Synthesis of Molecular Rulers to Study Distance and Orientation Dependent Förster Resonance Energy Transfer (FRET)

By

Dhananjaya Sahoo

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Department of Chemistry,
Bielefeld University, Bielefeld, Germany
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Approved, Thesis Committee:

Prof. Dr. Adelheid Godt

Prof. Dr. Markus Sauer

20th October 2009
Declaration of Authorship

I, Dhananjaya Sahoo, declare that this thesis entitled, “Synthesis of Molecular Rulers to Study Distance and Orientation Dependent Förster Resonance Energy Transfer (FRET)” and the work presented in it is my own. I confirm that:

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Date:

Signature:
To my family and friends
"The dream is not what you see in sleep, dream is the thing, which does not let you sleep" --Dr. A. P. J. Abdul Kalam
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## GLOSSARY

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<th>Definition</th>
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<tr>
<td>A</td>
<td>Acceptor</td>
</tr>
<tr>
<td>AcCN</td>
<td>Acetonitrile</td>
</tr>
<tr>
<td>CT</td>
<td>Charge transfer state</td>
</tr>
<tr>
<td>D</td>
<td>Donor</td>
</tr>
<tr>
<td>FRET</td>
<td>Förster Resonance Energy Transfer/Fluorescence Resonance Energy Transfer</td>
</tr>
<tr>
<td>HOM</td>
<td>Hydroxymethyl</td>
</tr>
<tr>
<td>HOE</td>
<td>Hydroxyethyl</td>
</tr>
<tr>
<td>HPLC</td>
<td>High performance liquid chromatography</td>
</tr>
<tr>
<td>IRF</td>
<td>Instrumental response function</td>
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<tr>
<td>LS</td>
<td>Local excited state</td>
</tr>
<tr>
<td>MeOH</td>
<td>Methanol</td>
</tr>
<tr>
<td>oligoPPEs</td>
<td>oligo(para-phenyleneethynylene)s</td>
</tr>
<tr>
<td>PMI</td>
<td>Perylenemonoimide</td>
</tr>
<tr>
<td>PMI(OAr)$_3$</td>
<td>Tri(aryloxy)-substituted perylenemonoimide</td>
</tr>
<tr>
<td>PMI(Me)$_2$</td>
<td>dimethylamino-substituted perylenemonoimide</td>
</tr>
<tr>
<td>PMI(Pip)</td>
<td>Piperinyl-substituted perylenemonoimide</td>
</tr>
<tr>
<td>PMI(Ethex)</td>
<td>2-Ethylhexylamino-substituted perylenemonoimide</td>
</tr>
<tr>
<td>PMI(Py)</td>
<td>Pyrrolidinyl-substituted perylenemonoimide</td>
</tr>
<tr>
<td>S&lt;sub&gt;0&lt;/sub&gt;</td>
<td>Ground electronic state</td>
</tr>
<tr>
<td>S&lt;sub&gt;1&lt;/sub&gt;</td>
<td>First excited singlet state</td>
</tr>
<tr>
<td>Term</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>(S_2)</td>
<td>Second excited singlet state</td>
</tr>
<tr>
<td>TFA</td>
<td>Trifluoro acetic acid</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>TIPS</td>
<td>Triisopropylsilyl</td>
</tr>
<tr>
<td>TICT</td>
<td>Twisted intramolecular charge-transfer state</td>
</tr>
<tr>
<td>W.R.T.</td>
<td>With respect to</td>
</tr>
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</table>

**Mathematical Terms**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>(E)</td>
<td>Efficiency of energy transfer</td>
</tr>
<tr>
<td>(R_0)</td>
<td>Förster distance in resonance energy transfer</td>
</tr>
<tr>
<td>(R)</td>
<td>Inter-fluorophore distance between donor and acceptor/reference</td>
</tr>
<tr>
<td>(\kappa_{nr})</td>
<td>Nonradiative decay rate constant</td>
</tr>
<tr>
<td>(\kappa_T)</td>
<td>Transfer rate in resonance energy transfer</td>
</tr>
<tr>
<td>(F)</td>
<td>Fluorescence or steady-state intensity</td>
</tr>
<tr>
<td>(J(\lambda))</td>
<td>Spectral overlap between donor emission and acceptor absorbance</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>Extinction coefficient</td>
</tr>
<tr>
<td>(\Phi)</td>
<td>Fluorescence quantum yield</td>
</tr>
<tr>
<td>(\kappa^2)</td>
<td>Orientation factor in resonance energy transfer</td>
</tr>
<tr>
<td>(\lambda_{ex})</td>
<td>Excitation wavelength</td>
</tr>
<tr>
<td>(\lambda_{em})</td>
<td>Emission wavelength</td>
</tr>
<tr>
<td>(\eta)</td>
<td>Refractive index</td>
</tr>
<tr>
<td>(OD)</td>
<td>Optical density</td>
</tr>
<tr>
<td>(\alpha_i)</td>
<td>Preexponential function in a multiexponential decay</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\chi_R^2$</td>
<td>Goodness-of-fit parameter, reduced chi-squared</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Fluorescence decay time or fluorescence lifetime</td>
</tr>
<tr>
<td>$\tau_D$</td>
<td>Donor fluorescence lifetime</td>
</tr>
<tr>
<td>$\tau_{DA}$</td>
<td>Donor lifetime in presence of acceptor</td>
</tr>
<tr>
<td>$\mu_e$</td>
<td>Dipole moment in excited state</td>
</tr>
<tr>
<td>$\mu_g$</td>
<td>Dipole moment in ground state</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Introduction

Förster resonance energy transfer/Fluorescence resonance energy transfer (FRET) is a non-radiative process, in which a donor fluorophore in its electronic excited state transfers the excitation energy to the nearby acceptor chromophore. A correlation between the efficiency ($E$) of resonance energy transfer and the distance ($R$) between donor and acceptor was established by the German physicist Theodor Förster in 1947.\(^1\) The FRET efficiency $E$ is proportional to the inverse sixth power of the distance $R$ between the donor and the acceptor, which is represented by

$$E = [1 + (R/R_0)^6]^{-1}$$  \hspace{1cm} (1.1)

where, $R_0$ is known as Förster radius that equals to the inter-fluorophore distance $R$ at $E = 50\%$.

In 1967 Stryer and Haugland reported FRET experiments using naphthyl and dansyl as the donor and acceptor, respectively and poly-L-prolines as the backbone for the FRET system.\(^2\) The authors found that the $R^6$ distance dependence predicted by Förster was nicely reproduced by the experimental results.\(^2\) This study has been subsequently considered as the proof of Förster theory and familiarly known as “spectroscopic ruler” for distance measurements, especially in the field of biosciences.\(^3\)-\(^9\)
Single-molecule spectroscopic technique has led to the rebirth of FRET.\textsuperscript{10-20} Eaton \textit{et al.}\textsuperscript{19} have used the single-molecule spectroscopic technique to determine the FRET efficiency taking Alex Fluor 488 maleimide and Alex Fluor 594 succinimidyl ester as the donor and the acceptor, respectively and poly-L-prolines as backbone, thereby testing once more the usefulness of FRET as a “spectroscopic ruler”. FRET at the single-molecule level had also been applied for measuring the end-to-end distance of molecules.\textsuperscript{19-23}

1.2 Principles of Förster resonance energy transfer

The FRET process involves the following steps.

i) Upon irradiation, the donor fluorophore gets excited from ground state to the excited state. Several excited states are available to the donor, however internal conversion and vibrational relaxation to the lowest excited state is very rapid (within picosecond).\textsuperscript{3,4}

ii) If a suitable acceptor is in close proximity to the donor, the non-radiative energy transfer takes place between the donor and the acceptor. This energy transfer involves a resonance between the singlet-singlet electronic transitions of the donor and acceptor, generated by the coupling of the emission transition dipole of the donor and the absorption transition dipole of the acceptor (Figure 1.1).\textsuperscript{3,4}
Figure 1.1 Jablonski energy level diagram showing FRET. The figure was adopted from http://www.olympusmicro.com/primer/techniques/fluorescence/fret/fretintro.html

The Jablonski diagram in figure 1.1 shows the coupled transitions between the donor emission and the acceptor absorbance involve in the process of fluorescence resonance energy transfer. Absorption and emission transitions are represented by linear vertical arrows (blue and orange or/and green respectively), while vibrational relaxation is indicated by wavy red arrows. The coupled transitions are drawn with dashed lines. In the presence of a suitable acceptor, the donor fluorophore can transfer excited state energy directly to the acceptor without emitting a photon (illustrated by a blue arrow in figure 1.1). As a result of that, the electron of the acceptor gets excited like the donor and consequently, returns to the ground state by emitting photon. The resulting sensitized emission has identical emission characteristics of the acceptor (See figure 1.2).
The extent of resonance energy transfer or FRET efficiency depends on the following factors:

i) The fluorescent quantum yield of the donor.\(^\text{3,4}\)

ii) The overlap of the emission spectrum of the donor and the absorption spectrum of the acceptor.\(^\text{3,4,39}\)

iii) The relative orientation of the transition dipole moment of the donor and that of the acceptor.\(^\text{3,4,40}\)

iv) The distance between the donor and the acceptor.\(^\text{2,3,4}\)

According to the Förster theory, the rate constant \(K_T\) for resonance energy transfer from a donor to an acceptor is given by

\[
K_T = \left( \frac{1}{\tau_0} \right) \left( \frac{R_0}{R} \right)^6
\]  

where, \(\tau_0\) is the excited-state lifetime of the donor in the absence of acceptor, \(R\) is the inter-fluorophore distance, and \(R_0\) is the Förster radius.

Förster radius \(R_0\) is the distance at which one half of the energy is transferred from the donor to the acceptor. \(R_0\) is expressed by

\[
R_0 = \left\{ 8.79 \times 10^{-5} \left[ \kappa^2 \eta^4 \phi_D J(\lambda) \right] \right\}^{-6} \text{ (in Å)} \]  

where, \(\phi_D\) = the fluorescence quantum yield of the donor only, \(\eta\) = refractive index of the environment, \(J(\lambda)\) = the spectral overlap integral of the donor and acceptor, and \(\kappa^2 = \)
the orientation factor, which depends on the relative orientation of the transition dipole moments of the donor and the acceptor.

The spectral overlap integral $J(\lambda)$ can be calculated according to eq. 1.4.

$$J(\lambda) = \frac{\int F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda}{\int F_D(\lambda) d\lambda} \quad \text{(in M}^{-1}\text{cm}^{-1}\text{nm}^4)$$

(1.4)

where, $F_D$ is the fluorescence intensity of the donor and $\varepsilon_A$ is the extinction coefficient of the acceptor with $\lambda$ as integral parameter.

**Figure 1.2** The figure shows spectral characteristics of fluorescein (donor) and tetramethylrhodamine (acceptor) undergoing energy transfer. As energy transfer takes place, the emission intensity of the donor decreases and emission intensity of the acceptor increases. The gray area represents the spectral overlap region of the donor emission and the acceptor absorption, which is responsible for energy transfer. The figure is taken from the *Ref*: 8.
The figure 1.2 shows the absorption and emission spectra of the donor fluorescein and the acceptor tetramethylrhodamine for their potential application as a FRET pair.\(^8\) Absorption spectra for both of the fluorophores are illustrated as solid lines, while the emission spectra are presented as dashed lines. The region of overlap between the donor emission and acceptor absorption spectra is represented by grey area. Whenever the spectral overlap of the fluorophores is high, a phenomenon known as spectral bleed-through or crossover occurs. In this phenomenon, the emission from the excited acceptor arises from the excitation of the donor, which transfers energy to the acceptor in a non-radiative fashion through dipole-dipole interaction and the direct excitation of the acceptor. The result is a high background signal that must be subtracted from the weak acceptor fluorescence emission.

**Figure 1.3** The figure on left shows visualization of the angles used to define the relative orientations of the donor (D) and acceptor (A) transition dipole moments and separated with distance vector \( R \) and on the right shows the value of \( \kappa^2 \) depending on the different orientation of D and A. The Figure on right hand side is taken from Ref. 4.
The orientation factor $\kappa^2$ or the relative orientations of the donor emission dipole and the acceptor absorption dipole is given by the eqs. 1.5 and 1.6.\(^3,8\)

$$\kappa^2 = (\cos \theta_T - 3\cos \theta_D \cos \theta_A)^2$$  \hspace{1cm} (1.5)

$$\kappa^2 = (\sin \theta_D \sin \theta_A \cos \varphi - 2\cos \theta_D \cos \theta_A)^2$$  \hspace{1cm} (1.6)

where, $\theta_T$ is the angle between the emission transition dipole of the donor and the absorption transition dipole of the acceptor, $\theta_D$ and $\theta_A$ are the angles between these dipoles and the vector joining the donor and the acceptor, and $\varphi$ is the angle between the planes containing the two transition dipoles (Figure 1.3, left).

The value of $\kappa^2$ is 0 when the orientation of transition dipole moments of the donor and that of the acceptor are orthogonal to each other (See the right and bottom of the circle in figure 1.3, right). On the other hand the value of $\kappa^2$ is 1 and 4 when the orientation of the transition dipole moments of the donor and acceptor are parallel and collinear, respectively (See the left and top of the circle in figure 1.3, right).

For FRET, the donor must be fluorescent however the acceptor chromophore is not necessarily to be fluorescent. The extent of resonance energy transfer can be determined from decreased fluorescence intensity of the donor in the presence of an acceptor or from the increased fluorescence intensity of the acceptor in the presence of the donor, in case that the acceptor is a fluorophore (Figure 1.2). Additionally, decrease in lifetime of the donor in the presence of the acceptor also gives information about the extent of resonance energy transfer.\(^3,4,7,8\)
The efficiency of resonance energy transfer \((E)\) can be calculated by the following three different ways.

I. Decrease in donor fluorescence intensity

\[
E = 1 - \frac{F_{DA}}{F_D} \tag{1.7}
\]

where, \(F_D\) is the fluorescence intensity of the donor only and \(F_{DA}\) is the fluorescence intensity of donor in the presence of the acceptor.

II. Increase in fluorescence intensity of the acceptor

\[
E = \left(\frac{\varepsilon_D}{\varepsilon_A}\right)\left[\frac{F_{AD}}{F_A}\right] - 1 \tag{1.8}
\]

where, \(F_A\) is the fluorescence intensity of the acceptor only, \(F_{AD}\) is the fluorescence intensity of the acceptor in the presence of the donor (sum of the fluorescence arising from the energy transfer and from the direct excitation of the acceptor), \(\varepsilon_A\) and \(\varepsilon_D\) are the molar extinction coefficients of the acceptor and the donor respectively, at the wavelength of donor excitation.

III. Decrease in excited state lifetime decay of the donor

\[
E = 1 - \frac{\tau_{DA}}{\tau_D} \tag{1.9}
\]

where, \(\tau_D\) is the excited state lifetime of the donor only and \(\tau_{DA}\) is the excited state lifetime of the donor in the presence of the acceptor.
The distance between the donor and the acceptor plays a key role for FRET efficiency. This is due to the dependence of the FRET efficiency $E$ on the inverse sixth power of the distance $R$ between the donor and the acceptor (Eq. 1.1). When the distance $R$ between the donor and acceptor is equal to the Förster radius $R_0$ of the system, the FRET efficiency $E$ is equal to 50% (Figure 1.4). When the distance $R$ decreases from $R_0$ to $0.5R_0$ the FRET efficiency $E$ approaches one. On the other hand by increasing the distance $R$ from $R_0$ to $2R_0$ the FRET efficiency $E$ approaches zero. The distance $R$ between the donor and the acceptor of a system can be measured within a range of $0.5R_0$ to $2R_0$. Beyond this range, the slope of the curve is too shallow to give reliable information on the distance $R$ between the two fluorophores.

**Figure 1.4** Distance $R$ between the donor and the acceptor versus efficiency $E$ of energy transfer. The figure is adopted from *Ref.* 3.
1.3 Applications and alternatives

Measurement of distance between the donor and the acceptor of macromolecules or biomolecules is just one of the several applications of FRET. The other applications of FRET are to measure the conformational changes,\textsuperscript{24} dynamic processes,\textsuperscript{25} rates of diffusion and distances of closest approach,\textsuperscript{7} and chemosensors for metal cations like Ag(I) and Hg(II).\textsuperscript{26-28} Hartwig and co-workers used FRET as a tool for reaction discovery and screening of catalyst for Heck coupling,\textsuperscript{29} arylation of ethyl cyanoacetate,\textsuperscript{30} and arylation of amines.\textsuperscript{31} For all of these cases dansyl was used as the donor and attached to one of the reactants whereas, azo-dye was used as the acceptor and attached to the other reactants which carrying a halide group. The catalyst was screened from the yield of the reaction. The yields of the reactions were determined by plotting the mole fraction of the products (FRET pair) versus emission intensity of the product, donor attached to the reactant, and acceptor attached with the reactant containing the halide group.\textsuperscript{29-31}

Generation of new fluorophores with spectral characteristics that combine the best of both the donor and the acceptor fluorophore is also one of the applications of FRET.\textsuperscript{32,33} In this case the donor and the acceptor attaches covalently to each other in a close proximity. In the simplest case, where the absorption and emission of the individual fluorophore do not change whereas, the absorption characteristic of the new fluorophore is the sum of the two individual fluorophores.\textsuperscript{33} Simultaneously, the emission of the new fluorophore is dominated by the acceptor emission with large stokes shifts and remarkably high quantum yield.\textsuperscript{33}

The alternative techniques which give structural information are X-ray crystallography, nuclear magnetic resonance (NMR), and electron paramagnetic
resonance (EPR). X-ray crystallography and NMR both produce potentially complete structural information but require large quantities of material. X-ray crystallography and NMR are limited to in vitro measurements and can analyze only relatively small molecules, restrictions which do not apply to FRET. Additionally, in case of X-ray crystallography, one could face the problem of crystallization and isomorphous replacement.

Interestingly, one can get structural information by using EPR technique on the spin labeled molecule of interest. This technique measures the dipole-dipole interaction between two spin labels in the nanometer range. Godt et al. reported the end to end distance distribution of oligo(para-phenyleneethynylene)s (oligoPPEs) by using EPR technique. Because EPR and FRET can measure end to end distances in the range of 1-10 nm, we are interested to compare these two methods. For that reason “molecular rulers” were developed for FRET study, taking oligoPPEs as the backbone for a fair comparison.

During my PhD work, I have synthesized the perylenemonoimide dye derivatives and studied their photophysical properties (chapter 2 and 5). Prerylenemonoimide dye derivatives with suitable photophysical properties were chosen as the donor and the acceptor of the molecular ruler. A series of shape persistant oligoPPEs with appropriate lengths were synthesized by following divergent and convergent approaches (chapter 3). Afterward these oligoPPEs were used as spacers for the construction of the molecular ruler (chapter 4). A series of linear dyads/donor-acceptor labeled oligoPPEs were synthesized as molecular ruler and the photophysical studies (Chapter 4) were performed to calculate end-to-end distance of oligoPPEs for comparison with EPR data.
A second series of kinked dyads/donor-acceptor oligoPPEs were synthesized keeping a fixed angle of 120 °C between the long axis of the fluorophores and the photophysical properties were studied to investigate the dependence of FRET efficiency on the relative orientation of fluorophores (Chapter 4).
Chapter 2

Perylenemonoimide derivatives and their photophysical studies

2.1 Introduction

Perylenemonoimide (PMI) dyes have found widespread applications ranging from industrial pigments\textsuperscript{41,42} to components of molecular photonic devices.\textsuperscript{43} PMI dyes have drawn attention due to their unique properties such as high fluorescence quantum yield (nearly unity),\textsuperscript{44-46} high thermal, chemical, and photochemical stability.\textsuperscript{47} PMI dyes have been implemented as a suitable candidate for energy transfer.\textsuperscript{48-51} The synthetic chemistry of PMI dyes has developed rapidly over the past few years, Langhal’s group has introduced a method to convert the commercially available perylene-dianhydride into PMI, which provides the starting point for the substituted PMI dyes.\textsuperscript{47} Müllen’s group and Lindsey’s group have developed methods for the halogenation and subsequent substitution of the halogenated PMI dyes.\textsuperscript{52-56}

2.2 Synthesis

A primary challenge in working with peryleneimide dyes is to overcome their poor solubility. A widespread approach with PMI has been to incorporate $2,6$-di-tert-butyl\textsuperscript{47,49,56,57} or $2,6$-diisopropyl\textsuperscript{52,57} phenyl group at the \textit{N}-atom of the imide moiety. Additional solubility has been achieved by introducing aryl-oxy substituents at the bay region of the PMI.\textsuperscript{52,54,57,58} We chose to incorporate $2,6$-diisopropyl phenyl group at the \textit{N}-atom of the imide group of the PMI. The objective was not only to improve the
solubility, but also to break the conjugation between the imide group and the phenylene unit of the PMI.

2.2.1 Perylenemonoimide

**Scheme 2.1** Synthesis of bromo aniline.

Treatment of the commercially available 2,6-diisopropylaniline with bromine in diethyl ether afforded the 4-bromo-2,6-diisopropylanilinehydrobromide (1a) in 71% yield. Treatment of the hydrobromide 1a with concentrated HCl afforded hydrochloride 1b. Similarly, treatment of the hydrobromide 1a with 0.1N NaOH solution afforded the free amine 1c (Scheme 2.1).

Following the procedure described by Lindsey *et al.*

commercially available perylene-dianhydride 2 and hydrobromide 1a were filled under argon into a thick walled pressure tube along with Zn(OAc)$_2$, imidazole, and distilled water. The tube was sealed with a Teflon screw cap and heated at 190 °C for 18 h to afford 3a in 30% yield. Debrominated perylenemonoimide 3b was isolated as a side product (Scheme 2.2). The yield of the reaction was low in comparison to the reported yield of 46%. The only difference between the reported procedure and ours was that in the former case free
aniline 1c was used, whereas we used the hydrobromide 1a. Therefore, we also performed the reaction taking the free aniline 1c and the hydrochloride 1b. Surprisingly, for both of these reactions the yields were only 26%, which was even lower than our previous finding. For all of these three variations debrominated product 3b was observed.

Lindsey et al.\textsuperscript{57} used 2,5-di-tert-butylaniline and performed the reaction in an autoclave at 190 °C for 20 h and isolated an analogue of 3b in 49% yield. We used 2,6-diisopropylaniline and followed the same reaction conditions as for the hydrobromide 1a. 3b was isolated in 47-48% yield which was nearly the same as that of the 3b analogue reported by Lindsey.\textsuperscript{57} Even though we used a different aniline than the reported one, it is fair to compare the results by considering the fact that the isopropyl group at 2 and 6 position of aniline will not change the nucleophilicity of the aniline dramatically in comparison to the tert-butyl group at 2 and 5 position. This result suggests that the low yield of 3a may be partly due to the formation of side product 3b. Secondly, the nucleophilicity of para-bromoaniline is somehow less than that of the aniline itself, which may be responsible for the low conversion of 3a.

**Scheme 2.2** Synthesis of perylenemonoimide.

\[
\begin{array}{c}
\text{Br} \quad \text{R} \\
1 \\
\end{array}
\quad +
\begin{array}{c}
\text{H} \quad \text{O} \\
2 \\
\end{array}
\quad \xrightarrow{\text{imidazole Zn(ACO)_{2}2H_{2}O}}
\begin{array}{c}
\text{N} \quad \text{O} \\
3 \\
\end{array}
\]

\[
\begin{array}{|c|c|c|}
\hline
1 & a & b & c \\
R & NH_{2} & HBr & NH_{2}HCl & NH_{2} \\
\hline
3 & a & b \\
R' & Br & H \\
\hline
\end{array}
\]
For the compounds 1b and 1c the yields of the reactions dropped from 26% to 20%, when the reactions were scaled up from 2.0 mmol to about 3.5 mmol. For these reactions the same thick walled tubes (35 mL, 17.8 cm x 25.4 mm) were used and as a consequence only a part of the reaction mixture was immersed in the oil bath, whereas for small scale reaction the reaction mixture was completely immersed. Therefore, the material above the oil layer gets insufficient heating in comparison to the counterpart inside the oil bath. We also found that the stirring was not sufficient enough to have a homogenous mixture. As a result of this, the material above the oil bath did not get sufficient heating to give the product, which may also be responsible for the lower yield.

At this point, we decided to run several parallel reactions on small scale and combine them for work up. The hydrobromide 1a was used for the scale up purpose because the yield of the reaction is higher than the reactions in which hydrochloride 1b and free aniline 1c were used. The other reason was the easier access of 1a. The scale-up was done in eight batches, out of which four batches consisted of three different thick walled pressure tubes whereas the other four batches consisted of two different thick walled tubes each. Each thick walled pressure tube (35 mL, 17.8 cm x 25.4 mm) was filled with 1.48 mmol of hydrobromide 1a and dianhydride 2 along with the required amount of Zn(OAc)$_2$, imidazole, and H$_2$O.

We had noticed that for reaction at small scales, a substantial amount of insoluble material remains on the top of the silica column after chromatography. These materials may be the unreacted anhydride or decomposed material. It would have taken much effort to isolate 3a from the crude products collected from eight batches. In order to reduce the workload, after aqueous work up the crude materials from eight batches
were combined in a flask (2.5 L in capacity) and suspended in CHCl₃ (1.5 L) for 48 h. The suspension was filtered and the solvent was evaporated to afford 4.81 g of red solid. The yield of 3a was estimated to be 26% from the ¹H NMR spectroscopy taking the consideration of PMI 3b and perylene. In order to make sure that there was no more 3a in the solid that had been filtered off from the suspension, this solid was resuspended in CHCl₃ and stirred for 48 h. After filtering the suspension and evaporating the solvents from the filtration only a few mg of material was found, which shows that substantially all of 3a had been extracted during the first filtration itself. 3.45 g (22%) of 3a was isolated by column chromatography. The remaining 4% material stuck on the silica during chromatography.

We found that the temperature plays a crucial role for the conversion. It was found that 190 °C is the optimal temperature as described by Langhals.⁴⁷ When the reaction was carried out at 180 °C, it failed to give the desired product emphasizing small changes in temperature. Also the amount of water plays a crucial role in the preparation of 3a: doubling the amount of water resulted in complete failure of the reaction.

2.2.2 Aryloxy-substituted perylenemonoimide

PMIs are known to undergo bromination selectively at the 1-, 6-, and 9-positions.⁵⁴-⁵⁸ Treatment of PMI 3a with excess bromine in refluxing chloroform afforded the brominated PMI derivative 4 in 45-52% yields (Scheme 2.3). The ¹H NMR spectrum shows the presence of 2-11% tetrabrominated product PMI(Br)₄ 4b. The compounds PMI(Br)₃ 4a and PMI(Br)₄ 4b have the same Rᵢ values so we decided to carry out the further reaction taking the mixture.
The mixture of PMI(Br)\textsubscript{3} \textit{4a} and PMI(Br)\textsubscript{4} \textit{4b} was taken along with 4-\textit{tert}-butylphenol and potassium carbonate in DMF and refluxed for 1 h to obtain \textit{5} in 49-66% yield (Scheme 2.3).\textsuperscript{56} About 3-10% of PMI(OAr)\textsubscript{2} \textit{5b} was estimated from the signals of \textsuperscript{1}H NMR spectroscopy. The structural identity of PMI(OAr)\textsubscript{2} \textit{5b} was confirmed by \textsuperscript{1}H-\textsuperscript{1}H COSY (Figure 2.1). Besides \textit{5a} and \textit{5b} tetraphenoxy substituted PMI \textit{5c} was isolated with traces of unknown impurity. From another reaction, a constitutional isomer of PMI(OAr)\textsubscript{2} \textit{5b} was isolated, which was confirmed by the \textsuperscript{1}H-\textsuperscript{1}H COSY (Figure 2.2).

Compounds PMI(OAr)\textsubscript{3} \textit{5a} and PMI(OAr)\textsubscript{2} \textit{5b} were not separable by standard chromatography, however separation was successful on analytical scale by HPLC using (60:40) THF and H\textsubscript{2}O as the mobile phase on bifunctional reverse phase column (octadecyl and phenyl, 4.6 x 250 mm, 5 µm). The mixture of compounds \textit{5a} and \textit{5b} were used as such for the next step.
Figure 2.1 $^1$H-$^1$H COSY of the mixture of compounds PMI(OAr)$_3$ 4a (A) and PMI(OAr)$_2$ 4b (B); solvent: CHCl$_3$, 500 MHz.

Figure 2.2 $^1$H-$^1$H COSY of the mixture of constitutional isomers of PMI(OAr)$_2$ 4b (I and II); solvent: CHCl$_3$, 500 MHz.
It was observed that when the reaction was carried out at a bath temperature of 185 °C, the formation of the PMI(OAr)$_2$ 5b was high (up to 23%), whereas at a bath temperature of 170 °C, the formation of the PMI(OAr)$_2$ 5b was low (up to 3%).

2.2.3 Amino-substituted perylenemonoimide

To the best of our knowledge, only three synthetic routes have been reported for amino-substituted PMI derivatives until now: Fieler et al.$^{47}$ used a conventional synthetic route to prepare a primary amino-substituted PMI by the nitration of PMI with nitrogen dioxide and reduction of the product with iron powder and HCl. Becker et al.$^{60}$ have developed a method to introduce diphenylmethyleniminino group at the 9-position of PMI by using palladium catalyzed $N$-aryl-coupling reaction. The amino compound was isolated by hydrolysis of the $N$-aryl coupling product by using catalytic amount of HCl in wet THF. Wasielewski’s group have introduced pyrrolidine at the 9-position of PMI with additional substituents at 1- and 6- position by nucleophilic substitution of bromine.$^{58,59}$ Later, Hudhomme’s group prepared the 9-pyrrolidino PMI by following the same procedure described by Wasielewski.$^{60}$ We followed the procedure reported by the Wasielewski’s group to synthesize the triamino substituted PMI starting from the PMI(Br)$_3$ 4a. Instead of getting the triamino substituted PMI, we isolated monoamino substituted PMI as the major product.

We synthesized a series of amino-substituted perylenemonoimide starting from a 1:20 mixture of PMI(Br)$_4$ 4b and PMI(Br)$_3$ 4a (Scheme 2.4). The compound 4 was refluxed with excess of the amines ($^{i}$Pr)$_2$NH, Et$_2$NH, piperidine, 2-ethylhexyl amine, and pyrrolidine in DMF for 3 h to obtained required products 6. However, for ($^{i}$Pr)$_2$NH and Et$_2$NH the reactions failed to give the product even after refluxing for 24 h.
Scheme 2.4 Synthesis of amino-substituted starting from PMI(Br)_3 4.

In case of the other amines, mono substitution product 6c-e were obtained within a reaction time of 3 h. A 1:20 mixture of PMI(Br)_4 4b and PMI(Br)_3 4a was refluxed with excess pyrrolidine in DMF for 3 h to afford the PMI(Py) 6e as a blue solid in 80% yield. However, later the amino-substituted compounds 6c-f were prepared from starting the monobromo PMI 4c (Scheme 2.5).

Scheme 2.5 Synthesis of amino-substituted PMI starting from PMI(Br) 4c.
The monobromo PMI 4c was synthesized starting from the PMI 3a following the procedure described by Lindsey.\textsuperscript{56} A solution of PMI 3a in chlorobenzene was treated with excess bromine and heated at 55 °C for 7 h to obtain the monobromo PMI 4c in quantitative yield (Scheme 2.5).\textsuperscript{56} The crude material was used as such for the next reactions. The PMI(Br) 4c was refluxed with excess amines (\textsuperscript{i}Pr)\textsubscript{2}NH, (Et)\textsubscript{2}NH, piperidine, 2-ethylhexylamine, pyrrolidine and imidazole in DMF (Scheme 2.5). The reactions for amines like piperidine, 2-ethylhexyl amine, and pyrrolidine completed within 3 h and the yield was 70-77%. For (Et)\textsubscript{2}NH and (\textsuperscript{i}Pr)\textsubscript{2}NH, the reaction mixture was refluxed for 24 h. There was no product or very little of the desired product for the former, whereas in case of later dimethylamino-substituted PMI PMI(Me)\textsubscript{2} 6g was isolated as major product instead of the desired product. Similarly, the reaction was slow for imidazole and it took around 24 h for completion. A very small amount of PMI(Me)\textsubscript{2} 6g was isolated as a side product along with the desired product 6f.
2.3 Photophysical studies

The absorption and emission spectra of the amino-substituted PMI (6c-6e and 6g) were recorded in various solvents of different polarity (toluene, THF, CHCl₃, and AcCN) and the spectral data have been collected in table 2.1 and the corresponding spectra are shown in figure 2.3.

Figure 2.3 Absorption (solid) and emission spectra (dashed) for PMI(Me)₂ 6g, PMI(Pip) 6c, PMI(EtHex) 6d, and PMI(Py) 6e in various solvents with different polarity (toluene (blue), THF (magenta), CHCl₃ (green), and AcCN (red). The absorption and emission spectra are normalized at their respective peak maximum. The excitation wavelength was at 465 nm with 5 nm slit widths.
Table 2.1 Absorption and emission spectral data of amino-substituted PMI (6c-6e and 6g) in various solvents with increasing polarity from left to right.\(^a,b\)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Absorption Max. (\lambda_{\text{max}}, \text{nm})</th>
<th>(\varepsilon^c)</th>
<th>Emission Max. (\lambda_{\text{max}}, \text{nm})</th>
<th>Stokes shift ((\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Toluene</td>
<td>THF</td>
<td>CHCl(_3)</td>
<td>AcCN(^d)</td>
</tr>
<tr>
<td>6g</td>
<td>542</td>
<td>542</td>
<td>550</td>
<td>549</td>
</tr>
<tr>
<td>6c</td>
<td>539</td>
<td>537</td>
<td>547</td>
<td>544</td>
</tr>
<tr>
<td>6d</td>
<td>578</td>
<td>604</td>
<td>593</td>
<td>614</td>
</tr>
<tr>
<td>6e</td>
<td>587</td>
<td>603</td>
<td>609</td>
<td>625</td>
</tr>
</tbody>
</table>

\(^a\)Emission spectra were measured after exciting the solution at 465 nm. \(^b\)Concentrations of the dyes 6g and 6c were set at 2.98 µM and 2.97 µM respectively, and for the dyes 6d and 6e were set at 2.93 µM in toluene, CHCl\(_3\), and THF. \(^c\)Molar extinction coefficient \((\text{mol}^{-1}\text{cm}^{-1}\text{L})\) measured in toluene at the respective absorption maxima. \(^d\)Dilute solutions with \(\text{OD} \approx 0.098\) at absorption maximum (typically corresponded to a concentration in micromolar range) were used for the measurements.

In principle, absorption of light excites the fluorophores from ground state \(S_0\) to the first singlet excited state \(S_1\). If the fluorophores further excited to the second singlet excited state \(S_2\), it rapidly decays to the \(S_1\) state in \(10^{-12}\) s due to internal conversion.\(^3,4\)

Emission from fluorophores generally occurs at higher wavelength than those at which absorption occurs. This loss of energy is due to the various processes i.e. internal conversion and vibrational relaxation that occur immediately after light absorption. Solvent effects shift the emission to still lower energy due to stabilization of the excited state by polar solvents; as a consequence the emission occurs in higher wavelength. The fluorophore has a larger dipole moment \((\mu_e)\) in excited state than the ground state.
(\(\mu_g\)). After excitation the solvent dipoles undergo reorientation or relaxation around the excited dipole moment \(\mu_e\) of the dye, which stabilize the energy further and lower the energy of the excited states and the solvent relaxation occurs within 10-100 ps.\(^3\)\(^4\) As the solvent polarity increases, this effect becomes larger and resulting emission occurs at higher wavelength. Usually absorption spectra are less sensitive to solvent effects, because absorption of light occurs in about \(10^{-15}\) s, which is too short for the motion of solvents or fluorophores.\(^3\)\(^4\)

The result in table 2.1 shows a 5-8 nm bathochromic shift of the absorption maxima for dyes 6g and 6c, whereas for the dyes 6d and 6e a bathochromic shift of 5-38 nm by changing solvent from toluene to acetonitrile. This big bathochromic shift observed in case of the later dyes is not explainable by the normal solvent effects. This could be due to some specific solvent effects like hydrogen bonding, preferential solvation, acid-base chemistry, or charge-transfers interactions.\(^3\)\(^4\)\(^62\)\(^63\) Specific solvent effects occur both in ground state or excited state. If it occurs in ground state, then one should expect changes in absorption spectrum,\(^3\) which we observed for the dyes 6d and 6e. For these dyes the specific solvent effects could be explained by the charge-transfer interactions.

The dashed lines in figure 2.3 consist of two emission bands, a short-wavelength band and a long-wavelength for all of the dyes 6c-6e and 6g. The short-wavelength emission band for the dyes 6g and 6c appears in 530-550 nm range, whereas for the dyes 6d and 6e, it appears in the range of 570-585 nm. The percentage of intensity of the short-wavelength emission bands w.r.t. the long-wavelength emission bands are presented in table 2.2. This result suggests that the intensity of short-wavelength band
increases with increase in polarity except 6g. Additionally, it shows that the intensities in the short-wavelength region of the dyes are higher for CHCl$_3$ and AcCN. The dyes 6d and 6e have higher intensity in comparison to the other two dyes in the short-wavelength region. The data on table 2.2 shows a good correlation between the solvent polarities with the intensity of short-wavelength band.

**Table 2.2** Percentage of the intensity of the short-wavelength emission bands w.r.t. the long-wavelength emission bands of the dyes 6c-6e and 6g in various solvents with increasing solvent polarity from toluene to AcCN.

<table>
<thead>
<tr>
<th>Solvents</th>
<th>PMI(Me)$_2$ 6g</th>
<th>PMI(Pip) 6c</th>
<th>PMI(EtHex) 6d</th>
<th>PMI(Py) 6e</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>6%</td>
<td>9%</td>
<td>20%</td>
<td>8%</td>
</tr>
<tr>
<td>THF</td>
<td>6%</td>
<td>12%</td>
<td>39%</td>
<td>6%</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>9%</td>
<td>13%</td>
<td>46%</td>
<td>28%</td>
</tr>
<tr>
<td>AcCN</td>
<td>6%</td>
<td>17%</td>
<td>53%</td>
<td>23%</td>
</tr>
</tbody>
</table>

According to the twisted intramolecular charge-transfer state (TICT) hypothesis, if a fluorophore contains both an electron donating and an electron-accepting group, for instance, the dyes 6c-6e and 6g contain the amino groups as the electron-donating group and the imides groups as the electron-accepting groups, after excitation at specific wavelength a short-wavelength emission band could be due to the coplanar state known as locally excited (LS) state and the long-wavelength emission band appears due to the twisted conformation, which causes full charge-separation/charge transfer (CT) between the amino group and the imide group of the perylene-core.$^{3,4,62-66}$ The charge-separation between the amino and imide group of the perylene-core in twisted state is further enhanced in comparison to the LS by increasing the solvent.
polarity, as a result stabilization of excited states occurs by the reorientation of the solvent dipoles giving emission in longer wavelength region.

The effect of the solvent polarity on emission maximum is more significant than that on the absorption maximum. A change of solvent from toluene to acetonitrile leads to a red shift of the absorption maximum of the dyes 6g and 6c by 7 nm and 5 nm respectively, whereas, the magnitude of the spectral shifts in emission are 8 and 12 times. This bathochromic shift in emission spectra could be well explained by the increase of solvent polarity and also specific solvent effects like TICT. These results also suggest that the excited state of the system is more polar than the ground state and also the dipole moment of excited state is higher than the ground state.

The excitation spectra of the dyes (the same solutions used for emission measurement) were recorded keeping the emission wavelength at 600 nm and 800 nm in various solvents with different polarity and a few representative spectra are shown in figure 2.4. A short-wavelength band is found in the excitation spectra upon emission at 600 nm which corresponds to the short-wavelength emission. This result suggests the presence of twisted state in the ground state.
Figure 2.4 Excitation spectra for PMI(EtHex) 6d and PMI(Py) 6e in CHCl₃ (green) and THF (magenta) at different emissions. The emissions were at 600 nm (solid line) and 800 nm (dotted line).

The lifetime decays of the dyes 6c-6e and 6g have been studied in toluene and AcCN and the data have been presented in table 2.3. The dyes in toluene were excited at 495 nm and lifetime decays were measured at 670 nm. Similarly, the dyes in AcCN were excited at 495 nm and the lifetime decays were measured at different emissions (570 nm, 670 nm, and 720 nm).

The data on table 2.3 shows relatively longer lifetime decays (τ₁) with major components for all of the dyes in AcCN (excitation at 495 nm and collected emission at...
720 nm). The shorter lifetime decays (τ<sub>2</sub>) are almost negligible (2-5%). This result suggests that the longer lifetime decays (τ<sub>1</sub>) are due to the long-wavelength emission of the dyes. Similarly, the data on table 2.3 shows predominantly longer lifetime decays (τ<sub>1</sub>) with major components (around 100%) for the dyes 6c and 6g in AcCN (excitation at 495 nm and collected emission at 670 nm).

**Figure 2.5** Lifetime decays of the PMI(Me)<sub>2</sub> 6g (blue), PMI(PiP) 6c (magenta), PMI(EtHex) 6d (cyan), PMI(Py) 6e (orange) and the prompt (black). The prompt is the instrument response function (IRF), which is the response of instrument to a zero lifetime sample. This curve is typically collected using a dilute scattering solution such as colloidal silica (Ludox) and no emission filter. The excitation wavelength was 495 nm and emission was 670 nm.
Table 2.3 Lifetime decays of amino-substituted PMI (6c-d, and 6g) in toluene\(^a\) and acetonitrile.\(^b\)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Toluene(^c) ((\lambda_{ex} = 495) nm)</th>
<th>Acetonitrile (^c)((\lambda_{ex} = 495) nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\lambda_{em} = 670) nm</td>
<td>(\lambda_{em} = 570) nm</td>
</tr>
<tr>
<td>(\tau) (ns)</td>
<td>(\alpha)</td>
<td>(\tau) (ns)</td>
</tr>
<tr>
<td>(\tau_1)</td>
<td>(\tau_2)</td>
<td>(\alpha_1)</td>
</tr>
<tr>
<td>6g</td>
<td>3.72</td>
<td>0.13</td>
</tr>
<tr>
<td>6c</td>
<td>3.24</td>
<td>0.12</td>
</tr>
<tr>
<td>6d</td>
<td>2.50</td>
<td>0.12</td>
</tr>
<tr>
<td>6e</td>
<td>4.41</td>
<td>2.54</td>
</tr>
</tbody>
</table>

\(^a\)The solutions were excited at 495 nm and the lifetime decays were measured at 670 nm. \(^b\)The solutions were excited at 495 nm and the lifetime decays were measured at different emissions (570 nm, 670 nm, and 720 nm). \(^c\)The lifetime decays for the dyes were fitted by a biexponential function. The lifetime decay fitting were done by Dr. Ralf Brune.
Again these lifetime decay values are similar to the previously obtained values at the emission of 720 nm. These results suggest that the lifetime decays for dyes 6c and 6g are due to the longer emission band and it is in good agreement with the result obtained from emission spectra. Whereas for the dyes 6d and 6e the data shows two lifetime decays, which suggest that the two lifetime decays arise due to the presence of the longer wavelength band and shorter wavelength band components of the dyes. The relatively longer lifetime decays are due to the short-wavelength band and the shorter lifetime decays are due to the long wavelength band of the dyes. The result shows predominantly longer lifetime decay with major component (around 100%) for the dyes 6c-6e in AcCN at the emission of 570 nm. This suggests that these lifetime decays arise exclusively due to the short-wavelength band. Whereas, for the dye 6g there are two lifetime decays one with longer lifetime decay and the other with shorter. These results suggest that the longer lifetime decay for the dye 6g is due to the short-wavelength band components and the the shorter lifetime decay is due to long-wavelength band. These results are in good agreement with our emission data and also explain the dual fluorescence.

It is fair to compare the obtained lifetime decays of the dyes in toluene and acetonitrile at the excitation wavelength of 495 nm and monitoring the emission at 670 nm (Table 2.3). These results show that the major components with relative longer lifetime decay for all dyes except for the dye 6g increases with polarity of the solvent. These results also support the fact that the percentage of the short-wavelength band increases with increasing polarity of the solvents.
The photophysical properties of the bench mark perylenemonoimide dyes 3b and 25a were reported on literature. The synthesis of dye 25a was discussed in chapter 4. Considering the photophysical properties the dye 25a was chosen as one of the fluorophores for FRET study.

The photophysical studies of the fluorophores 6c-6e and 6g show that the PMI(Py) 6e has higher absorption and emission maxima in comparison to the other fluorophores. Therefore, PMI(Py) was chosen as the second fluorophore for the construction of molecular ruler (Chapter 4, sec 4.2).
Chapter 3

Synthesis of oligo(\textit{para}-phenyleneethynylene)s as spacer

3.1 Introduction

Monodisperse and shape persistent oligomers, e.g. oligo(\textit{para}-phenyleethynylene)s (oligoPPEs) are attractive building blocks for molecular and supramolecular architectures.\textsuperscript{67,68} Recently Godt \textit{et al.}\textsuperscript{38} used the oligoPPEs as the backbone for the spin labeled oligomers for measuring the spin-to-spin distance distribution and extracted the end-to-end distance distribution of the oligoPPEs by EPR measurement. Similarly one can obtain such type of information on fluorescent labeled molecules by FRET.\textsuperscript{3-8} We were interested for comparing these two very different methods. For a fair comparison of these two methods, a series of oligoPPEs of different lengths were chosen as the backbone and attached to suitable fluorophores. In this section, I will discuss the details about the synthesis of oligoPPEs.

3.2 Synthesis of monodisperse oligoPPEs using hydroxymethyl (HOM) and TIPS as orthogonal protecting groups

A series of oligoPPEs of different lengths were synthesized following the divergent and convergent approach described by Kukula \textit{et al.}\textsuperscript{69} Previously synthesized compounds 1,4-dihexyl-2,5-diodobenzene and iodo monomer 7\textsubscript{a1}, which contain an iodo group at one end and the hydroxymethyl (HOM) at the other end were used as the starting material for the synthesis of the oligoPPEs.
The initial idea was to synthesize iodo dimer 7c2 with two repeating phenyleneethynylene units for the shortest fluorophore labeled oligoPPEs. Therefore, the iodo monomer 7a1 was coupled with TIPS acetylene to afford 8a1 (Scheme 3.1). The reaction was carried out at 50 °C for overnight and afterwards monitored by thin layer chromatography (TLC). The TLC analysis showed incomplete reaction, therefore 0.5 equiv. of TIPS acetylene and equal amounts of catalysts were added and the reaction was continued for another 8 h to obtain 8a1. A byproduct 8d1 (Figure 3.1) was formed in 35 mol% (estimated from the 1H-NMR spectrum of the crude product). However, later the monomer 8a1 was successfully synthesized by the coupling of the iodo monomer 7a1 with TIPS acetylene at room temperature for 18 h along with 5 mol% (estimated from the 1H-NMR spectrum of the crude products) of the carbometalation product 8d1.
(Figure 3.1). The monomer $8a_1$ contains two orthogonal acetylene protecting units HOM and TIPS at both ends of the compound.

![Figure 3.1: Structural representation of carbomatalation product $8d_n$.](image)

The monomer $8a_1$ was treated with $\gamma$-MnO$_2$/KOH in Et$_2$O to afford non-polar acetylene $9a_1$ as described by Kukula et al.\textsuperscript{69} and the yields were around 72-82%. The non-polar acetylene $9a_1$ was coupled with 1.5 equiv. of 1,4-dihexyl-2,5-diiodobenzene to afford the iodo dimer $7c_2$. In this reaction, the desired product $7c_2$ was formed along with other side products e.g. the disubstituted product $8c_3$, the acetylene dimerization product $10a_1$ and the unreacted 1,4-dihexyl-2,5-diiodobenzene. Unfortunately, the $R_f$ values of the compounds $7c_2$, $8c_3$, $10a_1$, and 1,4-dihexyl-2,5-diiodobenzene are very close to each other with a $R_f$ value of 0.15 in 1:1 Et$_2$O and $n$-pentane. Therefore, isolation of the desired product $7c_2$ was not successful by flash chromatography. At this point, I decided to run further reaction by treating the crude material with excess 2-propynol to obtain dimer $8a_2$ instead of isolating the iododimer $7c_2$ by chromatographic separation.
Chapter 3  Synthesis of oligo(para-phenyleneethylene)s as spacer

The crude material containing the mixture of compounds $7c_2$, $8c_3$, $10a_1$, and 1,4-dihexyl-2,5-diiodobenzene was treated with excess 2-propynol, so that the iodo dimer $7c_2$ gave the desired product $8a_2$, which has one HOM group and comparatively more polar than compounds $8c_3$, and $10a_1$. Simultaneously, the unreacted 1,4-dihexyl-2,5-diiodobenzene coupled with two equivalents of 2-propynol to afford highly polar disubstituted compound with two HOM groups. The TLC analysis showed three spots with $R_f$ values 0.15, 0.43, and 0.74. The desired product $8a_2$ ($R_f = 0.43$) was isolated by flash chromatography. However, later the dimer $8a_2$ was synthesized by the coupling of the iodo monomer $7a_1$ with the non-polar acetylene $9a_1$ in 80-87% yields. Traces amount of separable carbometalation product $8d_2$ was formed as a byproduct (Figure 3.1).

The next target was to synthesize the higher homologs of $8a_n$. Therefore, the dimer $8a_2$ was treated with the $\gamma$-MnO$_2$/KOH in Et$_2$O to afford non-polar acetylene $9a_2$ in 72-80% yields (Scheme 3.2). On the other hand, the dimer $8a_2$ was treated with $\gamma$Bu$_4$NF in THF to afford polar acetylene $9c_2$ quantitatively. The polar acetylene $9c_2$ was coupled with 1.5 equiv. of 1,4-dihexyl-2,5-diiodobenzene to afford iodo trimer $7a_3$ in 53-58% yields. The iodo trimer $7a_3$ was coupled with the non-polar acetylene $9a_2$ to afford pentamer $8a_5$ in 72-73% yields and subsequently the HOM group was removed to isolate the non-polar acetylene $9a_5$ in 67-72% yields (Scheme 3.2).
The previously synthesized tetramer $8a_4$ was treated with the $\gamma$-MnO$_2$/KOH in Et$_2$O to afford non-polar acetylene $9a_4$ in 94% yield, which was subsequently coupled with the iodo trimer $7a_3$ to afford heptamer $8a_7$ in 92% yield (Scheme 3.2).
3.3 Synthesis of monodisperse oligoPPEs using hydroxyethyl (HOE) and TIPS as orthogonal protecting groups

Kukula et al.\textsuperscript{69} have reported the carbometalation product as a side product in the synthesis of the monomer $8a_1$ whereas, I have also found the carbometalation product in the synthesis of both the monomer $8a_1$, and the dimer $8a_2$. Ms. Schulte has demonstrated that the formation of carbometalation product can be suppressed by using 3-butyn-2-ol instead of the 2-propynol. She has also demonstrated that the 4-aryl-3-butyn-2-ol can be deprotected to give the arylethylene with $\gamma$-MnO$_2$/KOH in Et$_2$O at room temperature. Therefore, we were interested to investigate whether the same methodology can be applied for the higher homologs of $8a_n$. The iodo dimer $7b_2$, which was used for the synthesis of hexamer $8b_6$, heptamer $8b_7$, and nonamer $8b_9$ was synthesized by Ms. Schulte. Later, I have also synthesized the iodo dimer $7b_2$ (Scheme 3.3).

The 3-butyn-2-ol was coupled with 1.5 equiv. of 1,4-dihexyl-2,5-diiodobenzene to afford iodo monomer $7b_1$ in 62% yield, which subsequently coupled with the TIPS acetylene at room temperature to afford monomer $8b_1$ in 75% yield. Unfortunately, the carbometalation product was found in 2 mol% (estimated from the $^1$H-NMR spectra of the crude product) as a byproduct. The monomer $8b_1$ was treated with $\text{n}^\text{Bu}_4\text{NF}$ in THF at room temperature to afford the polar acetylene $9b_1$ in quantitative amount. The polar acetylene $9b_1$ was coupled with 1.5 equiv. of 1,4-dihexyl-2,5-diiodobenzene to afford iodo dimer $7b_2$ in 52% yield (Scheme 3.3).
Scheme 3.3 Synthesis of iodo monomer 7b₁ and iodo dimer 7b₂.

The iodo dimer 7b₂ was coupled with non-polar acetylene 9a₄ and 9a₅ to afford hexamer 8b₆ and heptamer 8b₇ respectively, in 79-97% yields, which contain two orthogonal protecting groups TIPS and hydroxyethyl (HOE). As expected, the HOE group of the hexamer 8b₆ and the heptamer 8b₇ was removed by the γ-MnO₂/KOH in Et₂O at room temperature to afford the respective non-polar acetylenes 9a₆ and 9a₇. Treatment of the heptamer 8a₇ with γ-MnO₂/KOH in Et₂O at room temperature also afforded non-polar acetylene 9a₇. The nonamer 8b₉ was synthesized by coupling the iodo dimer 7b₂ and the non-polar acetylene 9a₇ and the yield was 71-94%. The nonamer 8b₉ was not sufficiently soluble in Et₂O, so THF was used as solvent for the removal of HOE group. The nonamer 8b₉ was treated with the γ-MnO₂/KOH in THF to afford 9a₉ in 70-79% yields (Scheme 3.4).
**Scheme 3.4** Synthesis of oligomers $8b_n$, and non-polar acetylenes $9b_n$ ($n = 6, 7, 9$).

When the nonamer $8b_9$ was treated with $\gamma$-MnO$_2$/KOH from a previously synthesized batch (more than six months old), the nonamer $8b_9$ was oxidized to give the ketone $11b_9$ rather than the free acetylene $9a_9$ (Scheme 3.5). For our curiosity, to check the reactivity of the $\gamma$-MnO$_2$, we treated the pentamer $8a_5$ with $\gamma$-MnO$_2$/KOH from the same batch which was used in the former case. The pentamer $8a_5$ was oxidized to
give aldehyde $11a_5$ in preference to the free acetylene $9a_5$. This clearly shows that, freshly prepared $\gamma$-MnO$_2$ is required for the removal of HOM and HOE groups.

**Scheme 3.5** Schematic representation of aldehyde $11a_5$ and ketone $11b_9$.

The intermediate aldehyde $11a_5$ was treated with excess powdered KOH to afford the free acetylene $9a_5$ (Scheme 3.5). Similarly, the intermediate $11a_9$ was treated with excess KOH and the reaction was monitored for 24 h, but there was no change in the reaction. These observations show that the $\gamma$-MnO$_2$ might have some influence for the conversion of ketone to free acetylene.

In summary, I have synthesized the oligoPPEs $8a_n$ with $n = 2, 5$ and oligoPPEs $8b_n$ with $n = 6, 7, 9$. The former molecules contain HOM and TIPS as the orthonal protecting groups and the HOM group was removed by treatment of $\gamma$-MnO$_2$/KOH in Et$_2$O. In the later series all of molecules contain HOE and TIPS as the orthogonal protecting groups. Interestingly, the HOE group was successfully removed by treatment with the $\gamma$-MnO$_2$/KOH. Freshly prepared $\gamma$-MnO$_2$ is required for the removal of
HOM/HOE group. The oligoPPEs $9a_n$ with $n = 2, 5, 7, \text{ and } 9$, which contain a TIPS group at one end and the ethynylene group at the other end were used as spacer for the construction of the molecular ruler, which will be discussed in next chapter.
Chapter 4

Molecular rulers and their photophysical studies

4.1 Introduction

FRET is used as a “spectroscopic ruler”, particularly in the field of biosciences.\textsuperscript{3-8} Two fluorophores are required for this technique and out of the two, one acts as donor and the other one as acceptor, which is not necessarily fluorescent. The energy transfer process takes place through a non-radiative long-range dipole-dipole interaction, only when the two fluorophores are in a close proximity of 1-10 nm.

One can also determine the end-to-end distances by EPR on spin labeled molecules.\textsuperscript{35-38} The aim of the present work is to compare these two different methods FRET and EPR. For that reason, a molecular ruler was constructed taking oligoPPEs as the spacer.

Perylenemonoimide dye was chosen as fluorescent probe due to the following outstanding properties: i) high fluorescence quantum yield, ii) high thermal and photochemical stability, iii) absorbs and emits at higher wavelength than oligoPPEs.\textsuperscript{56,69,71,72}

4.2 Molecular ruler for the inter-fluorophore distance measurements

\textsuperscript{PMI(OAr)}_3 was chosen as fluorescent probe due to the above mentioned outstanding properties. The photophysical properties of different amino-substituted compounds as discussed in chapter 2, show that the PMI(Py) \textsuperscript{6e} has higher absorption and emission maxima in comparison to the other amino-substituted PMI. Secondly, it
absorbs and emits at higher wavelength than the PMI(OAr)₃ (see figure 4.1) and also the absorption of the former overlaps with the emission of the latter. Therefore we chose PMI(Py) 6e as the second fluorophore for the construction of the molecular ruler for FRET study.

The objective was to build linear PMI(OAr)₃-(PPE)ₙ-PMI(Py) dyads 1₄ₙ. The synthesis can be achieved by two approaches (Scheme 4.1). In the first approach, Pd-catalyzed coupling of PMI(Py) 6e with the oligoPPEs 9ₐₙ bearing TIPS protected ethynyl unit at the other end produces PMI(Py) labeled oligoPPEs. Removal of the TIPS group would provide the free acetylene, which subsequently couples with the mixture of PMI(OAr)₃ 5a and PMI(OAr)₂ 5b to achieve the desired dyads 1₄ₙ.

**Scheme 4.1** Structural representation of PMI(OAr)₃-(PPE)ₙ-PMI(Py) dyad 1₄ₙ and their corresponding building blocks.

In the second approach, Pd-catalyzed coupling of the mixture of PMI(OAr)₃ 5a and PMI(OAr)₂ 5b with the oligoPPEs 9ₐₙ followed by removal of TIPS group would give the free acetylene. The resulting free acetylene couples with PMI(Py) 6e to achieve the required product 1₄ₙ.
4.2.1 Synthesis of PMI(OAr)$_3$-(PPE)$_2$-PMI(Py) dyad 14$_2$

**Scheme 4.2** Synthesis of PMI(OAr)$_3$-(PPE)$_n$-PMI(Py) dyad 14$_2$.

Following the first approach, the PMI(Py) 6e was attached to the oligoPPEs 9$_a$ by Pd-catalyzed acynyl-aryl coupling to afford 12$_n$ with n = 0, 2, and 5 as a blue solid in 60-80% yields (Scheme 4.2). The PMI(Py) labeled oligoPPEs 12$_n$ with n = 0, 2 were treated with $n$Bu$_4$NF in THF to afford the free acetylene 13$_n$ in 85% yield. The free acetylene 13$_2$ was coupled with the mixture of PMI(OAr)$_3$ 5a and PMI(OAr)$_2$ 5b to afford dyad 14$_2$ in 75% yield (Scheme 4.2).
4.2.2 Photophysical studies

![Structural representations of dyes PMI 3b, PMI(OAr)3 25a, and PMI(Py) 130](image)

**Figure 4.1** The figure on left shows structural representation of dyes for PMI 3b, PMI(OAr)3 25a, and PMI(Py) 130. Absorption spectra (top right) and emission spectra (bottom right) for PMI 3b (black), PMI(OAr)3 25a (red) and PMI(Py) 130 (green) in toluene. The emission spectra were normalized with the maximum and excitation wavelength is 475 nm.

The photophysical studies were conducted for the dye 130 in toluene and compared with the benchmark perylene dyes PMI 3b and PMI(OAr)3 25a. The absorption and emission spectra for the dyes PMI 3b, PMI(OAr)3 25a, and PMI(Py) 130 were recorded in toluene (Figure 4.1). Dilute solutions with OD ≈ 0.05 at absorption maxima (typically corresponded to a concentration in micromolar range) were used for the measurements.
The absorption spectrum shows that the absorption maximum of PMI(Py) **13₀** was red shifted by 80 nm and 52 nm in comparison to the absorption maximum of PMI **3b** and PMI(OAr)₃ **25a** respectively. Similarly, the emission maximum of the PMI(Py) **13₀** was red shifted by 157 nm and 112 nm in comparison to the emission maximum of PMI **3b** and PMI(OAr)₃ **25a** respectively (Table 4.1).

![Figure 4.2](image.png)

**Figure 4.2.** Emission spectra for PMI **3b** (black), PMI(OAr)₃ **25a** (red) and PMI(Py) **13₀** (green) in toluene. The emission spectra were normalized with the OD, at their respective excitation wavelength. Excitation wavelength: 475 nm.

The fluorescence quantum yield of PMI(Py) **13₀** was measured by using Eq. 4.1. PMI **3b** and PMI(OAr)₃ **25a** were used as the references⁷³ (Figure 4.2, Table 4.1).

\[
\phi = \phi_n \left(\frac{I}{I_n}\right) \left(\frac{OD_R}{OD}\right) \left(\frac{\eta^2}{\eta_R^2}\right)
\]

(4.1)

where, \(\phi\) is the quantum yield, \(I\) is the integrated intensity, \(OD\) is the optical density, and \(\eta\) is the refractive index of the solvent used.
The subscript $R$ refers to the reference fluorophore of known quantum yield.

**Table 4.1**: The photophysical data of PMI 3b, PMI(OAr)$_3$ 25a, and PMI(Py) 13$_0$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\lambda_{abs}$ (nm)</th>
<th>$\lambda_{em}$ (nm)</th>
<th>$\phi_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3b</td>
<td>479, 506</td>
<td>529, 569</td>
<td>0.91$^{73}$</td>
</tr>
<tr>
<td>25a</td>
<td>511, 536</td>
<td>577, 623</td>
<td>0.86$^{73}$</td>
</tr>
<tr>
<td>13$_0$</td>
<td>586</td>
<td>687</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The absorption and emission spectra of the donor 25a, acceptor 13$_0$, and the dyad 14$_2$ were shown in figure 4.3. The absorption spectrum of dyad 14$_2$ shows a short wavelength peak at 350 nm, which is due to the oligoPPE and the second peak at 540 nm due to the sum of the absorbance of the donor 25a and the acceptor 13$_0$.

**Figure 4.3** Absorption spectra (left) and emission spectra (right) for donor 25a (solid line), acceptor 13$_0$ (dashed line) and PMI(OAr)$_3$-(PPE)$_2$-PMI(Py) dyad 14$_2$ (dotted line) in toluene. The emission spectra were normalized with the OD, at their respective excitation wavelength. Excitation wavelength: 475 nm.
The emission spectrum of the dyad 14₂ (Figure 4.3) shows a longer wavelength peak, corresponding to the emission of the acceptor 13ₐ, whereas the shorter wavelength peak corresponds to the emission of the donor 25ₐ. Considering the emission intensity of the donor only and the emission intensity of dyad 14₂ in the relevant region, it is clear that the energy transfer takes place from the PMI(OAr)₃ to PMI(Py). This result proves that PMI(OAr)₃-(PPE)₂-PMI(Py) dyad 14₂ can be used as a molecular ruler for FRET study, where PMI(OAr)₃ acts as the donor and PMI(Py) as the acceptor.

The absorption and emission spectra for the dye 6e are broad, structureless, and also red-shifted as compared to those of PMI and PMI(OAr)₃ (Figure 4.1). Stracke et al.⁷⁴ reported similar amino substituted peryleneimide derivatives. The unstructured absorption spectrum of the reported amino compound resembles that of the PMI(Py). This unstructured spectrum is due to the charge transfer transition resulting from donation of electron density from the lone-pair on the nitrogen atom of amino group into perylene core.⁷⁴,⁷⁵ The extended π-conjugation/donation of electron density is possible only when the overlap of orbital containing the amino lone-pair with the π-system of the perylene core is maximized and this is achieved when the amino group adopts an sp² hybridisation. Zoon et al.⁷⁶ reported for pyrrolidine substituted PMI that the amino group adopts an intermediate hybridization between sp² and sp³. Therefore the above mentioned hypothesis is applicable for the unstructured absorbance of PMI(Py) and this hypothesis was supported by the protonation and deprotonation of the pyrrolidine nitrogen (Figure 4.4).
Figure 4.4 Absorption spectra (left) and emission spectra (right) for PMI(Py) 6e (solid line), PMI(Py) 6e + TFA (dashed line), PMI(Py) 6e + TFA + TEA (dotted line) in toluene. The emission spectra were normalized with the OD, at their respective excitation wavelengths. Excitation wavelength: 500 nm.

The absorption and emission spectra for PMI(Py) were measured in toluene. The same sample was protonated by the addition of a drop of trifluoroacetic acid (TFA), so that the lone-pair electron present on pyrrolidine nitrogen will no longer be available for conjugation and the absorption and the emission spectra were measured (Figure 4.4). As expected, there was a blue shift in the absorption and emission maxima of the protonated PMI(Py) 6e (dashed line, Figure 4.4). Drop of Et$_3$N was added to the above protonated PMI(Py) 6e solution to obtain the free PMI(Py) and the absorption and emission spectra were recorded. Interestingly, a bathochromic shift was observed for the absorption and emission spectrum and these spectra appear in the same wavelength region as that of the parent PMI(Py) (dotted line, Figure 4.4). Additionally, it was observed that, the absorbance and emission of protonated PMI(Py) 6e appear in the same region as that of PMI 3b (Figure 4.5). This result suggests that when the lone-pair electron of pyrrolidine nitrogen is no longer available, the system behaves as the PMI 3b. Similarly, the absorption and emission of the dye PMI(OAr)$_3$ 25a was measured after protonation. There was no shift in the peak except the peak gets broader.
Figure 4.5 Absorption spectra (left) and emission spectra (right) for PMI (solid line) and PMI(Py) $6_e +$ TFA (dashed line) in toluene. The emission spectra were normalized with the OD, at their respective excitation wavelength. Excitation wavelength: 475 nm.

These interesting results motivated us to investigate the photophysical properties of the protonated dyad $14_2$. The absorbance and emission of the donor $25a$, the acceptor $13_0$, and the dyad $14_2$ were measured in toluene and then the same solutions were protonated by addition of a drop of TFA.

The absorption and emission of the above protonated solution were measured (Figure 4.6). The absorption spectrum for the protonated dyad $14_2$ shows two peaks, one at the shorter wavelength (350 nm) due to the oligoPPE. The second peak at longer wavelength (540 nm) is the sum of the absorbance of the protonated donor $25a$ and acceptor $13_0$. The shoulder of the dyad $14_2$ around 700 nm disappears after protonation.
Chapter 4  Molecular rulers and their photophysical studies

Figure 4.6. Absorption (left) and emission spectra (right) for 25a (solid line), 130 (dashed line), and PMI(OAr)_3-(PPE)_2-PMI(Py) dyad 14_2 (dotted line) after protonation with TFA in toluene. The emission spectra were normalized with the OD, at their respective excitation wavelength. Excitation wavelength: 475 nm.

Figure 4.7. Structural representation of the direction of energy transfer for PMI(OAr)_3-(PPE)_2-PMI(Py) dyad 14_2 before and after protonation.
The emission spectrum of the protonated dyad 142 (Figure 4.6) obtained by excitation at 475 nm shows just one major peak which corresponds to emission of the PMI(OAr)₃ after protonation. The emission intensity of the protonated dyad 142 at the shorter wavelength (540 nm) had almost disappeared. Considering the emission intensity of protonated 13₀ and the protonated dyad 14₂ in the relevant region, it is clear that the energy transfer is highly efficient and takes place from protonated PMI(Py) to PMI(OAr)₃ (Figure 4.6). That means the direction of energy transfer for the dyad 14₂ gets reversed upon protonation.
4.3 An improved molecular ruler for the inter-fluorophore distance measurements

In the previous section, I discussed about the PMI(OAr)$_3$-(PPE)$_2$-PMI(Py) dyad 14$_2$, where the energy transfer takes place from PMI(OAr)$_3$ to PMI(Py). The same system in acidic environment undergoes energy transfer from the protonated PMI(Py) to the PMI(OAr)$_3$. Interestingly, the UV-vis and emission spectrum of the protonated PMI(Py) are identical to that of the PMI (Figure 4.4). This gave me the idea that PMI can be used as donor along with PMI(OAr)$_3$ for FRET study. Additionally, by using PMI as donor, the number of synthetic steps involved for the synthesis of PMI-(PPE)$_n$-PMI(OAr)$_3$ dyads could be reduced by 2-3 steps in comparison to the protonated dyad 14$_2$. Therefore, the PMI(Py) of PMI(OAr)$_3$-(PPE)$_2$-PMI(Py) dyad 14$_2$ was replaced by PMI, to achieve PMI-(PPE)$_n$-PMI(OAr)$_3$ dyads (Scheme 4.3).

4.3.1 Linear PMI-(PPE)$_n$-PMI(OAr)$_3$ dyads

The target dyads PMI-(PPE)$_n$-PMI(OAr)$_3$ can be synthesized in two different approaches and either of the two approaches follows Pd-catalyzed coupling reactions. In approach A, a mixture of PMI(OAr)$_3$ 5$_a$ and PMI(OAr)$_2$ 5$_b$ couples with oligoPPEs 9$_a_n$ to afford fluorescent labeled oligoPPEs 15$_n$. Treatment of the fluorescent labeled oligoPPEs 15$_n$ with $^n$Bu$_4$NF affords free acetylene 16$_n$, which subsequently couples with the PMI 3$_a$ to get the required dyads 19$_n$. In approach B, firstly the PMI 3$_a$ couples with the oligoPPEs 9$_a_n$ to afford the precursor 17$_n$. Treatment of 17$_n$ with $^n$Bu$_4$NF affords free acetylene 18$_n$, which subsequently couples with the mixture of PMI(OAr)$_3$ 5$_a$ and PMI(OAr)$_2$ 5$_b$ to afford the desired linear dyads 19$_n$. 
We found that PMI(OAr)₃ has better solubility than PMI as described in the literature.⁵⁴⁻⁵⁸ I was not expecting that there will be a dramatic change in the solubility of PMI after attaching the oligoPPEs. Therefore, the oligoPPEs were attached to the more soluble PMI(OAr)₃ expecting that the resulting PMI(OAr)₃ labeled oligoPPEs would have better solubility than the PMI labeled oligoPPEs. Following approach A, the dyads 19₂, 19₅, and 19₉ were synthesized. However, later it was found that when the PMI 3ₐ was coupled to the oligoPPEs, the solubility of resulting compounds 17ₙ were dramatically improved in comparison to that of the PMI 3ₐ. These results showed that one can achieve the desired dyads PMI-(PPE)ₙ-PMI(OAr)₃ 19ₙ by following either of the two approaches. The dyad 19₇ was successfully synthesized by following the approach B.
Scheme 4.4 Synthesis of linear PMI-(PPE)\textsubscript{n}-PMI(OAr)\textsubscript{3} dyads.

**Approach A**

\textbf{n} = 2, 5, 9

\[ \text{TIPS} \equiv \begin{array}{c} \equiv \text{Hex} \equiv \text{H} + \text{Br} \equiv \text{N} \equiv \text{O} \equiv \text{Ar} \equiv \text{R}^1 \end{array} \]

\[ 9a_n \]

\[ n = 2, 5, 7, 9 \]

\[ \text{Pd}_2(\text{dba})_3, \]
\[ \text{P} \text{(o-tolyl)}_3, \]
\[ \text{toluene, Et}_3\text{N}, \]
\[ 65 \degree \text{C}, 18 \text{ h} \]

\[ \text{OAr} = \begin{array}{c} \equiv \text{C(Me)}_3 \equiv \text{O} \equiv \text{Ar} \equiv \text{H} \end{array} \]

\[ \text{Approach B} \]

\textbf{n} = 7

\[ \text{nBu}_4\text{NF}, \]
\[ \text{THF, 2 h, rt} \]

\[ 19_n \]

\[ n = 2, 5, 7, 9 \]

\[ \text{Pd}_2(\text{dba})_3, \]
\[ \text{P} \text{(o-tolyl)}_3, \]
\[ \text{toluene, Et}_3\text{N}, \]
\[ 65 \degree \text{C}, 18 \text{ h} \]
The oligoPPEs $9a_n$ were coupled with a mixture of PMI(OAr)$_3$ $5a$ and PMI(OAr)$_2$ $5b$ to afford $15_n$ in 70-80% yield (Scheme 4.4). The PMI(OAr)$_3$ labeled oligoPPEs $15_n$ were treated with $^7$Bu$_4$NF to afford the free acetylenes $16_n$ in 90-95% yield. For the synthesis of $15_2$, a 93:7 mixture of compounds $5a$ and $5b$ was used, whereas in other cases ($15_5$, $15_7$, and $15_9$) a 97:3 mixture of compounds $5a$ and $5b$ was used.

The PMI $3a$ was coupled with the free acetylenes $16_n$ (n =2, 5, and 9) to afford the required linear dyads $19_n$ in 67-80% yields (Scheme 4.4). Unfortunately, the yield of $19_5$ was only 51% due to the necessary repeated chromatography for purification. The compound $19_5$ has very good solubility in common organic solvents (Et$_2$O, CH$_2$Cl$_2$, CHCl$_3$, and THF). At this point the main aim was to take advantage of the good solubility and avoid the solvent CHCl$_3$ for chromatography. Therefore, a 1:1 mixture of Et$_2$O and n-pentane was used for chromatography. Unfortunately, I was not able to isolate pure product after chromatography for several times. Finally, the compound $19_5$ was purified with chromatography using the usual 1:1 mixture of CHCl$_3$ and n-hexane.

Following the second approach, the PMI $3a$ was coupled with the oligoPPEs $9a_n$ to afford $17_n$ in 70-80% yields. The PMI labeled oligoPPEs $17_n$ (n = 5, 7, and 9) were treated with $^7$Bu$_4$NF to afford the free acetylenes $18_n$ in 90-95% yield (Scheme 4.4). The alkyne $18_7$ was coupled with a 97:3 mixture of PMI(OAr)$_3$ $5a$ and PMI(OAr)$_2$ $5b$ to afford $19_7$ in 65% yield (Scheme 4.4).
4.3.2 Kinked PMI-(PPE)_n-PMI(OAr)_3 dyads

According to Förster theory, the efficiency of energy transfer is dependent on the inverse sixth power of the inter-fluorophore distance and also on the Förster radius of the fluorophore pair (Chapter 1.1, eq. 1.1). The Förster radius depends on the relative orientation of the transition dipoles of the two fluorophores. As a consequence the rate of energy transfer depends on the fluorophore alignment. In order to investigate this fact, kinked PMI-(PPE)_n-PMI(OAr)_3 dyads were designed with a fixed angle of 120° between the long axis of PMI and PMI(OAr)_3 (Scheme 4.5).
The initial idea was to incorporate the kink moiety into the PMI labeled oligoPPEs 18<sub>n</sub> and then couple with the PMI(OAr)<sub>3</sub> to achieve the kinked dyads 24<sub>n</sub>. The free acetylene 18<sub>s</sub> was coupled with bromo compound 21 using Pd-mediated coupling reaction to afford the compound 22<sub>s</sub> in 34% yields. The bromo compound 21 was synthesized in 89% yield by Pd/Cu catalyzed coupling of 1-bromo-3-iodobenzene (20) with 2-propynol (Scheme 4.6).
From our previous experience with the synthesis of oligoPPEs, it was noticed that the TMS acetylene coupled product and starting iodo compounds have nearly same $R_f$ values as a result of that one could face difficulties in chromatographic separation. Therefore, polar protecting group 2-propanol was chosen instead of TMS acetylene for the synthesis of bromo compound 21. As expected, a big difference in the $R_f$ values of 20 and 21 was found.

The hydroxymethyl protected compound $22_5$ was treated with $\gamma$-MnO$_2$ and powdered KOH in CH$_2$Cl$_2$ to afford free acetylene $23_5$ in 67% yield. Treatment of the unprotected acetylene $23_5$ with a 97:3 mixture of PMI(OAr)$_3$ 5a and PMI(OAr)$_2$ 5b by the usual Pd-mediated coupling reaction afforded $24_5$ in 70% yield (Scheme 4.7). The compound $22_5$ has poor solubility in comparison to linear molecule $17_5$ which has a TIPS end group. Additionally, the free acetylene $23_5$ has better solubility in comparison to $22_5$. These facts support that the poor solubility of $22_5$ is due to the hydroxymethyl group.

As we encountered low solubility of $22_5$ and also low yield, a different synthetic approach was followed for the synthesis of kinked dyads $24_n$ with $n = 7, 9$. There are two possible alternate routes (Scheme 4.7) to the earlier synthetic route followed for $24_5$ (Scheme 4.6). In route A, the kink moiety 20 will be attached individually with each of the free acetylene $18_n$ and subsequently couple with the free acetylene 25 to afford the desired dyads $24_n$. 
Scheme 4.7 Retro synthesis of kinked PMI-(PPE)_n-PMI(OAr)_3 dyads 24_n (n = 7, 9.).
By following route B, the kink moiety 20 will couple with the free acetylene 25 to afford bromo compound 26 which subsequently couples with 18\textsubscript{n} to afford the desired dyads 24\textsubscript{n} (Scheme 4.7).

By following either of the two routes one needs to go through two step synthesis. The key difference between the two routes lies in the first step of the synthesis. By following route A, one will couple the kink moiety 20 with the limited amount of precious material 18\textsubscript{n} to achieve bromo compound 27\textsubscript{n} in the first step and run the reaction for “n” number of time. Whereas by following route B, one would couple the kink moiety 20 with the acetylene 25 to afford bromo compound 26 in the first step and run the reaction only once. Then in the second step for either of the two routes, one would run the same number of reactions to achieve the desired product 24\textsubscript{n}. Therefore, there are two advantages for following route B over route A. Firstly, as a whole the number of reactions in first step will be reduced. Secondly, the loss of precious material 18\textsubscript{n} will be less.

Therefore route B was followed and the kink moiety 20 was attached with the free acetylene 25. The unprotected acetylene 25 was synthesized by coupling of a 97:3 mixture of PMI(OAr)\textsubscript{3} 5a and PMI(OAr)\textsubscript{2} 5b with TMS acetylene to obtain the TMS protected PMI(OAr)\textsubscript{3}, which was subsequently treated with 5N NaOH in a 1:1 mixture of THF and MeOH. The kink moiety 20 was coupled with the unprotected acetylene 25 to achieve the bromo compound 26 in 73% yield (Scheme 4.8).\textsuperscript{72} The bromo compound 26 was coupled with the free acetylenes 18\textsubscript{7} and 18\textsubscript{9} to afford 24\textsubscript{7} and 24\textsubscript{9} in 60% and 63% yields, respectively (Scheme 4.8).
4.3.3 Photophysical studies

The donor PMI 3b, the acceptor PMI(OAr)₃ 25a, the linear PMI-(PPE)ₙ-PMI(OAr)₃ dyads 19ₙ, and kinked PMI-(PPE)ₙ-PMI(OAr)₃ 24ₙ are shown in Figure 4.8. The distance $R$ between the two fluorophores for the linear dyads 19ₙ and kinked dyads 24ₙ were calculated taking the standard bond lengths and are summarized in table 4.2.\textsuperscript{77,79}
The distance $R$ for the linear and kinked dyads ($n = 5, 7, \text{ and } 9$) are nearly same (Figure 4.8 and table 4.2).

**Figure 4.8** Figures representing the structure of PMI 3b, PMI(OAr)$_3$ 25a, linear dyads 19$_n$ ($n = 2, 5, 7, \text{ and } 9$), and kinked dyads 24$_n$ ($n = 5, 7, \text{ and } 9$). $R$ is the calculated distance between the centers of the two fluorophores.
The UV-vis absorption and emission spectra of PMI 3b, PMI(OAr)$_3$ 25a, and the linear dyads 19$_n$ were measured in toluene. The Förster radius $R_0$ for the above mentioned fluorophores was calculated from the spectral overlap integral of the emission spectrum of the PMI and the absorption spectrum of the PMI(OAr)$_3$ by using Eq. 1.3 and found to be 7.1 nm (Figure 4.9).

**Figure 4.9** Emission spectrum (blue) of the donor PMI 3b and absorption spectrum (red) of the acceptor PMI(OAr)$_3$25a in toluene and the area cover by gray color is their overlap.

**Figure 4.10** Emission spectra of PMI 3b (magenta), the PMI(OAr)$_3$ 25a (cyan), the sum of the emission of PMI and PMI(OAr)$_3$ (black), and linear PMI-(PPE)$_n$-PMI(OAr)$_3$ dyads 19$_n$ (n = 2 (orange), 5 (blue), 7 (red), and 9 (green)) on left. The emission spectra of PMI 3b (magenta), the PMI(OAr)$_3$ 25a (cyan), the
sum of the emission of PMI and PMI(OAr)$_3$ (black), and kinked PMI-(PPE)$_n$-PMI(OAr)$_3$ dyads 24$_n$ ($n = 5$ (blue-dashed), 7 (red-dashed), and 9 (green-dashed)) are shown on the right. Excitation wavelength was 450 nm and the emission spectra were normalized with the concentration.

The black curve in Figure 4.10 is the sum of the emission of the donor PMI and the acceptor PMI(OAr)$_3$ with equal concentrations. This type of curve appears when there is no interaction between the two fluorophores. The left side spectra show the emission of PMI 3b, PMI(OAr)$_3$ 25a, and linear PMI-(PPE)$_n$-PMI(OAr)$_3$ dyads 19$_n$ ($n = 2, 5, 7, \text{ and } 9$). The orange curve represents the emission of the PMI-(PPE)$_2$-PMI(OAr)$_3$, and the emission intensity at the PMI emission region (510-540 nm) almost vanished. This decrease in emission intensity of the PMI-(PPE)$_2$-PMI(OAr)$_3$ dyad 19$_2$ at the PMI emission region clearly suggests that there is energy transfer from PMI to PMI(OAr)$_3$. When one goes from $n = 2$-$9$, the emission intensity at the donor’s emission region increases. That means, the emission intensity of donor in presence of acceptor increases as the distance between the donor and the acceptor increases, which suggests that the energy transfer depends on the inter-fluorophore distance $R$.

The spectra on the right side of Figure 4.10 show the emission of PMI 3b, PMI(OAr)$_3$ 25a, and kinked PMI-(PPE)$_n$-PMI(OAr)$_3$ dyads 24$_n$ ($n = 5, 7, \text{ and } 9$), where the angle between the long axes of the fluorophores is 120°. The kinked PMI-(PPE)$_5$-PMI(OAr)$_3$ dyad 24$_5$ has smaller emission intensity at the donor emission region in comparison to the donor PMI 3b. This reduced emission intensity in the donor emission region suggests that there is energy transfer in the dyad 24$_5$. As the inter-fluorophore distances increases with $n = 5$-$9$, the emission intensity at the donor region increases. This clearly shows that the efficiency of energy transfer decreases as the inter-fluorophore distance increases. By comparing the emission spectra of the linear dyads
19_n and kinked dyads 24_n (n = 5, 7, and 9), we found that the emission intensities of the kinked dyads 24_n in the donor emission region are higher than the corresponding linear dyads. This suggests that the FRET efficiencies for kinked dyads are lower in comparison to their linear counterparts. This proves that the FRET efficiency depends on the alignment of the fluorophores.

The FRET efficiencies for the linear and kinked molecules were calculated from the decrease in emission intensity of donor and also from the increase in acceptor emission intensity by using Eq.1.7 and Eq. 1.8 and the results are summarized in table 4.3.

**Figure 4.11** Excited-state lifetime decays of the PMI 3b (magenta), PMI(OAr)_3 25a (cyan), linear PMI-(PPE)_n-PMI(OAr)_3 dyads 19_n (n = 2 (orange), 5 (blue), 7 (red), and 9 (green)) and the prompt (black) (left). The prompt is the IRF. The figure on the right side shows the excited-state lifetime decays of the kinked PMI-(PPE)_n-PMI(OAr)_3 dyads 25_n (n = 5 (blue), 7 (red), and 9 (green)), and the prompt (black). The excited-state lifetime decays were measured by exciting the donor at 450 nm and the emission was detected at 525 nm in toluene.
The time-resolved lifetime decays of PMI 3b, PMI(OAr)$_3$ 25a, and the linear dyads 19$_n$ are determined by time-correlated single photon counting in toluene by exciting at 450 nm and fluorescence decays were collected at 525 nm (Figure 4.11 left). The lifetime decays for the donor PMI 3b and the acceptor PMI(OAr)$_3$ 25a were fitted by a biexponential function and the lifetime decays were found to be 4.84 and 4.52 respectively (Table 4.2), which suggests that these dyes have single exponential decay.

The dyes 3b and 25a are integral part of the dyads 19$_n$ with n = 2, 5, 7, and 9. When one would measure the lifetime decay of dyads 19$_n$, one would expect to obtain two lifetime decays corresponding to the respective donor 3a and the acceptor 25 since both the dyes have emission at 450 nm. If there will be energy transfer process between the donor and the acceptor, one would expect that the lifetime of donor in presence of acceptor should be less than the lifetime decay of the donor only. Keeping these facts in mind the lifetime decays for the linear dyads 19$_n$ with n = 2, 5, 7, and 9 were fitted by a biexponential function keeping the lifetime of the acceptor (4.52 nm) fixed and the results are summarized in table 4.2 (entry 3-6). The result shows that the shorter lifetime decays due to the donor in presence of acceptor $\tau_{DA}$ for the dyads 19$_n$ are smaller than the lifetime $\tau_D$ of the donor only. This decrease in lifetime of the donor in presence of acceptor supports once again that the energy transfer takes place from PMI to PMI(OAr)$_3$. The FRET efficiencies were calculated from the decrease in lifetime of the donor by using Eq.1.9 and the results are summarized in table 4.3.
Table 4.2 The lifetime decays of PMI, PMI(OAr)$_3$, linear dyads 19$_n$ ($n = 2, 5, 7, \text{and} \ 9$), and kinked dyads 24$_n$ ($n = 5, 7, \text{and} \ 9$) in toluene. The excited-state lifetime decays were measured by exciting the donor at 450 nm and the emission was detected at 525 nm in toluene.

<table>
<thead>
<tr>
<th>Entries</th>
<th>Compounds</th>
<th>Linear dyads 19$_n$</th>
<th>Kinked dyads 24$_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\tau^a$</td>
<td>$\alpha^b$</td>
</tr>
<tr>
<td>1</td>
<td>PMI 3b</td>
<td>4.84</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>PMI(OAr)$_3$ 25a</td>
<td>4.52</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>n = 2</td>
<td>0.53</td>
<td>4.52</td>
</tr>
<tr>
<td>4</td>
<td>n = 5</td>
<td>0.67</td>
<td>4.52</td>
</tr>
<tr>
<td>5</td>
<td>n = 7</td>
<td>1.81</td>
<td>4.52</td>
</tr>
<tr>
<td>6</td>
<td>n = 9</td>
<td>3.01</td>
<td>4.52</td>
</tr>
</tbody>
</table>

$^a\tau_1$, $\tau_2$, and $\tau_3$ are the lifetime components obtained from the biexponential and triexponential fitting, by keeping the lifetime of the acceptor fixed.

$^b$The amplitude of the lifetime component.

The lifetime decay fitting and calculation for FRET efficiency for the linear dyads 19$_n$ and kinked dyads 24$_n$ were conducted by Dr. Brune.\textsuperscript{79}
Similarly, the lifetime decays of kinked PMI-(PPE)$_n$-PMI(OAr)$_3$ dyads $24_n$ were determined by time-correlated single photon counting in toluene by exciting at 450 nm and lifetime decays were collected at 525 nm (Figure 4.11 left). The decays were fitted by a triexponential function and the results are summarized in table 4.2. As expected, the lifetimes of the donor in presence of acceptor $\tau_{DA}$ for the dyads $24_n$ are smaller than the lifetime $\tau_D$ of the donor only. Comparing the lifetime decay $\tau_{DA}$ for the linear dyads $19_n$ and kinked dyads $24_n$, the lifetime $\tau_{DA}$ of kinked dyads are higher than the linear ones, which suggests that the efficiencies of energy transfer for kinked dyads are less than the linear dyads. This result supports the fact that FRET efficiency depends on the alignment of fluorophores. The FRET efficiencies were calculated from the decrease in lifetime of the donor using Eq.1.9 and the results are summarized in table 4.3.

Table 4.3 The FRET efficiencies $E$ of PMI-(PPE)$_n$-PMI(OAr)$_3$ dyads $19_n$ and $24_n$ with respect to the decrease in emission intensity of donor ($F_D$), increase in emission intensity of acceptor ($F_A$) and decrease in the lifetime decays of donor ($\tau_D$) in toluene. $R$ is the calculated distance between the fluorophores.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Linear PMI-(PPE)$_n$-PMI(OAr)$_3$ dyads $19_n$</th>
<th>Kinked PMI-(PPE)$_n$-PMI(OAr)$_3$ dyads $24_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R$ (nm)</td>
<td>$E_D$</td>
</tr>
<tr>
<td>$n = 2$</td>
<td>3.47</td>
<td>1.031</td>
</tr>
<tr>
<td>$n = 5$</td>
<td>5.53</td>
<td>0.827</td>
</tr>
<tr>
<td>$n = 7$</td>
<td>6.90</td>
<td>0.552</td>
</tr>
<tr>
<td>$n = 9$</td>
<td>8.27</td>
<td>0.272</td>
</tr>
</tbody>
</table>
The FRET efficiencies $E$ calculated by the decrease in emission intensity of donor, increase in emission intensity of acceptor, and decrease in lifetime decay are plotted against the distance $R$ (calculated distance between the centers of the donor and the acceptor; see Figure 4.8 and table 4.3) (Figure 4.12).

*Figure 4.12 FRET efficiency $E$ versus calculated inter-fluorophore distances $R$. The gray-dashed curve and wine-dashed curve are the typical FRET curves due to the fitting of the FRET efficiency $E$ versus $R_0$ for linear dyads and kinked dyads respectively. The solid gray curve and solid wine curve were generated by plotting the FRET efficiencies $E$ versus the calculated inter-fluorophore distance $R$ for linear molecules and the kinked molecules, respectively $[(PMI-(PPE))_nPMI(OAr)]_3$, where $n = 2$.}
(orange), 5 (blue), 7 (red), and 9 (green)]. The FRET efficiencies due to decrease in fluorescent intensity of donor, increase in fluorescence intensity of acceptor, and decrease in lifetime decay of donor in presence of acceptor are represented by circle, square and triangle respectively.

The solid gray and wine curves in Figure 4.12 show the correlation between the FRET efficiencies \( E \) and the calculated inter-fluorophore distances \( R \) for the linear and kinked dyads. These results are in good agreement with Förster theory and it also proves that the FRET efficiency \( E \) depends on the inverse sixth power of the inter-fluorophore distance \( R \). Additionally, the FRET efficiencies for the kinked dyads \( 24_n \) are smaller than that of the strait dyads \( 19_n \). This finding also supports the fact that the FRET efficiency depends on the direction of the transition dipole moment of fluorophores.

In summary, I have successfully synthesized the PMI(OAr)\(_3\)-(PPE)\(_2\)-PMI(Py) dyad \( 14_2 \) and studied the photophysical properties, which show the energy transfer takes place from PMI(OAr)\(_3\) to PMI(Py). The photophysical studies for the dyad \( 14_2 \) show that the direction of the energy transfer changed upon protonation. Additionally, PMI(Py) was found to be a suitable candidate for proton sensor.

I have also successfully synthesized a series of PMI/PMI(OAr)\(_3\) labeled oligoPPEs, where the angle between the long alixs of PMI and PMI(OAr)\(_3\) is 0°. The steady-state and time-resolved measurements show the energy transfer process takes place from the PMI to the PMI(OAr)\(_3\). The FRET efficiency decreases as the distance between the centers of the donor and acceptor increases, which is in good agreement
with the Förster theory. A second series of PMI/PMI(OAr)$_3$ labeled oligoPPEs was synthesized, where the angle between the long axis of PMI and PMI(OAr)$_3$ is 120°. The steady-state and time-resolved measurements show that the FRET efficiencies for these kinked molecules are comparatively smaller than those of their linear counterparts, which is in good agreement with the Förster theory, that the FRET efficiency depends on the relative orientation of the fluorophores. These studies show that the PMI/PMI(OAr)$_3$ labeled oligoPPEs are an efficient system and can be used as molecular ruler for FRET study.
Chapter 5

Alkynyl-substituted perylenemonoimide

(On-going Project)

5.1 Introduction

Perylenemonoimide dye and its derivatives are attractive due to their high quantum yield, photophysical stability, and thermal stability.\textsuperscript{41-44} In chapter 4, I have shown that PMI(OAr)\textsubscript{3} and PMI(Py) can be used as an acceptor fluorophore for energy transfer. The PMI(Py) is also used as donor for electron transfer process.\textsuperscript{58} PMI dye derivatives having absorbance and emission at higher wavelength and high fluorescence quantum yield are still in high demand, due to their potential applications for FRET study and also electron transfer process.

By introducing substituents on the bay region of PMI not only the solubility changes, but also the spectral properties change. The presence of three p-(tert)-butylphenoxy substituents at the bay region of the PMI show a red shift of approximately 30 nm and 45 nm in the absorption and emission maximum, respectively.\textsuperscript{73} Similarly, N-pyrrolidiny1 substituents at the 9-postion of PMI results in a bathochromic shift of the absorption and emission maximum by 80 nm and 156 nm respectively, and the fluorescence quantum yield drops to 0.15 (See Chapter 2.3, Table 2.1). These spectral changes are due to the fact of extended π-conjugation of the substituents with the perylene core.\textsuperscript{60} Keeping this fact in mind, a PMI derivative was designed, where the substituents are para-alkoxyphenyleneethynylene units (Scheme 4. 1). Recently, Edvinsson et al.\textsuperscript{78} reported similar PMI-derivatives for the purpose of solar cells.
5.2 Strategy

**Scheme 5.1** Retro synthesis of akynyl-substituted perylenemonoimide.

The akynyl-substituted PMI 30 carrying a bromo phenylene unit at the imide position will be an ideal fluorophore for attaching with a suitable fluorophore for FRET (Scheme 5.1). For synthesis of the compound 30, the ideal starting point will be the PMI 3b. Bromination of the PMI 3b will produce tribrominated PMI 27, which subsequently
couples with the ethyne to produce the alkynyl-substituted PMI 28. The compound 28 can be hydrolyzed under basic condition to achieve the anhydride 29, which will subsequently treated with 4-bromo-2,6-diisopropylaniline to produce the desired product 30.

5.3 Synthesis

Scheme 5.2 Synthesis of alkynyl-substituted perylenemoiimide.

A solution of PMI 3b in chloroform was refluxed with excess bromine to afford brominated PMI derivatives 27 in 45-52 % yield (Scheme 5.2). The compound 27 was characterized by $^1$H NMR which confirms that it contains a mixture of tribrominated
PMI 27a and 6-7 mol% of tetrabrominated PMI 27b. The compounds 27a and 27b have same Rf on TLC, so we decided to carry out the further reaction taking the mixture.

The mixture of tribrominated PMI 27a with 6-7 mol% of tetrabrominated PMI 27b was coupled with the 3-(4-methoxyphenyl)ethyne by Pd-catalyzed coupling to afford the alkynyl-substituted perylenemonoimide 28 as a pink solid in 34% yield (Scheme 5.2). The compound 28 is only soluble in CHCl₃.

5.4 Photophysical studies

The absorption and emission spectra of compound 28 was measured in toluene and the fluorescence quantum yield was determined taking the benchmark perylene dyes 3b and 25a (Figure 4.8) as the reference.

![Figure 5.1 Absorption (left) and emission (right) spectra of 3a (black), 25a (red), and 28 (blue). The spectra are normalized at their maximum for a good comparability. The excitation wavelength was 475 nm.](image)

The blue line in figure 5.2 left is the absorption of compound 28 and shows two peaks; a shorter wavelength around 345 nm is due to the phenyleneethylene unit. The
peak at higher wavelength around 579 is due to the perylene core. The absorption maximum shows a bathochromic shift of 73 nm and 43 nm in comparison to the benchmark perylene dyes 3b and 25a respectively.

Similarly, the emission spectrum of compound 28 (blue line) shows a bathochromic shift of 85 nm and 40 nm in comparison to the dyes 3b and 25a (Figure 5.1, right).

![Normalized emission spectra](image)

**Figure 5.2** The normalized emission spectra for 25a (red) and 28 (blue).

The fluorescent quantum yield of the compound 28 was determined to be 0.49 by using Eq. 2.1 and the dye 25a was taken as reference with a quantum yield of 0.86 (Figure 5.2).

In summary, alkynyl-substituted perylenemonoimide dye 28 was synthesized successfully. The photophysical studies show that the dye has absorption maximum at 585 nm, emission maximum at 615 nm with a fluorescence quantum yield of 0.49. This fluorophore has poor solubility and also poor yield (34%). In order to improve the solubility, synthetic modifications are necessary. By exchanging the methoxy group for isopropoxy group, the solubility might increase.
Chapter 6

Summary

Perylenemonoimide and aryloxy-substituted perylenemonoimide were synthesized successfully. Amino-substituted perylenemonoimide dyes 6c-6e were synthesized successfully starting from tribrominated perylenemonoimide. These dyes have also been synthesized following a different route starting from monobrominated perylenemonoimide. The photophysical studies show that there is dual fluorescence for the amino-substituted PMI and it is structure specific. The dual fluorescence predominantly observed for the dyes 6d and 6e and this effect increases with increase in the solvent polarity. The dye 6e was used as an acceptor for FRET study and this can be used as proton sensor.

Similarly, alkynyl-substituted dye 28 was synthesized and the phophysical studies show absorption maximum at 585 nm and emission maximum at 615 nm with a fluorescence quantum yield of 0.49.

A series of oligoPPEs with HOM and TIPS as the orthogonal protecting groups, were synthesized by the usual convergent-diversent process. Similarly, another series of oligoPPEs was synthesized by following same convergent-diversent approach where HOE and TIPS are the orthogonal protecting groups. The HOE group was sucessfully removed by the $\gamma$-MnO$_2$/KOH. Freshly prepared $\gamma$-MnO$_2$ is necessary for the removal of HOM and HOE groups. The resulting free acetylenes were used as spacer for the construction of molecular ruler.
A PMI(OAr)₃/PMI(Py) labeled oligoPPE or dyad 14₂ was successfully synthesized. The photophysical studies show that the energy transfer process takes place from PMI(OAr)₃ to the PMI(Py). Interestingly, reverse FRET was observed for the protonated dyad 14₂. This dyad can be used as proton sensor.

A series of linear and kinked dyads were synthesized, where PMI 3b and PMI(OAr)₃ 25a were used as fluorescent probes. In both of these dyads, the energy transfer process takes place from PMI 3b to the PMI(OAr)₃ 25a. The FRET efficiencies for both of the linear and kinked dyads were calculated from the decrease in emission intensities and decrease in lifetime decays of the donor in presence of the acceptor and also from the increase in emission intensity of the acceptor. The correlation between $E$ and the calculated inter-fluorophore distance $R$ shows that the efficiency $E$ decreases as the distance $R$ increases. This result is in very good agreement with the dependency of FRET efficiency on the inverse sixth power of distance $R$. Secondly, the FRET efficiencies of the linear dyads were comparatively higher than the kinked dyads, which suggests that the FRET efficiency depends on the relative orientation of the transition dipole moments of the fluorophores. This is in good agreement with the Förster theory. Therefore, the PMI/PMI(OAr)₃ labeled oligoPPEs are the appropriate molecular ruler for FRET studies.
Chapter 7

Experimental

7.1 General methods and instruments

Perylene-dianhydride, 2,6-diisopropylaniline, Imidazole, Zn(OAc)$_2$·2H$_2$O, $^n$Bu$_4$NF (1M in THF), pyrrolidine, and DMF (anhydrous) were purchased from Acros Organics and Pd$_2$(dba)$_3$, p(o-toly)$_3$ were from Aldrich. Bromine, Et$_3$N, toluene and 4-tert-butylphenol were purchased from Merck. All chemicals were used as received. CDCl$_3$ and CD$_2$Cl$_2$ were obtained from Flora Chemicals. Previously synthesized compounds 1,4-dihexyl-2,6-diiodobenzene, iodomonomer 7a$_1$, iododimer 7b$_2$ and tetramer 8a$_4$ were available from our laboratory. PMI(pip) 6c, PMI(EtHex) 6d, PMI(Py) 6e, and PMI(Me)$_2$ 6g, used for the photophysical studies were synthesized by Ms. Miriam Schulte starting from monobromo perylenemonoimide PMI(Br) 4c under my assistance.

The photophysical studies were carried out in cooperation with Prof. Dr. Markus Sauer’s group at the Department of Physics, Bielefeld University. These experiments were carried out together with Dr. Ralf Brune.

Absorption spectra were taken on a UV/Vis spectrophotometer (Perkin Elmer). Fluorescence spectra were recorded with a spectrofluorimeter (Cary Eclipse) at concentrations of below $10^{-6}$ M. Ensemble fluorescence lifetime measurements were performed on a 5000 MC spectrometer (IBH, Glasgow, UK) using time-correlated single-photon counting (TCSPC). As excitation source a pulsed light emitting diode (center 450 nm) with a repetition rate of 1 MHz and a pulse length of 1~ns (FWHM) was used. With
this setup an instrument response function (IRF) of 1 ns (FWHM) was measured. Typically, 3000 photon counts were collected in the maximum channel using 2048 channels. The decay parameters were determined by least-square deconvolution, and their quality was judged by the reduced $\chi^2$ values and the randomness of the weighted residuals. All fluorescence decays measured could be described satisfactorily by a monoexponential model. Measurements were performed at room temperature (20 °C).

- **Thin layer chromatography (TLC)**
  
  Silica gel coated on aluminium plate with fluorescent indicator from Merck, silica gel size 60, $F_{254}$, layer thickness 0.25 mm
  
  Detection: UV-Lamp, Beneda 366/254, heidelberg

- **Column chromatography**
  
  Silica gel MN-60 (Mesh size 40-63 μm and 63-200 μm) from Merck

- **HPLC**
  
  Aligant 1200 series
  
  Detector: UV-Vis, Emission
  
  Reverse Phase Column: $C_{18}$ Spiex from Macherey & Nagel.

- **Nuclear magnetic resonance spectroscopy (NMR)**
  
  $^1H$ NMR
  
  Instruments: Bruker AM 250 (250.133 MHz), DRX 500 (500.132, MHz), DRX 600 (600.133, MHz), with internal standards: $CDCl_3$ (7.25 ppm), $CD_2Cl_2$ (5.32 ppm).
  
  Measurement Temperature: 300 K
The chemical shifts are given in ppm, coupling constants \( (J) \) are given in Hz. The multiplicity of the signals are given as \( s = \) singlet, \( d = \) doublets, \( t = \) triplets, \( q = \) quartets, and \( m = \) multiplets.

\(^{13}\)C NMR

Instrument: Bruker AM 250 (62.896 MHz), DRX 500 (125.772, MHz), with internal standards: CDCl\(_3\) (77.0 ppm), CD\(_2\)Cl\(_2\) (53.5 ppm).

Measurement Temperature: 300 K

- MALDI TOF

MALDI TOF mass spectra were recorded with a Vozager\(^\text{®}\) DE instrument mounted with 1.2 m flight tube. Isolation was achieved using LSI nitrogen laser (337 nm beam wavelength, 3 ns pulse width, 3 Hz repetition rate). Depending on the mass range the ions were accelerated with 15 to 20 kV. If not mentioned differently, 2-[(2E)-3-(4-t-butylphenyl)-2-methylpro-2-enylidene]malononitrile was used as the matrix and THF as the solvent to prepare the samples.

7.2 General procedures

7.2.1 General procedure A: Alkyny-Aryl coupling for oligoPPEs

In a Schlenk flask the coupling components were taken along with dry THF and dry piperidine. The reaction mixture was degassed through freeze-pump-thaw cycles for three times.\(^69,70\) To the degassed reaction mixture Pd(PPh\(_3\))\(_2\)Cl\(_2\) (1 mol % with respect to the aryl halide) and CuI (2 mol % with respect to the aryl halide) were added. The reaction mixture was stirred at room temperature for 18 h. After 18 h, Et\(_2\)O and 2 N HCl
was added successively. The phases were separated and the aqueous phase was extracted with Et₂O. The combined organic phases were washed with water and then dried over Na₂SO₄. The products were isolated by column chromatography. In case of oligomers, the first fractions were collected as the dimer of the respective non-polar acetylene used for the coupling.

7.2.2 General procedure B: Synthesis of acetylene

To a solution of 8aₙ, 15ₙ, and 17ₙ in THF, 1 M nBuN₄F in THF (2 equiv.) was added and stirred at room temperature. After 2 h, Et₂O and water were added to the reaction mixture and stirred for 5 minutes. The aqueous phase was separated and extracted with Et₂O. The combined organic phases were washed with water. The organic phase was dried over Na₂SO₄ and the solvent was evaporated to get the required products.

7.2.3 General procedure C: Synthesis of non-polar acetylene 9aₙ

The solution of oligoPPEs 8aₙ (n = 5), and 8bₙ (n = 6, 7, 9) in Et₂O were treated with activated γ-MnO₂/KOH in four portions, each at the interval of every one hour. After completion of reaction, the reaction mixture was filtered through a pad of silica gel and subsequent evaporation of the solvent gave compounds 9aₙ (n= 5-9).

In case of 8bₙ THF was used as solvent and excess MnO₂/KOH was added till completion of reaction. The duration of reaction for 9bₙ was about 5-6 h.

7.2.4 General Procedure D: Alkynyl-aryl coupling using Pd₂(dba)₃ and P(o-tolyl)₃

In a Schlenk flask the coupling components (aryl halide, free acetylene) were taken along with toluene and Et₃N and degassed for three times through freeze-pump-
thaw cycles. To the degassed reaction mixture in frozen state Pd$_2$(dba)$_3$ (10 mol% with respect to the aryl halide) and P(o-tolyl)$_3$ (65 mol% with respect to the aryl halide) were added under argon.$^{56}$ The flask was evacuated and refilled with argon for three times. The reaction mixture was stirred at 65 °C. After 18 h, the reaction mixture was cooled to room temperature. Et$_2$O and 2 N HCl were added successively to it and the reaction mixture was stirred for 5 min. The aqueous phase was separated and extracted with Et$_2$O. The combined organic phases were washed with water and then dried over Na$_2$SO$_4$. The products were isolated by column chromatography.

7.2.5 General Procedure E: Synthesis of amino-substituted perylenemonoimide

A sample of 4, and the corresponding amines (excess) were taken in a flask along with anhydrous DMF under argon. The reaction mixture was refluxed for 3 h. After cooling the reaction mixture to room temperature, Et$_2$O, 2N HCl were added successively and stirred for 5 min. The organic phase was separated out and the aqueous phase was extracted with Et$_2$O (3 x). The combined organic phases were washed with distilled water. The organic phase was dried over Na$_2$SO$_4$ and the solvent was evaporated to get the crude materials. The products were isolated by column chromatography.

7.3 Synthesis of perylenemonoimide derivatives

7.3.1 Synthesis of perylenemonoimide 3a
Following the procedure described by Lindsey et al., hydrobromide 1a (600 mg, 2.05 mmol), perylene dianhydride 2 (1.58 g, 4.04 mmol), Zn(OAc)$_2$·2H$_2$O (540 mg, 2.46 mmol), imidazole (7.8 g), and distilled water (3.5 mL) were heated at 190 °C for 18 h in a thick walled pressure tube (35 mL, 17.8 cm x 25.4 mm). After cooling the reaction mixture to room temperature, the pressure was released. The crude material was suspended in distilled water and the suspension was filtered. The solid that had been filtered from the suspension was resuspended in (1:1) conc. HCl, MeOH and filtered. Finally the solid that had been filtered from the second suspension was suspended in MeOH and filtered. The solid was dried under vacuum. The solid obtained after drying was suspended in CHCl$_3$ (15 mL) and loaded on a column (silica gel, 4 x 30 cm$^2$) and eluted with CHCl$_3$. A slightly yellow byproduct (perylene) was eluted first, which was not collected. Subsequently, the required product 3a was eluted in the 2nd fraction. The solvent was evaporated to afford 3a as a red solid (303 mg, 30%). $^1$H NMR data is identical to those reported by Lindsey.

7.3.2 Synthesis of perylenemonoimide 3b

Following the procedure described by Lindsey et al. for imidation and double decarboxylation in an autoclave but in a thick walled pressure tube (35 mL, 17.8 cm x 25.4 mm), a commercially available perylene dianhydride 2 (1.9 g, 4.04 mmol), 2,6-diisopropylaniline (470 mg, 2.65 mmol), Zn(OAc)$_2$·2H$_2$O (693 mg, 3.16 mmol), imidazole (9.9 g), and distilled water (4.0 mL) were heated at 190 °C for 18 h. After cooling the
reaction mixture to room temperature, the pressure was released. The crude material was suspended in distilled water and the suspension was filtered. The solid that had been filtered from the suspension was resuspended in (1:1) conc. HCl, MeOH and filtered. Finally the solid that had been filtered from the second suspension was suspended in MeOH and filtered. The solid was dried under vacuum. The solid obtained after drying was suspended in CHCl₃ (15 mL) and loaded on a column (silica gel, 4 × 25 cm², CHCl₃) and eluted with CHCl₃. A slightly yellow byproduct (perylene) was eluted first, which was not collected. Subsequently, the required product 3b was eluted in the 2nd fraction. The solvent was evaporated to afford 3b as red solid (600 mg, 47%, \( R_f = 0.13 \)).

\(^1\)H NMR (500 MHz): \( \delta = 1.17 \) (d, \( J = 6.9 \) Hz, 12 H, CH(CH₃)₂), 2.73-2.79 (m, 2 H, CH(CH₃)₂), 7.33 (d, \( J = 7.8 \) Hz, 2 H, Ar-H ortho to CH(CH₃)₂), 7.47 (t, \( J = 7.8 \) Hz, 1 H, Ar-H meta to CH(CH₃)₂), 7.65 (t, \( J_1 = 7.8 \) Hz, 2 H, H-8, H-11), 7.92 (d, \( J = 8.1 \) Hz, 2 H, H-9, H-10/H-7, H-12). 8.47 and 8.48 (2 d, \( J_1 = 8.5 \) Hz, \( J_2 = 8.0 \) Hz, 4 H, H-1, H-2, H-5, and H-6), 8.66 (d, \( J = 8.0 \) Hz, 2 H, H-7, H-12/H-9, H-10). - MALDI TOF: \( m/z = 482.6 \).

7.3.3 Synthesis of bromo-substituted perylenemonoimide 4

The procedure described by Lindsey et al. \(^{56} \) was followed. Br₂ (0.85 mL, 16.41 mmol) was added to a solution of 3a (460 mg, 0.82 mmol) in CHCl₃ (25 mL) and heated to reflux. After 3 h and 5 h, identical amounts of Br₂ were added. After a total reaction
time of 8 h, the reaction mixture was cooled to room temperature with an ice bath. The cooled reaction mixture was treated with saturated aqueous Na$_2$SO$_3$ solution (40 ml) and stirred for 3-4 min. suddenly; the reaction mixture came out from the flask due to exothermic reactions. The reaction mixture was collected and washed with Na$_2$SO$_3$ solution. Finally, the organic phase was washed with water and then dried over Na$_2$SO$_4$. The solvent was evaporated to get the crude product. Column chromatography (4 x 30 cm$^2$ silica gel, (1:1) CHCl$_3$/n-hexane) afforded a 12.6:1.0 mixture (340 mg, $R_f$ = 0.61 in 3:1 CHCl$_3$ and n-hexane) of 4a (313 mg, 48%) and 4b (27 mg, 4%) as a red solid.

$^1$H NMR (500 MHz) of 4a: $\delta$ = 1.15 (d, $J$ = 6.8 Hz, 12 H, CH(CH$_3$)$_2$), 2.63-2.68 (m, 2 H, CH(CH$_3$)$_2$), 7.44 (s, 2 H, Ar-H ortho to CH(CH$_3$)$_2$), 7.81 (t, $J$ = 8.1 Hz, 1 H, H-11), 7.99 (d, $J$ = 8.3 Hz, 1 H, H-7/8), 8.46 (d, $J$ = 8.4 Hz, 1 H, H-12/10), 8.90 and 8.92 (2 s, 1 H each, H-2, H-5), 9.11 (d, $J$ = 8.3 Hz, 1 H, H-8/7), 9.33 (d, $J$ = 7.5 Hz, 1 H, H-10/12). - MALDI TOF: $m/z$ = 797.7.

These signals have higher intensity than expected and this higher intensity is due to the additional signal for the phenylene group at the imides moiety of 4b. The remaining signals due to the compound 4b are $\delta$ = 8.11 (d, $J$ = 8.3 Hz, 2 H, H-7, H-12/H-8, H-11), 8.88 (s, 2 H, H-2, H-5), 8.94 (d, $J$ = 8.3 Hz, 2 H, H-8, H-11/H-7, H-12).
7.3.4 Synthesis of aryloxy-substituted perylenemonoimide 5

Following the procedure described by Lindsey et al. a (12.6:1) mixture of 4a and 4b (340 mg, 0.43 mmol), 4-tert-butylphenol (767.8 mg, 5.11 mmol), and K$_2$CO$_3$ (848 mg, 6.13 mmol) were dissolved in DMF (25 mL, anhydrous) under argon and refluxed at a bath temperature of 170 °C for 1 h. After cooling down the reaction mixture, the DMF was distilled off by vacuum distillation using the diaphragm pump and heating the reaction mixture to 60 °C. Water (100 mL) and CHCl$_3$ (100 mL) were added to the residue and stirred for 10 min. The organic phase was separated out and the aqueous phase was extracted with CHCl$_3$ (3 x 25 mL). The combined organic phases were dried over Na$_2$SO$_4$. The solvent was evaporated to get the crude product. Column chromatography (silica gel, 4 x 30 cm$^2$, CHCl$_3$/n-hexane (4:6)) afforded a 13.7:1.0 mixture (65 mg, $R_f$ = 0.33) of 5a (61 mg, 16%) and 5b (4 mg, 1%) as a magenta solid in the first fraction. In the second fraction a 32:1.0 mixture (180 mg) of 5a (175 mg, 44%) and 5b (5 mg, 1.5%) was isolated as a magenta solid. A 1.5:1.0 mixture (40 mg) of 5a
(23 mg, 16%) and 5c (17 mg, 44%) was isolated as third fraction, and subsequently 5c was isolated (8 mg, 22%) with traces of unknown impurity in the 4th fraction.

\(^1\)H NMR (500 MHz): \(\delta = 1.12 \text{ (d, } J = 6.6 \text{ Hz, } 12 \text{ H, } \text{CH(CH}_3_2^*\text{), 1.31, (3s, 9 H, } t\text{-butyl), 1.33, and 1.34 (s, 9 H each, } t\text{-butyl), 2.62-2.71 (m, 2 H, } \text{CH(CH}_3_2^*\text{), 6.89 (d, } J = 8.8 \text{ Hz, 1 H, } H\text{-8/7), 7.00 (2 H, half of AA'XX' spinsystem, } O\text{Ar-H meta to } t\text{-butyl), 7.06 and 7.09 (2 H each, half of AA'XX' spinsystem, } O\text{Ar-H meta to } t\text{-butyl), 7.36 (2 H, half of AA'XX' spinsystem, } O\text{Ar-H ortho to } t\text{-butyl), 7.38 (s, 2 H, } \text{Ar-H ortho to } \text{CH(CH}_3_2^*\text{), 7.41 (4 H, half of AA'XX' spinsystem, } \text{Ar-H ortho to } t\text{-butyl), 7.64 (t, } J = 8.0 \text{ Hz, 1 H, } H\text{-11), 8.28 and 8.32 (2 s, 1 H each, } H\text{-2, } H\text{-5'), 8.48 (d, } J = 8.1 \text{ Hz, 1 H, } H\text{-10/12), 9.24 (d, } J = 8.8 \text{ Hz, 1 H, } H\text{-7/8), 9.44 (d, } J = 7.5 \text{ Hz, 1 H, } H\text{-12/10). MALDI TOF: } m/z = 1005.22.

These signals have higher intensity than expected and this higher intensity is due to the additional signals for the phenylene group at the imide position and the aryloxy group present at the bay region (1 and 9 position) of 5b. The remaining signals due to the compound 5b are \(\delta = 7.59 \text{ (t, } J = 7.9 \text{ Hz, 2 H, } H\text{-8, } H\text{-11), 7.91 (d, } J = 8.1 \text{ Hz, 2 H, } H\text{-9, } H\text{-10/H-7, } H\text{-12), 9.36 (d, } J = 7.9 \text{ Hz, 2 H, } H\text{-7, } H\text{-12/H-9, } H\text{-10).}

7.3.5 Piperidinyl-substituted perylenemonoimide 6c

Following general procedure E, the mixture of 4a and 4b (25 mg, 0.03 mmol), piperidine (1.0 mL, 10.123 mmol) were refluxed with anhydrous DMF (3 mL) under argon for 3 h to obtain the required product 6c. Column chromatography [4 x 15 cm,
silica gel, CHCl$_3$:$n$-Hexane (1:1) and then the solvent was changed to CHCl$_3$ and later MeOH:CHCl$_3$ (1:20)] afforded desired product 6c as violet solid (9 mg, 45%).

$^1$H NMR (250 MHz) $\delta = 1.16$ (d, $J = 6.75$ Hz, 12 H, CH(CH$_3$)$_2$), 1.72 (m, 2 H, $CH_2\gamma$ to N), 1.89 (m, 4 H, $CH_2\beta$ to N), 2.75 (m, 2 H, CH(CH$_3$)$_2$), 3.19 (m, 4 H, $CH_2\alpha$ to N), 7.19 (d, $J = 8.3$ Hz, 1 H, H-8), 7.43 (s, 1 H, Ar-H ortho to CH(CH$_3$)$_2$), 7.61-7.67 (t, $J = 7.75$ Hz, 1 H, H-11), 8.25 (d, $J = 8.5$ Hz, 1 H, H-10), 8.31 (d, $J = 8.3$ Hz, 1 H, H-7), 8.38 and 8.42 (2d, $J = 7.25$ Hz, 1 H each, H-1, H-6), 8.47 (d, $J = 6.8$ Hz, 1 H, H-12), 8.56 and 8.62 (2d, $J = 5.5$ Hz, 1 H each, H-2, H-5).

7.3.6 2-Ethylhexylamine-substituted perylenemonoimide 6d

Following general procedure E, a sample of 4 (25 mg, 0.03 mmol), 2-ethylhexylamine (1.5 mL, 10.613 mmol) were refluxed with anhydrous DMF (3 mL) under argon for 3 h to obtain the required product 6d. Column chromatography [4 x 15 cm$^2$ silica gel, 1:1 mixture of CHCl$_3$ and n-Hexane. Later the solvent was changed to CHCl$_3$ and finally a 1:20 mixture of MeOH and CHCl$_3$] afforded desired product 6d as a blue solid (12 mg, 57%).

$^1$H NMR (600 MHz) $\delta = 0.94$ (m, 3 H, CH$_2$CH$_3$), 1.01 (m, 3 H, CH$_2$CH$_3$), 1.15 (d, $J = 6.6$ Hz, 12 H, CH(CH$_3$)$_2$), 1.38 (m, 4 H, CH$_2$), 1.52 (m, 4 H, CH$_2$), 1.80 (m, 1 H, CHCH$_2$NH), 2.72 (m, 2 H, CH(CH$_3$)$_2$), 3.34 (t, $J = 11.1$ Hz, 2 H, CH$_2$NH), 5.02 (t, $J = 4.8$
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Hz, 1 H, NH), 6.77 (d, J = 8.4 Hz, 1 H, H-8), 7.42 (s, 1 H, Ar-H ortho to CH(CH₃)₂), 7.60 (t, J = 7.8 Hz, 1 H, H-11), 7.86 (d, J = 8.4 Hz, 1 H, H-10), 8.19 (d, J = 8.4 Hz, 1 H, H-7), 8.37 and 8.39 (2d, J = 8.4 Hz, 1 H each, H-1, H-6), 8.52 (d, J = 7.2 Hz, 1 H, H-2/5), 8.54 (d, J = 7.8 Hz, 1 H, H-5/2), 8.59 (d, 1H, J = 7.8 Hz, H-12).

7.3.7 Pyrolidnyl-substituted perylenemonoimide 6e

Following general procedure E, the mixture of 4a and 4b (202 mg, 0.25 mmol), pyrrolidine (4 mL, 48.7 mmol) and anhydrous DMF (10 mL) under argon were refluxed for 3 h to obtained 6e. Column chromatography (4 x 22 cm² silica gel, Et₂O) afforded 6e as blue solid (132 mg, 82%).

¹H NMR (250 MHz): δ = 1.15 (d, J = 7.5 Hz, 12 H, CH(CH₃)₂), 2.09 (t, J = 6.5 Hz, 4 H, CH₂), 2.73 (m, 2 H, CH(CH₃)₂), 3.70 (t, J = 6.5 Hz, 4 H, CH₂), 6.95 (d, J = 8.7 Hz, 1 H, H-8), 7.42 (s, 1 H, Ar-H ortho to CH(CH₃)₂), 7.52-7.59 (t, J = 7.7 Hz, 1 H, H-11), 8.21 (d, J = 8.5 Hz, 1 H, H-10), 8.33-8.39 (3d, J₁ = 7.7 Hz, J₂ = 8.8 Hz, J₃ = 8.2 Hz, 1 H each H-1, H-6, H-7), 8.50 (d, J = 7.2 Hz, 1 H, H-12), 8.55 and 8.59 (2 d, J = 8.2 Hz, 1 H each, H-2, H-5).
7.4 Synthesis of oligoPPEs

7.4.1 Iodotrimer 7a₃

Following the general procedure A, a solution of free acetylene 9c₂ (4.0 g, 6.75 mmol), 1,4-dihexyl-2,5-diiodobenzene (33.6 g, 67.46 mmol) in THF (95 mL) and piperidine (30 mL) was degassed for three times. Pd(PPh₃)₂Cl₂ (46.5 mg, 0.9 mol% with respect to 9c₂) and Cul (26.3 mg, 2.0 mol% with respect to 9c₂) were added to the degassed reaction mixture and stirred at room temperature for 18 h to afford the iodotrimer 7a₃. Flash chromatography (6 x 30 cm² silica gel, n-pentane) gave the 1,4-dihexyl-2,5-diiodobenzene (31.1 g, 92%, \( R_f = 0.84 \)) and 7a₃ (3.42 g, 53%, \( R_f = 0.4 \)) as a yellow-brown solid by eluting with n-pentane/CH₂Cl₂, 3:1 v/v.

M.p.: 72-73°C. - \(^1\text{H} \text{NMR (250 MHz, CD₂Cl₂):} \delta = 7.72 \text{ (s, 1 H, Ar-H ortho to iodo), 7.39 (s, 2 H, Ar-H), 7.36, 7.34, and 7.31 (3 s, 3 H, Ar-H), 4.53 (d, } J = 6.1 \text{ Hz, 2 H, CH}_2\text{OH), 2.87-2.65 (m, 12 H, Ar-CH}_2\text{), 1.80-1.58 (m, 12 H, ArCH}_2\text{CH}_2\text{), 1.37-1.32 (m, 36 H, CH}_2\text{), 1.06 (s), 1.05 (s, 1 H), 0.92-0.86 (m, 18 H, CH}_3\text{).} \) \(^{13}\text{C} \text{NMR:} \delta = 144.3 \text{ (C, I-C-C-Hexyl), 143.4, 142.8, 142.5 and 142.4 (5 C, C-Hexyl), 139.9 (CH, arom.CH ortho to iodo), 132.9, 132.8 and 132.7 (4 CH, arom. CH), 123.4, 123.2, 123.1 and 122.4 (5 C, C- C=C), 101.2 (C, C-I), 93.3, 92.9, 92.8 and 92.5 (4 C, C=C), 84.5 (C, C=CCH}_2\text{OH), 52.0 (CH}_2\text{, CH}_2\text{OH), 40.6 (CH}_2\text{, Ar-CH}_2\text{ ortho to iodo) 34.5, 34.3 and 34.2 (4 CH}_2\text{, Ar-CH}_2\), 32.2, 32.1, 31.1, 30.9, 30.6, 29.7, 29.6, 29.5, 29.4, 23.1 and 23.0 (14 CH}_2\text{), 17.9

7.4.2 Pentamer 8a₅

Following the general procedure A, a solution of iodotrimer 7a₃ (1.64 g, 1.71 mmol) and the free acetylene 9a₂ (1.33 g, 1.85 mmol) in THF (50 mL) and piperidine (15 mL) was degassed for three times. Pd(PPh₃)₂Cl₂ (12.2 mg, 1.0 mol%) and CuI (6.7 mg, 2.0 mol%) were added to the degassed reaction mixture and stirred at room temperature for 18.5 h to afford pentamer 8a₅. Column chromatography (5 x 25 cm² silica gel, n-pentane/CH₂Cl₂, 3:1 v/v) afforded 8a₅ as a yellow solid with traces amount of impurity in 2nd fraction (1.19 g) and 3rd fraction (1.23 g) respectively. The 3rd fraction was recolumned to afford 8a₅ (985 mg) as a yellow solid with traces of impurity. However the 2nd fraction of the first column was dissolved in CH₂Cl₂ (2-3 ml) and MeOH was slowly added to it. 8a₅ was precipitated out and filtered to afford 971 mg with reasonable purity (Rf = 0.47).

M.p.: 109-110 °C. ¹H NMR (250 MHz, CD₂Cl₂): δ = 7.42-7.36 (m, 8 H, Ar-H), 7.34 (s, 1 H, Ar-H), 7.32 (s, 1 H, Ar-H), 4.53 (s, 2 H, CH₂OH), 2.90-2.72 (m, 20 H, Ar-CH₂), 1.74-1.69 (m, 20 H, ArCH₂-CH₂), 1.37-1.25 (m, 60 H, CH₂), 1.18 (s, 21 H, TIPS), 0.93-0.91 (m, 30 H, CH₃). ¹³C NMR: δ = 143.2, 142.8, 142.5 and 142.4 (4 C, C-Hexyl), 133.3, 132.9, and 132.8 (3 CH, arom. CH), 123.4, 123.3 and 122.4 (3 C, C=C=C), 106.1 and 95.9 (2 C, C≡CTIPS), 93.5, 93.4, 92.5 (3 C, C≡C), 84.5 (C, C≡CCH₂OH), 52.0
(CH₂, CH₂OH), 34.8, 34.6 and 34.3 (3 CH₂, ArCH₂), 32.3, 32.1, 31.4, 31.3, 31.2, 31.1, 31.0, 29.7, 29.5, 23.1 and 22.8 (12 CH₂), 18.9 (CH₃, CH₂OHCH₃), 14.3 (CH₃, CH₂CH₃), 11.9 (CH, SiCH(CH₃)₃). – MALDI TOF: m/z 1553.98. Anal. Calcd for C₁₁₂H₁₆₄OSi (1554.64): C, 86.53; H, 10.63. Found C, 85.92; H, 11.09.

7.4.3 Hexamer 8b₆

Following the general procedure A, a solution of iododimer 7b₂ (160 mg, 0.23 mmol) and the free acetylene 9a₄ (303 mg, 0.24 mmol) in THF (13 mL) and piperidine (4 mL) was degassed for three times. Pd(PPh₃)₂Cl₂ (1.6 mg, 1.0 mol%), CuI (1.3 mg, 3.0 mol%) were added to the degassed reaction mixture and stirred at room temperature for 18 h to afford hexamer 8b₆. The product was isolated as a yellow solid (334 mg, 80%, Rᵣ = 0.61) by flash chromatography (4 x 35 cm², silica gel, n-pentane/CH₂Cl₂ (1:1)).

M.p. : 119-121 °C. -¹H NMR (500 MHz, CD₂Cl₂): δ = 7.41-7.39 (m, 8 H, Ar-H), 7.35 (s, 2 H, Ar-H), 7.33 (s, 1 H, Ar-H), 7.29 (s, 1 H, Ar-H), 4.81-4.76 (m, 1 H, CHOH), 2.86-2.71 (m, 24 H, Ar-CH₂), 1.98 (d, J = 5.0 Hz, 1 H, OH), 1.73-1.61 (m, 24 H, ArCH₂-CH₂), 1.56 (d, J = 6.2 Hz, 3 H, CH(OH)CH₃), 1.44-1.35 (m, 72 H, CH₂), 1.16 (s, 21 H, TIPS), 0.91-0.90 (m, 36 H, CH₃). – ¹³C NMR: δ = 143.1, 142.7, 142.4 and 142.3 (4 C, C-Hexyl), 133.2, 132.8 and 132.7 (3 CH, arom. CH), 123.1 and 122.4 (2 C, C=C≡C), 106.0 and 96.2 (2 C, C≡CTIPS), 95.8, 93.4, and 93.2 (3 C, C≡C), 82.8 (C, C≡CCHOH), 59.2 (CH, CHOCH), 34.7, 34.5, 34.4 and 34.3 (4 CH₂, ArCH₂), 32.2, 32.1, 31.3, 31.2, 31.1,
31.0, 29.7, 29.6, and 23.1 (12 CH$_2$), 24.7 (CH$_3$, CHOCH$_3$), 18.9 (CH$_3$, CH(CH$_3$)$_2$), 14.3 (CH$_3$, CH$_2$CH$_3$), 11.8 (CH, SiCH(CH$_3$)$_3$). – MALDI TOF: $m/z$ 1836.53. Anal. Calcd for C$_{133}$H$_{194}$OSi (1837.11): C, 86.96; H, 10.64. Found C, 86.93; H, 10.84

7.4.4 Heptamer 8b$_7$

Following the general procedure A, a solution of iododimer 7b$_2$ (195 mg, 0.28 mmol) and the free acetylene 9a$_5$ (442 mg, 0.29 mmol) in THF (12 mL) and piperidine (4 mL) was degassed for three times. Pd(PPh$_3$)$_2$Cl$_2$ (3.0 mg, 1.5 mol%), Cul (1.5 mg, 2.8 mol%) were added to the degassed reaction mixture and stirred at room temperature for 19 h to afford heptamer 8b$_7$. The product was isolated as a yellow solid (565 mg, 97 %, $R_f = 0.57$) by flash chromatography (4 x 25 cm$^2$ silica gel, n-pentane/Et$_2$O, 4:1 v/v).

M.p. : 133-135°C. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ = 7.41-7.39 (m, 10 H, Ar-H), 7.35 (s, 2 H, Ar-H), 7.33 (s, 1 H, Ar-H), 7.29 (s, 1 H, Ar-H), 4.79-4.77 (m, 1 H, CHOH), 2.87-2.71 (m, 28 H, Ar-CH$_2$), 1.96 (d, $J = 5.4$ Hz, 1 H, OH), 1.76-1.61 (m, 28 H, ArCH$_2$), 1.55 (d, $J = 8.1$ Hz, 3 H, CH(OH)CH$_3$), 1.44-1.34 (m, 84 H, CH$_2$), 1.16 (s, 21 H, TIPS), 0.91-0.89 (m, 42 H, CH$_3$). – $^{13}$C NMR: $\delta$ = 143.1, 142.7, 142.4 and 142.3 (4 C, C-Hexyl), 133.2, 132.8 and 132.7 (3 CH, arom. CH), 123.1 and 122.3 (2 C, C-C=C), 106.0 and 96.2 (2 C, C=C=CTIPS), 95.8, 93.4, and 93.2 (3 C, C=C), 82.7 (C, C=C=CHOH), 59.2 (CH, CHOHOH), 34.7, 34.5, and 34.3 (3 CH$_2$, ArCH$_2$), 32.2, 32.1, 31.3, 31.2, 31.1, 30.9, 29.7, 29.5 and 23.1 (10 CH$_2$), 24.7 (CH$_3$, CHOHOHCH$_3$), 18.8 (CH$_3$, CH(CH$_3$)$_2$), 14.3 (CH$_3$, CH$_2$CH$_3$).
CH$_2$CH$_3$), 11.7 (CH, SiCH(CH$_3$)$_3$). – MALDI TOF: $m/z = 2103.44$. Anal. Calcd for C$_{153}$H$_{222}$OSi (2105.56): C, 87.28; H, 10.63. Found C, 87.28; H, 10.45.

7.4.5 Heptamer 8a$_7$

Following the general procedure A, a solution of iodotrimer 7a$_3$ (110 mg, 0.11 mmol), and the free acetylene 9a$_4$ (152 mg, 0.12 mmol) in THF (10 mL) and piperidine (4 mL) was degassed for three times. Pd(PPh$_3$)$_2$Cl$_2$ (1.2 mg, 1.4 mol%) and CuI (1.0 mg, 4.0 mol%) were added to the degassed reaction mixture and stirred at room temperature for 19 h to afford the heptamer 8a$_7$. The product was isolated as a yellow solid (221 mg, 92 %, $R_f = 0.63$) by flash chromatography (4 x 25 cm$^2$ silica gel, n-pentane/CH$_2$Cl$_2$, 1:1 v/v)

M.p. : 148-149°C. $^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ = 7.40-7.39 (m, 8 H, Ar-H), 7.35, 7.33, 7.30 (4 s, 1 H each, Ar-H), 7.32 (s, 2 H, Ar-H), 4.52 (d, $J = 6.1$ Hz, 2 H, CH$_2$OH), 2.87-2.72 (m, 28 H, Ar-CH$_2$), 1.75-1.63 (m, 28 H, ArCH$_2$-CH$_2$), 1.50-1.26 (m, 84 H, CH$_2$), 1.16 (s, 21 H, TIPS), 0.90-0.88 (m, 42 H, CH$_3$). $^{13}$C NMR (250 MHz, CD$_2$Cl$_2$): $\delta$ = 143.1, 142.8, 142.5 and 142.4 (4 C, C-Hexyl), 133. 3 and 132.8 (2 CH, arom. CH$_3$), 123.4, 123.2 and 122.4 (3 C, C=C=C), 106.1 and 95.9 (2 C, C=C=CTIPS), 93.5, 93.3, 92.5 (3C, C=C), 84.5 (C, C=CCCH$_2$OH), 77.9 (c), 52.0 (CH$_2$, CH$_2$OH), 34.8, 34.6 and 34.2 (3 CH$_2$, ArCH$_2$), 32.3, 32.1, 31.3, 31.2, 31.1, 30.9, 29.7, 29.5, 23.1 and 23.0 (10 CH$_2$), 18.9 (CH$_3$, CH$_2$OHCH$_3$), 14.3 (CH$_3$, CH$_2$CH$_2$), 11.8 (CH, SiCH(CH$_3$)$_3$). – MALDI TOF: $m/z = 2090.01$. Anal. Calcd for C$_{152}$H$_{220}$OSi (2091.53): C, 87.29; H, 10.60. Found C, 86.51; H, 10.69.
7.4.5 Nonamer \(8b_9\)

Following the general procedure A, a solution of iododimer \(7b_2\) (45 mg, 0.06 mmol) and the free acetylene \(9a\) (140 mg, 0.07 mmol) in THF (5 mL) and piperidine (2 mL) was degassed for three times. \(\text{Pd(PPh}_3\text{)}_2\text{Cl}_2\) (1.1 mg, 2.5 mol%) and \(\text{CuI}\) (1.0 mg, 8.3 mol%) were added to the degassed reaction mixture and stirred at room temperature for 20 h to afford the iodotrimer \(8b_9\). The product \(8b_9\) (133 mg, 79 %, \(R_f = 0.20\)) was isolated as a yellow solid by flash chromatography (4 x 25 cm\(^2\) silica gel, \(n\)-pentane/CH\(_2\)Cl\(_2\), 3:1 v/v).

\(\text{M.p. : 162-165}^\circ\text{C.} \quad \text{\(^1H\ NMR}\ (500 \text{MHz, CD}_2\text{Cl}_2):} \quad \delta = 7.41-7.39 \text{ (m, 12 H, Ar-}H), 7.35 \text{ (s, 2 H, Ar-}H), 7.33 \text{ (s, 1 H, Ar-}H), 7.32 \text{ (s, 2 H, Ar-}H), 7.28 \text{ (s, 1 H, Ar-}H), 4.79-4.77 \text{ (m, 1 H, CHOH), 2.87-2.45 \text{ (m, 36 H, Ar-}CH_2), 1.74-1.61 \text{ (m, 36 H, ArCH}_2\text{-}CH_2)\), 1.55 \text{ (d, } J = 6.5 \text{ Hz, 3 H, CH(OH)}\text{-}CH_3), 1.44-1.26 \text{ (m, 108 H, CH}_2\text{), 1.16 \text{ (s, 21 H, TIPS), 0.91-0.88 \text{ (m, 54 H, CH}_3).} \quad \text{\(^{13}C\ NMR:} \quad \delta = 143.1, 142.7, 142.4 \text{ and 142.3 (4 C, C-Hexyl), 133.2, 132.8 and 132.7 (3 CH, arom. } CH), 123.1 \text{ and 122.3 (2 C, C-C=C), 106.0 and 96.2 (2 C, C=CTIPS), 95.8, 95.6, 95.4, 93.4, and 93.2 (3 C, C=C), 82.7 (C, C=CCHOH), 59.2 (CH, CHOH), 34.7, 34.5, and 34.3 (3 CH}_2, ArCH_2), 32.2, 32.1, 31.3, 31.2, 31.1, 30.9, 30.1, 29.7, 29.5 \text{ and 23.1 (11 CH}_2), 24.7 (CH}_3, CHOHCH}_3), 18.8 (CH}_3, CH(CH}_3)_2), 14.3 (CH}_3, CH}_2CH}_3), 11.7 (CH, SiCH(CH}_3)_3). \quad \text{MALDI TOF:} \quad m/z = 2640.68. \quad \text{Anal. Calcd for C}_{193}H_{278}OSi (2642.45):} \quad \text{C, 87.73%; H, 10.60. Found C, 87.10; H, 10.27.} \)
7.4.10 Polar acetylene 9b₁

Following the general procedure B, a solution of 8a₂ (5.16 g, 6.89 mmol) in THF (250 mL, PA grade), n-Bu₄NF (13.8 mL, 13.78 mmol, 1 M in THF) was added and was stirred for 2 h at room temperature. After 2 h Et₂O (200 mL) and water (100 mL) were added to the reaction mixture. The aqueous phase was separated and extracted with Et₂O (50 mL x 3). The combined organic phases were washed with water. The organic phase was dried with Na₂SO₄ and the solvent was evaporated to get a yellow oil. Column chromatography (5 x 20 cm² silica gel, n-pentane/CH₂Cl₂, 3:1 v/v) afforded the product 9c₂ (4.38 g, 107 %, Rf = 0.36) as a yellow oil.

¹H NMR (250 MHz, CDCl₃): δ = 7.32 and 7.31 (2 s, 3 H, Ar-H), 7.27 (s, 1 H, Ar-H), 4.53 (s, 2 H, CH₂O), 3.29 (s, 1 H, C≡CH), 2.81-2.68 (m, 8 H, Ar-CH₂), 1.72-1.53 (m, 12 H, ArCH₂-CH₂), 1.39-1.21 (m, 24 H, CH₂), 1.05 (s, 15 H, ?), 0.91-0.83 (m, 12 H, CH₃).

7.4.11 Non-polar acetylene 9a₅

Following the general procedure C, γ-MnO₂ (3.69 g, 42.48 mmol) and powdered KOH (1.21 g, 20.91 mmol) were added in four portion at a interval of 1 h to a solution of 8a₅ (971 mg, 0.63 mmol) in Et₂O (50 mL) to afford 9a₅. Column chromatography (4 x 20
cm$^2$, silica gel, $n$-pentane/Et$_2$O, 3:1 v/v) afforded 9a$_6$ as a yellow solid (694 mg, 72%, $R_f = 0.96$).

M.p. : 91-93°C. -$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta = 7.40$-7.39 (m, 6 H, Ar-H), 7.36 (s, 1 H, Ar-H), 7.35 (s, 2 H, Ar-H), 7.33 (s, 1 H, Ar-H), 3.37 (s, 1 H, C=CH), 2.87-2.74 (m, 20 H, Ar-CH$_2$), 1.72-1.61 (m, 20 H, ArCH$_2$-CH$_2$), 1.43-1.31 (m, 60 H, CH$_2$), 1.16 (s, 21 H, TIPS), 0.90-0.86 (m, 30 H, CH$_3$). $^{13}$C NMR: $\delta = 143.3, 143.1, 142.4$ and 142.3 (4 C, C-Hexyl), 133.3, 133.2, 132.8 and 132.7 (4 CH, arom. CH), 123.6, 123.1, 123.0 and 121.7 (5 C, C=C=C), 106.0 and 95.8 (2 C, C=CTIPS), 93.4, 93.2 and 93.1 (4 C, ArC=CAR), 82.6 and 81.9 (2 C, C=CH), 34.7, 34.5, 34.4 and 34.2 (4 CH$_2$, ArCH$_2$), 32.2, 32.0, 31.3, 31.2, 31.1, 31.0, 30.9, 29.7, 29.6, 29.5, and 23.0 (13 CH$_2$), 18.8 (CH$_3$, SiCH(CH$_3$)$_3$), 14.2 (CH$_3$, CH$_2$CH$_3$), 11.7 (CH, SiCH(CH$_3$)$_3$). – MALDI TOF: $m/z = 1523.77$. Anal. Calcd for C$_{111}$H$_{162}$Si (1524.61): C, 87.45; H, 10.71. Found C, 87.59; H, 10.71

7.4.12 Non-polar acetylene 9a$_6$

Following the general procedure C, $\gamma$MnO$_2$ (312 mg, 3.59 mmol) and powdered KOH (105 mg, 1.84 mmol) were added in six portion at a interval of 1 h to a solution of 8b$_6$ (50 mg, 0.03 mmol) in Et$_2$O (5 mL) to afford 9a$_6$. 9a$_6$ (48 mg, 98%, $R_f = 0.79$) was isolated as a yellow solid.
M.p. : 113-114°C. -^1^H NMR (500 MHz, CD_2Cl_2): \( \delta = 7.42-7.41 \) (m, 8 H, Ar-H), 7.40-7.34 (s, 4 H, Ar-H), 3.38 (s, 1 H, C=CH), 2.88-2.75 (m, 24 H, Ar-CH_2), 1.77-1.63 (m, 24 H, ArCH_2-CH_2), 1.45-1.35 (m, 72 H, CH_2), 1.17 (s, 21 H, TIPS), 0.92-0.90 (m, 36 H, CH_3). ^1^C NMR: \( \delta = 143.3, 143.1, 142.5 \) and 142.3 (4 C, C-Hexyl), 133.4, 133.2, 132.8 and 132.7 (4 CH, arom. CH), 123.7, 123.2, 123.1 and 121.8 (4 C, C=C=CH), 106.0 and 95.8 (2 C, C=CTIPS), 93.4, 93.3 and 93.1 (3 C, ArC=CAr), 82.6 and 81.9 (2 C, C=CH), 34.8, 34.6, 34.5, and 34.2 (4 CH_2, ArCH_2), 32.2, 32.0, 31.3, 31.2, 31.1, 30.9, 30.1, 29.8, 29.7, 29.6, 29.5, 23.1 and 23.0 (14 CH_2), 18.9 (CH_3, SiCH(CH_3)_3), 14.3 (CH_3, CH_2CH_3), 11.8 (CH, SiCH(CH_3)_3). – MALDI TOF: \( m/z = 1793.27 \). Anal. Calcd for C_{131}H_{190}Si (1793.06): C, 87.75; H, 10.68. Found C, 87.57; H, 10.53.

7.4.13 Non-polar acetylene 9a

Following the general procedure C, \( \gamma\)-MnO_2 (822 mg, 9.46 mmol) and powdered KOH (441mg, 7.72 mmol) were added in six portion at a interval of 1 h to a solution of 8b (400 mg, 0.19 mmol) in Et_2O (50 mL) to afford 9a. Column chromatography (4 x 20 cm^2, silica gel, n-pentane/ Et_2O, 20:1 v/v) afforded 9a (352 mg, 94%, \( R_f = 0.84 \) in n-pentane/ Et_2O, 4:1 v/v) as a yellow solid.

M.p. : 131-133°C. -^1^H NMR (250 MHz, CD_2Cl_2): \( \delta = 7.41 \) (s, 10 H, Ar-H), 7.37 (s, 1 H, Ar-H), 7.36 (s, 2 H, Ar-H), 7.34 (s, 1 H, Ar-H), 3.37 (s, 1 H, C=CH), 2.90-2.74 (m, 28 H, Ar-CH_2), 1.74-1.68 (m, 28 H, ArCH_2-CH_2), 1.51-1.37 (m, 84 H, CH_2), 1.17 (s, 21
H, TIPS), 0.93-0.90 (m, 42 H, CH$_3$). $^{13}$C NMR: $\delta$ = 143.3, 143.1, 142.5, and 142.4 (5 C, C-Hexyl), 133.4, 133.3, and 132.8 (4 CH, arom. CH), 125.8, 123.7, 123.3, and 121.9 (4 C, C=C=C), 106.1 and 95.9 (2 C, C=C(TIPS)), 93.5, 93.3 and 93.2 (3 C, ArC=CAr), 82.7 and 81.9 (2 C, C=CH), 34.8, 34.6 and 34.2 (4 CH$_2$, ArCH$_2$), 32.3, 32.1, 31.3, 31.2, 31.0, 30.5, 29.7, 29.5, 23.4, 23.1 and 23.0 (13 CH$_2$), 18.9 (CH$_3$, SiCH(CH$_3$)$_3$), 14.3 (CH$_3$, CH$_2$CH$_3$), 11.9 (CH, SiCH(CH$_3$)$_3$). – MALDI TOF: m/z = 2060.38. Anal. Calcd for C$_{151}$H$_{218}$Si (2061.51): C, 87.98; H, 10.66. Found C, 87.49; H, 10.70.

7.4.14 Non-polar acetylene 9a

Following general procedure C, □-MnO$_2$ (849 mg, 9.77 mmol) and powdered KOH (412 mg, 7.21 mmol) were added in five portioning, in a interval of 1 h, to a solution of 8b (130 mg, 0.05 mmol) in THF (15 mL) to afford 9a. Column chromatography (4 x 30 cm$^2$, silica gel, n-pentane/CH$_2$Cl$_2$, 3:1 v/v) afforded 9a (85 mg, 67%, $R_f$ = 0.96) as yellow solid in first fraction and 8b (17 mg, 13%, $R_f$ = 0.50) as a yellow solid in third fraction.

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ = 7.37-7.36 (m, 14 H, Ar-H), 7.33 (s, 2 H, Ar-H), 7.31 (s, 1 H, Ar-H), 7.29 (s, 1 H, Ar-H), 3.29 (s, 1 H, C=CH), 2.85-2.82 (m, 36 H, Ar-CH$_2$), 1.74-1.64 (m, 36 H, ArCH$_2$-CH$_2$), 1.42-1.25 (m, 108 H, CH$_2$), 1.14 (s, 21 H, TIPS), 0.89-0.87 (m, 54 H, CH$_3$).
7.5 Synthesis of PMI(Py) labeled oligoPPEs

7.5.1 PMI(Py) labeled oligoPPE 12\textsubscript{0}

Following the general procedure D, a sample of 6e (106 mg, 0.17 mmol) was coupled with TIPS acetylene (45 µL, 0.20 mmol) in toluene (3.0 mL) and Et\textsubscript{3}N (0.5 mL) to afford 12\textsubscript{0}. The crude material was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (1-2 mL) and to it MeOH was added drop by drop. A blue solid was tops out, which was filtered and dried to afford 12\textsubscript{0} as a blue solid (95mg, 77%, R\textsubscript{f} = 0.54 in Et\textsubscript{2}O).

\(^1\)H NMR (250 MHz): δ = 0.88-0.92 (m, 12 H, CH(CH\textsubscript{3})\textsubscript{2}), 1.15 (s, 21 H, TIPS), 2.09 (t, J = 6.3 Hz, 4 H, H \gamma to N), 2.73-2.87 (m, 2 H, CH(CH\textsubscript{3})\textsubscript{2}), 3.70 (t, J = 6.3 Hz, 4 H, H \beta to N), 6.95 (d, J = 7.5 Hz, 1 H, H-8), 7.29-7.41 (4s, 1 H each, Ar-\textit{H}), 7.48 (s, 2 H, Ar-\textit{H} ortho to CH(CH\textsubscript{3})\textsubscript{2}), 7.56 (t, J = 8.2 Hz, 1 H, H-11), 8.22 (d, J = 8.5 Hz, 1 H, H-10), 8.33-8.39 (m, 3 H, H-1, H-6, H-7), 8.50 (d, J = 7.5 Hz, 1 H, H-12), 8.55 (d, J = 8.3 Hz, 1 H, H-5), 8.61 (d, J = 8.0 Hz, 1 H, H-2).

7.5.2 PMI(Py) labeled oligoPPE 12\textsubscript{2}
Following the general procedure D, a sample of 6e (41 mg, 0.065 mmol) was coupled with 9a\textsubscript{2} (52 mg, 0.072 mmol) in toluene (3.5 mL) and Et\textsubscript{3}N (0.7mL). Chromatography, (silica gel (4 x 25 cm), n-Pentane, Et\textsubscript{2}O (1:1)), afforded 12\textsubscript{2} as a blue solid (66mg, 80%, \( R_i = 0.59 \) in Et\textsubscript{2}O).

\(^1\)H NMR (250 MHz): \( \delta = 0.88-0.92 \) (m, 12 H, CH\((CH_3)_2\)), 1.15 (s, 21 H, TIPS), 1.31-1.43 (m, 24 H, \( CH_2 \)), 1.63-1.78 (m, 8 H, ArCH\textsubscript{2}-CH\textsubscript{2}), 2.09 (t, \( J = 6.3 \) Hz, 4 H, H \( \gamma \) to N), 2.73-2.87 (m, 10 H, Ar-\( CH_2 \), \( CH(CH_3)_2 \)), 3.70 (t, \( J = 6.3 \) Hz, 4 H, H \( \beta \) to N), 6.95 (d, \( J = 7.5 \) Hz, 1 H, H-8), 7.29-7.41 (4s, 1 H each, Ar-\( H \)), 7.48 (s, 2 H, Ar-\( H \) ortho to CH\((CH_3)_2\)), 7.56 (t, \( J = 8 \) Hz, 1 H, H-11), 8.22 (d, \( J = 8.5 \) Hz, 1 H, H-10), 8.33-8.39 (m, 3 H, H-1, H-6, H-7), 8.50 (d, \( J = 7.5 \) Hz, 1 H, H-12), 8.55 (d, \( J = 8.3 \) Hz, 1 H, H-5), 8.61 (d, \( J = 8.0 \) Hz, 1 H, H-2).

7.5.3 PMI(Py) labeled oligoPPE 12\textsubscript{5}

Following the general procedure D, a sample of 6e (45 mg, 0.07 mmol) was coupled with 9a\textsubscript{5} (112 mg, 0.07 mmol) in toluene (7.5 mL) and Et\textsubscript{3}N (1.5mL). Chromatography, (4 x 25 cm\textsuperscript{2} silica gel, 1:1 mixture of n-Pentane and Et\textsubscript{2}O) afforded 12\textsubscript{5} as a blue solid (150 mg) in 3\textsuperscript{rd} fraction, which was further dissolved in CH\textsubscript{2}Cl\textsubscript{2} (2 mL) and MeOH was added slowly drop by drop. A blue solid was tops out (115mg, 77%, \( R_i = 0.70 \) in Et\textsubscript{2}O).
\(^1\)H NMR (500 MHz, CD\(_2\)Cl\(_2\)): \(\delta = 0.91-0.93\) (m, 30 H, CH\(_2\)CH\(_3\)), 1.16 (s, 21 H, TIPS), 1.19 (d, \(J = 6.8\) Hz, 12 H, CH(CH\(_3\))\(_2\)), 1.31-1.52 (m, 60 H, CH\(_2\)), 1.64-1.79 (m, 20 H, ArCH\(_2\)CH\(_2\)), 2.08 (t, \(J = 6.2\) Hz, 4 H, H \(\gamma\) to N), 2.76-2.91 (m, 22 H, Ar-H, CH(CH\(_3\))\(_2\)), 3.72 (t, \(J = 6.2\) Hz, 4 H, H \(\beta\) to N), 6.92 (d, \(J = 8.7\) Hz, 1 H, H-8), 7.40-7.43 (m, 7 H, Ar-H), 7.47 (s, 1 H, Ar-H) 7.52 (s, 2 H, Ar-H ortho to CH(CH\(_3\))\(_2\)), 7.55 (t, \(J = 8.0\) Hz, 1 H, H-11), 8.17 (d, \(J = 8.4\) Hz, 1 H, H-6), 8.32 (d, 1 H, \(J = 9.0\) Hz, H-7), 8.37 (d, 2 H, \(J = 8.7\) Hz, H-1, H-10), 8.49 (d, \(J = 7.4\) Hz, 1 H, H-12), 8.51 (d, \(J = 8.1\) Hz, 1 H, H-5), 8.56 (d, \(J = 8.1\) Hz, 1 H, H-2).

7.5.4 Free acetylene 13\(_0\)

Following general procedure B, a sample of 12\(_0\) (95 mg, 0.13 mmol) was treated with "Bu\(_4\)NF (260 \(\mu\)L, 2 equiv., 1M in THF) in THF (5 mL). After 2 h distilled water (50 mL) was added to the reaction mixture and a blue solid was tops out. The solid was filtered and dried to afford 13\(_0\) (64 mg, 85%, \(R_f = 0.59\) in Et\(_2\)O).

\(^1\)H NMR (250 MHz): \(\delta = 0.88-0.92\) (m, 12 H, CH(CH\(_3\))\(_2\)), 2.09 (t, \(J = 6.3\) Hz, 4 H, H \(\gamma\) to N), 2.73-2.87 (m, 2 H, CH(CH\(_3\))\(_2\)), 3.09 (s, 1 H, C=CH\(_2\)), 3.70 (t, \(J = 6.3\) Hz, 4 H, H \(\beta\) to N), 6.95 (d, \(J = 7.5\) Hz, 1 H, H-8), 7.29-7.41 (4s, 1 H each, Ar-H), 7.48 (s, 2 H, Ar-H ortho to CH(CH\(_3\))\(_2\)), 7.56 (t, \(J = 8.2\) Hz, 1 H, H-11), 8.22 (d, \(J = 8.5\) Hz, 1 H, H-10), 8.33-8.39 (m, 3 H, H-1, H-6, H-7), 8.50 (d, \(J = 7.5\) Hz, 1 H, H-12), 8.55 (d, \(J = 8.3\) Hz, 1 H, H-5), 8.61 (d, \(J = 8.0\) Hz, 1 H, H-2). MS (MALDI TOP, 22 KV) \(m/z = 574.55\).
7.5.5 Free acetylene $\text{13}_2$

Following the general procedure B, a solution of $\text{12}_2$ (66 mg, 0.052 mmol) in THF (4 mL) was treated with $^6\text{Bu}_4\text{NF}$ (100 µL, 0.104 mmol, 1M in THF) to afford $\text{13}_2$ as a blue solid (52 mg, 89%, $R_f = 0.70$ in Et$_2$O). The product was used as such for next step.

$^1\text{H NMR}$ (250 MHz): $\delta = 1.18$-$1.21$ (d, $J = 7.0$ Hz, 12 H, CH$(\text{CH}_3)_2$), 1.31-$1.43$ (m, 24 H, $\text{CH}_2$), 1.63-$1.74$ (m, 8 H, Ar$\text{CH}_2$.CH$_2$), 2.09 (t, $J = 6.5$ Hz, 4 H, H $\gamma$ to N), 2.62-2.84 (m, 10 H, Ar-$\text{CH}_2$, CH(CH$_3$)$_2$), 3.29 (s, 1 H, C≡CH), 3.71 (t, $J = 6.5$ Hz, 4 H, H $\beta$ to N), 6.97 (d, $J = 9.3$ Hz, 1 H, H-8), 7.29-7.41 (4s, 1 H each, Ar-$H$), 7.47 (s, 2 H, Ar-$H$ ortho to CH(CH$_3$)$_2$), 7.56 (t, $J = 8.2$ Hz, 1 H, H-11), 8.23 (d, $J = 8.5$ Hz, 1 H, H-10), 8.33-8.41 (m, 3 H, H-1, H-6, H-7), 8.51 (d, $J = 7.5$ Hz, 1 H, H-12), 8.57 (d, $J = 8.3$ Hz, 1 H, H-5), 8.62 (d, $J = 8.0$ Hz, 1 H, H-2). MS (MALDI TOP, 22 KV) $m/z = 1111.58$. 
7.5.6 PMI(OAr)$_3$-(PPE)$_2$-PMI(Py) dyad 14$_2$

Following the general procedure D, a 93:7 mixture of compounds 5a and 5b (31 mg, 0.03 mmol) was coupled with free acetylene 13$_2$ (37.7 mg, 0.03 mmol) in toluene (3.5 mL) and Et$_3$N (0.7 mL). Chromatography (4 x 30 cm$^2$ silica gel, 1:1 mixture of n-pentane and Et$_2$O) afforded 14$_2$ as a blue solid (48 mg, 76%).

$^1$H NMR (500 MHz): $\delta = 0.86$-$0.91$ (m, 12 H), 1.15-1.16 (d, $J = 6.75$ Hz, 12 H), 1.16-1.19 (d, $J = 6.50$ Hz, 12 H), 1.31, 1.33, and 1.34 (3s, 9 H each, t-butyl), 1.39-1.47 (m, $CH_2$, 24 H), 1.69-1.76 (m, 8 H, ArCH$_2$-CH$_2$), 2.09 (broad singlet, 4 H, $H$-γ to N), 2.69-2.84 (m, 12 H, ArCH$_2$, CH(CH$_3$)$_2$), 3.71 (broad singlet, 4 H, $H$-α to N), 6.89 (d, $J = 9.0$ Hz, 1 H, $H$-8), 6.97 (d, $J = 8.5$ Hz, 1 H, $H$-8'), 7.01 (2 H, half of AA'XX' spinsystem, OAr-H meta to t-butyl), 7.08 (4 H, half of AA'XX' spinsystem, OAr-H-meta to t-butyl), 7.35-7.46 (m, 13 H, Ar-H, OAr-H ortho to t-butyl, Ar-H ortho to CH(CH$_3$)$_2$), 7.48 (s, 1 H, Ar-H), 7.57 (t, $J = 8.0$ Hz, 1 H, $H$-8'), 7.64 (t, 1 H, $J = 8.0$ Hz, $H$-8), 8.23 (d, $J = 8.0$ Hz, 1 H, $H$-10), 8.30 (s, 1 H, $H$-5), 8.34-8.40 (m, 4 H, $H$-2, $H$-1', $H$-6', $H$-7), 8.48 (d, $J = 8.0$ Hz, 1 H, $H$-10).
Hz, 1 H, H-10), 8.52 (d, J = 8.0 Hz, 1 H, H-12'), 8.58 (d, J = 8.0 Hz, 1 H, H-5'), 8.62 (d, J = 8.0 Hz, 1 H, H-2'), 9.25 (d, J = 7.0 Hz, 1 H, H-7), 9.45 (d, J = 7.0 Hz, 1 H, H-12).

7.6 PMI(OAr)_3 labeled oligoPPEs 15_n (n = 2, 5, 7, and 9)

7.6.1 PMI(OAr)_3 labeled oligoPPEs 15_2

Following the general procedure D, a 93:7 mixture of 5a and 5b (63 mg, 0.06 mmol) was coupled with the free acetylene 9a_2 (49.6 mg, 0.07 mmol) in toluene (4 mL) and Et₃N (0.8 mL). Column chromatography (4 × 30 cm² silica gel, 1:1 CHCl₃ and n-hexane) afforded 15_2 as a magenta solid (75 mg, 72%, R_f = 0.84) in 3rd fraction. A mixture of the required product and traces amount of dba was isolated in the 4th fraction (42 mg, 41%).

¹H NMR (500 MHz): (CD₂Cl₂) δ = 0.85-0.88 (m, 12 H, CH₂CH₃), 1.12 (d, J = 7.0 Hz, 12 H, CH(CH₃)₂), 1.14 (s, 21 H, tips), 1.29-1.41 (m, 51 H, t-butyl, CH₂), 1.68-1.72 (m, 8 H, ArCH₂-CH₂), 2.81-2.83 (m, 10 H, Ar-CH₂, CH(CH₃)₂), 6.91 (d, J = 8.9 Hz, 1 H, H-8/7), 7.05 (2 H, half of AA'XX' spin system, OAr-H meta to t-butyl), 7.09-7.13 (m, 4 H,
OAr-\(H\) meta to \(t\)-butyl, \(7.33, 7.35, 7.39\) and \(7.40\) (4 s, 1 H each, \(Ar-H, p\)-polyphenylenes), \(7.37-7.45\) (m, 8 H, \(Ar-H, OAr-H\) ortho to \(t\)-butyl, \(Ar-H\) ortho to \(CH(CH_3)_2\)), \(7.67\) (t, \(J = 8.1\) Hz, 1 H, \(H-11\)), \(8.25\) and \(8.28\) (2 s, 1 H each, \(H-2, H-5\)), \(8.50\) (dd, \(J_1 = 8.2\) Hz, \(J_2 = 1.2\) Hz, 1 H, \(H-10/12\)), \(9.28\) (d, \(J = 8.8\) Hz, 1 H, \(H-7/8\)), \(9.48\) (d, \(J = 8.2\) Hz, 1 H, \(H-12/10\)); MS (MALDI TOP, 22 KV) \(m/z = 1644.6\).

These signals have higher intensity than expected and this higher intensity is due to the additional signal for the PMI(OAr)\(_2\) (5b) coupled product. The remaining additional signals are: \(\delta = 7.63\) (t, \(J = 8.0\) Hz, 2 H, \(H-8, H-11\)), \(7.96\) (d, \(J = 8.0\) Hz, 2 H, \(H-7, H-12/H-9, H-10\)), \(8.27\) (s, 2 H, \(H-2, H-5\)), \(9.40\) (d, \(J = 7.7\) Hz, 2 H, \(H-9, H-10/H-7, H-12\)).

7.6.2 PMI(OAr)\(_3\) labeled oligoPPEs 15\(_5\)

\[\begin{array}{c}
\text{Hex} \\
\text{Hex} \\
\text{TIPS} \\
\end{array}\]

\[\begin{array}{c}
\text{Hex} \\
\text{Hex} \\
\text{TIPS} \\
\end{array}\]

Following the general procedure D, a 97:3 mixture of 5a and 5b (47 mg, 0.05 mmol) was coupled with the free acetylene 9a\(_5\) (74 mg, 0.05 mmol) in toluene (5 mL) and Et\(_3\)N (1 mL). Column chromatography (4 \(\times\) 30 cm\(^2\) silica gel, 1:1 CHCl\(_3\) and \(n\)-hexane) afforded 15\(_5\) as a magenta solid (93 mg, 82\%, \(R_f = 0.74\)).
$^1$H NMR (500 MHz): (CD$_2$Cl$_2$) $\delta$ = 0.88-0.91 (m, 30 H, CH$_2$CH$_3$), 1.14-1.16 (m, 33 H, tips, CH(CH$_3$)$_2$), 1.31-1.46 (m, 87 H, t-butyl, CH$_2$), 1.64-1.76 (m, 20 H, ArCH$_2$-CH$_2$), 2.72-2.88 (m, 22 H, Ar-CH$_2$, CH(CH$_3$)$_2$), 6.91 (d, $J$ = 8.8 Hz, 1 H, H-8/7), 7.05 (2 H, half of AA’XX’ spin system, OAr-H meta to t-butyl), 7.10-7.13 (m, 4 H, OAr-H meta to t-butyl), 7.33 and 7.35 (2 s, 1 H each, Ar-H of p-(polyphenylene)s), 7.39-7.48 (m, 16 H, Ar-H of p-(polyphenylene)s, OAr-H ortho to t-butyl, Ar-H ortho to CH(CH$_3$)$_2$), 7.67 (t, $J$ = 8.0 Hz, 1 H, H-11), 8.25 and 8.28 (2 s, 1 H each, H-2, H-5), 8.50 (d, $J$ = 9.0 Hz, 1 H, H-10/12), 9.28 (d, $J$ = 8.8 Hz, 1 H, H-7/8), 9.49 (d, $J$ = 7.4 Hz, 1 H, H-12/10); MS (MALDI TOP, 22 KV) m/z = 2447.94.

7.6.3 PMI(OAr)$_3$ labeled oligoPPEs 15$_7$  

Following the general procedure D, a 97:3 mixture of 5a and 5b (21 mg, 0.02 mmol) was coupled with the free acetylene 9a$_7$ (40 mg, 0.02 mmol) in toluene (5 mL) and Et$_3$N (1 mL). Column chromatography (4 × 20 cm$^2$ silica gel, 1:1 mixture of CHCl$_3$ and n-hexane) afforded 15$_7$ as a magenta solid (6 mg, 10%, $R_f$ = 0.85) and (20 mg,
34%) in 2\textsuperscript{nd} and 3\textsuperscript{rd} fraction respectively. Around 22 mg of compound was isolated in 4\textsuperscript{th} fraction which contains the product and traces amount of dba.

\(^1\)H NMR (500 MHz): (CD\(_2\)Cl\(_2\)) \(\delta = 0.88-0.91\) (m, 42 H, CH\(_2\)CH\(_3\)), 1.15 (d, \(J = 7.4\) Hz, 12 H, CH(CH\(_3\))\(_2\)), 1.16 (s, 21 H, \text{tips}), 1.31-1.46 (m, 111 H, \text{t-butyl}, CH\(_2\)), 1.69-1.76 (m, 28 H, ArCH\(_2\)-CH\(_2\)), 2.71-2.88 (m, 30 H, Ar-CH\(_2\), CH(CH\(_3\))\(_2\)), 6.91 (d, \(J = 8.8\) Hz, 1 H, H-8/7), 7.05 (2 H, half of AA'XX' spinsystem, OAr-H meta to t-butyl), 7.10-7.13 (m, 4 H, OAr-H meta to t-butyl), 7.33 and 7.35 (2 s, 1 H each, Ar-H of \(p\)-(polyphenylene)s), 7.39-7.47 (m, 20 H, Ar-H of \(p\)-(polyphenylene)s, OAr-H ortho to t-butyl, Ar-H ortho to CH(CH\(_3\))\(_2\)), 7.68 (t, \(J = 8.0\) Hz, 1 H, H-11), 8.25 and 8.28 (2 s, 1 H each, H-2, H-5), 8.50 (d, \(J = 9.0\) Hz, 1 H, H-10/12), 9.28 (d, \(J = 8.8\) Hz, 1 H, H-7/8), 9.49 (d, \(J = 7.4\) Hz, 1 H, H-12/10); MS (MALDI TOP, 22 KV) m/z = 2983.7.

7.6.4 PMI(OAr)\(_3\) labeled oligoPPEs 15\(_9\)

Following the general procedure D, a 97:3 mixture of 5\(_a\) and 5\(_b\) (30 mg, 0.03 mmol) was coupled with the free acetylene 9\(_a\)\(_9\) (81 mg, 0.03 mmol) in toluene (5 mL)
and Et₃N (1 mL). The crude material was purified by column chromatography (4 × 20 cm² silica gel, a 1:1 mixture of CHCl₃ and n-hexane). and the 3rd fraction was recolumned (4 × 20 cm² silica gel, a 1:1 mixture of CHCl₃ and n-hexane). The 2nd and 3rd fractions of the 2nd column were isolated and solvent was evaporated to obtain red solids of 2 mg (2%) and 6 mg (6%) respectively, which contains a substantial amount of PMI(OAr)₂ related compound along with the required product. The 4th (62 mg, 59%, Rᵣ = 0.67) and 5th (2 mg, 2%, Rᵣ = 0.67) fraction gave 15₉ as a red solid in reasonable pure.

¹H NMR (500 MHz): (CD₂Cl₂) δ = 0.89-0.91 (m, 54 H, CH₂CH₃), 1.14-1.16 (m, 33 H, tips, CH(CH₃)₂), 1.31-1.46 (m, 135 H, t-butyl, CH₂), 1.64-1.76 (m, 36 H, ArCH₂-CH₂), 2.72-2.88 (m, 38 H, Ar-CH₂, CH(CH₃)₂), 6.91 (d, J = 8.8 Hz, 1 H, H-8/7), 7.05 (2 H, half of AA’XX’ spinsystem, OAr-H meta to t-butyl), 7.10-7.12 (m, 4 H, OAr-H meta to t-butyl), 7.33 and 7.35 (2 s, 1 H each, Ar-H of p-(polyphenylene)s), 7.39-7.47 (m, 24 H, Ar-H of p-(polyphenylene)s, OAr-H ortho to t-butyl, Ar-H ortho to CH(CH₃)₂), 7.68 (t, J = 8.0 Hz, 1 H, H-11), 8.25 and 8.28 (2 s, 1 H each, H-2, H-5), 8.50 (d, J = 8.6 Hz, 1 H, H-10/12), 9.28 (d, J = 8.9 Hz, 1 H, H-7/8), 9.49 (d, J = 7.3 Hz, 1 H, H-12/10); MS (MALDI TOP, 22 KV) m/z = 3518.9.
Chapter 7 | Experimental

7.7 Free acetylene $16_n$ ($n = 2, 5, 7, \text{and} 9$)

7.7.1 Free acetylene $16_2$

Following the general procedure B, 1 M $^n$BuN$_4$F in THF (50 µL, 2 equiv.) was added to a solution of $15_2$ (40 mg, 0.02 mmol) in THF (3.5 mL) and stirred for 2 h at room temperature to afford $16_2$ as a magenta solid (35 mg, 96%, $R_f = 0.62$ in 3:7 CHCl$_3$/n-hexane, v/v). The material was used as such for next reaction.

$^1$H NMR (500 MHz): $\delta = ^\circ$0.85-0.99 (m, 12 H, CH$_2$CH$_3$), ^$1.14-1.16 (12 H, CH(CH$_3$)$_2$), ^$1.31-1.45 (m, 51 H, t-butyl, CH$_2$), ^$1.63-1.73 (m, 8 H, ArCH$_2$-CH$_2$), ^$2.69-2.83 (m, 10 H, Ar-CH$_2$, CH(CH$_3$)$_2$), ^$3.29 (s, 1 H, C≡CH ), 6.89 (d, $J = 8.8$ Hz, 1 H, H-8/7), 7.01, 7.07, and 7.09 (6 H, 3 halves of 3 AA'XX' spinsystems, OAr-H meta to t-butyl), ^$7.32-7.46 (m, 12 H, Ar-H of p-(polyphenylene)s, OAr-H ortho to t-butyl, Ar-H ortho to CH(CH$_3$)$_2$), 7.64 (t, $J = 8.1$ Hz, 1 H, H-11), 8.30 and 8.33 (2 s, 1 H each, H-2, H-5), 8.48 (d, $J = 8.2$ Hz, 1 H, H-10/12), 9.24 (d, $J = 8.8$ Hz, 1 H, H-7/8), 9.45 (d, $J = 7.7$ Hz, 1 H, H-12/10).

$^1$These signals have higher intensity than expected and this higher intensity is due to the additional signal for the PMI(OAr)$_2$ (5b) coupled product. The remaining
signals are: $\delta = 7.59 \ (t, \ J = 8.0 \text{ Hz}, 2 \ H, H-8 \text{ and } H-11)$, $7.91 \ (d, \ J = 7.8 \text{ Hz}, 2 \ H, H-7, H-12/ H-9, H-10)$, $8.32 \ (s, 2 \ H, H-2, H-5)$, $9.36 \ (d, \ J = 7.9 \text{ Hz}, 2 \ H, H-9, H-10/H-7, H-12)$; MS (MALDI TOP, 22 KV) $m/z = 1487.80$.

7.7.2 Free acetylene $16_5$

Following the general procedure B, 1 M TBAF in THF (42 µL, 2 equiv.) was added to a solution of $15_5$ (58 mg, 0.02 mmol) in THF (5 mL) and stirred for 2 h at room temperature to afford $16_5$ as a magenta solid (53 mg, 97%, $R_f = 0.67$ in 1:1 CHCl$_3$ and $n$-hexane). The material was used as such for next reaction.

$^1$H NMR (500 MHz): $\delta = 0.86$-$0.99 \ (m, 30 \ H, CH$_2$CH$_3$)$, $1.14$-$1.16 \ (12 \ H, CH(CH$_3)_2$)$, $1.31$-$1.48 \ (m, 87 \ H, t$-$butyl, CH$_2$)$, $1.64$-$1.74 \ (m, 20 \ H, ArCH$_2$-CH$_2$)$, $2.71$-$2.84 \ (m, 22 \ H, Ar-CH$_2$, CH(CH$_3)_2$), $3.30 \ (s, 1 \ H, \text{C}=\text{C}H)$, $6.89 \ (d, \ J = 8.8 \text{ Hz}, 1 \ H, H-8/7)$, $7.01$, $7.07$, and $7.08 \ (6 \ H, 3 \ halves \ of \ 3 \ AA'XX'$ spinsystems, OAr-H meta to $t$-$butyl)$, $7.33 \ (s, 2 \ H, \text{Ar-H of } p$-(polyphenylene)s), $7.35$-$7.43 \ (m, 16 \ H, \text{Ar-H of } p$-(polyphenylene)s, OAr-H ortho to $t$-$butyl, \text{Ar-H ortho to CH(CH$_3)_2$}, 7.64 \ (t, \ J = 8.1 \text{ Hz}, 1
H, H-11), 8.30 and 8.34 (2 s, 1 H each, H-2, H-5), 8.49 (d, J = 8.9 Hz, 1 H, H-10/12), 9.25 (d, J = 8.8 Hz, 1 H, H-7/8), 9.45 (d, J = 7.4 Hz, 1 H, H-12/10).

7.7.3 Free acetylene 16g

Following the general procedure B, 1 M TBAF in THF (30 µL, 2 equiv.) was added to a solution of 15g (53 mg, 0.02 mmol) in THF (3 mL) and stirred for 2 h at room temperature. Flash chromatography (4 x 30 cm² silica gel, 3:7 CHCl₃ and n-hexane) afforded 16g as a magenta solid (46 mg, 91 %, Rᵓ = 0.69 in 1:1 CHCl₃ and n-hexane).

¹H NMR (500 MHz): δ = 0.87-0.88 (m, 54 H, CH₂CH₃), 1.15 (d, J = 6.4 Hz, 12 H, CH(CH₃)₂), 1.31-1.41 (m, 135 H, t-butyl, CH₂), 1.62-1.72 (m, 36 H, ArCH₂-CH₂), 2.62-2.83 (m, 38 H, Ar-CH₂, CH(CH₃)₂), 3.30 (s, 1 H, C≡CH), 6.89 (d, J = 8.6 Hz, 1 H, H-8/7), 7.01, 7.07, and 7.09 (6 H, 3 halves of 3 AA’XX’ spin systems, OAr-H meta to t-butyl), 7.30-7.46 (m, 26 H, Ar-H of p-polyphenylene)s, OAr-H ortho to t-butyl, Ar-H ortho to CH(CH₃)₂), 7.64 (t, J = 7.9 Hz, 1 H, H-11), 8.30 and 8.33 (2 s, 1 H each, H-2, H-
5), 8.49 (d, $J = 8.3$ Hz, 1 H, $H\text{-}10/12$), 9.25 (d, $J = 8.5$ Hz, 1 H, $H\text{-}7/8$), 9.45 (d, $J = 7.5$ Hz, 1 H, $H\text{-}12/10$). MS (MALDI TOP, 22 KV) m/z = 3366.80.

7.8 PMI labeled oligoPPEs $17_n$ ($n = 2, 5, 7, \text{ and } 9$)

7.8.1 PMI labeled oligoPPE $17_2$

Following the general procedure D, PMI $3a$ (14 mg, 0.03 mmol) was coupled with the free acetylene $9a_2$ (20 mg, 0.03 mmol) in toluene (5 mL) and Et$_3$N (1 mL). Column chromatography (4 × 30 cm$^2$ silica gel, 3:1 mixture of CHCl$_3$ and $n$-hexane) afforded $17_2$ as a red solid (24 mg, 80%, $R_f = 0.44$).

$^1$H NMR (500 MHz): δ = 0.86-0.90 (m, 12 H, CH$_2$CH$_3$), 1.14 (s, 21 H, $tips$), 1.20 (d, $J = 6.8$ Hz, 12 H, CH(CH$_3$)$_2$), 1.30-1.41 (m, 24 H, CH$_2$), 1.68-1.73 (m, 8 H, ArCH$_2$-CH$_2$), 2.74-2.84 (m, 10 H, Ar-CH$_2$), CH(CH$_3$)$_2$), 7.30, 7.32, 7.36 and 7.41 (4 s, 1 H each, Ar-H of $p$-(polyphenylene)s), 7.48 (s, 2 H, Ar-H ortho to CH(CH$_3$)$_2$), 7.67 (t, $J = 7.9$ Hz, 2 H, H-8, H-11), 7.95 (d, $J = 8.2$ Hz, 2 H, H-9, H-10/H-7, H-12), 8.49 and 8.51 (2 d, $J_1 = 8.4$ Hz, $J_2 = 8.2$ Hz, 2 H each, H-1, H-2, H-5, and H-6), 8.68 (d, $J = 8.0$ Hz, 2 H, H-7, H-12/H-9, H-10); MS (MALDI TOP, 22 KV) m/z = 1199.82.
7.8.2 PMI labeled oligoPPEs 17₅

Following the general procedure D, PMI 3a (59 mg, 0.11 mmol) was coupled with the free acetylene 9a₅ (169 mg, 0.11 mmol) in toluene (5 mL) and Et₃N (1 mL). Column chromatography (4 × 30 cm² silica gel, a 3:1 mixture of CHCl₃ and n-hexane) afforded 15₅ as a red solid (158 mg, 75%, Rᵣ = 0.73).

¹H NMR (500 MHz): δ = 0.88-0.92 (m, 30 H, CH₂CH₃), 1.15 (s, 21 H, tips), 1.22 (d, J = 6.8 Hz, 12 H, CH(CH₃)₂), 1.30-1.42 (m, 60 H, CH₂), 1.71-1.74 (m, 20 H, ArCH₂-CH₂), 2.77-2.84 (m, 22 H, Ar-CH₂, CH(CH₃)₂), 7.30, 7.32, (2 s, 1 H each, Ar-H of p-(polyphenylene)s), 7.36-7.39 (m, 7 H, Ar-H of p-(polyphenylene)s), 7.43 (s, 1 H, Ar-H of p-(polyphenylene)s), 7.50 (s, 2 H, Ar-H ortho to CH(CH₃)₂), 7.65 (t, J = 7.8 Hz, 2 H, H-8, H-11), 7.93 (d, J = 8.2 Hz, 2 H, H-9, H-10/H-7, H-12), 8.47 and 8.48 (2 d, J₁ = 8.3 Hz, J₂ = 7.5 Hz, 2 H each, H-1, H-2, H-5, and H-6), 8.67 (d, J = 7.9 Hz, 2 H, H-7, H-12/H-9, H-10); MS (MALDI TOP, 22 KV) m/z = 2004.21.

7.8.3 PMI labeled oligoPPEs 17₇
Following the general procedure D, the PMI 3a (58 mg, 0.10 mmol) was coupled with the free acetylene 9a7 (200 mg, 0.10 mmol) in toluene (6 mL) and Et₃N (1.5 mL). Column chromatography (4 × 30 cm² silica gel, 3:1 mixture of CHCl₃ and n-hexane) afforded 17₇ as a red solid (171 mg, 69%, Rᵣ = 0.56).

¹H NMR (500 MHz): δ = 0.88-0.91 (m, 42 H, CH₂CH₃), 1.14 (s, 21 H, tips), 1.21 (d, J = 6.8 Hz, 12 H, CH(CH₃)₂), 1.28-1.42 (m, 84 H, CH₂), 1.67-1.73 (m, 28 H, ArCH₂-CH₂), 2.76-2.84 (m, 30 H, Ar-CH₂, CH(CH₃)₂), 7.30, 7.32 (2 s, 1 H each, Ar-H of p-(polyphenylene)s), 7.36-7.38 (m, 11 H, Ar-H of p-(polyphenylene)s), 7.43 (s, 1 H, Ar-H of p-(polyphenylene)s), 7.50 (s, 2 H, Ar-H ortho to CH(CH₃)₂), 7.67 (t, J = 7.8 Hz, 2 H, H-8, H-11), 7.94 (d, J = 8.2 Hz, 2 H, H-9, H-10/H-7, H-12), 8.49 and 8.50 (2 d, J₁ = 8.3 Hz, J₂ = 7.9 Hz, 2 H each, H-1, H-2, H-5, and H-6), 8.68 (d, J = 7.9 Hz, 2 H, H-7, H-12/H-9, H-10); MS (MALDI TOP, 22 KV) m/z = 2540.71.

7.8.4 PMI labeled oligoPPEs 17₉

Following the general procedure D, the PMI 3a (13 mg, 0.02 mmol) was coupled with the free acetylene 6a₉ (60 mg, 0.02 mmol) in toluene (5 mL) and Et₃N (1. mL). Column chromatography (4 × 20 cm² silica gel, 1:1 mixture of CHCl₃ and n-hexane) afforded 17₉ as a red solid (57 mg, 80%, Rᵣ = 0.28).
\[^1\text{H} \text{NMR} (500 MHz): \delta = 0.87-0.92 (m, 54 \text{ H}, \text{CH}_2\text{CH}_3), 1.14 (s, 21 \text{ H}, \text{tips}), 1.20 (d, J = 6.8 \text{ Hz}, 12 \text{ H}, \text{CH(\text{CH}_3)_2}, 1.29-1.47 (m, 108 \text{ H}, \text{CH}_2), 1.70-1.73 (m, 36 \text{ H}, \text{ArCH}_2-\text{CH}_2), 2.74-2.84 (m, 36 \text{ H}, \text{Ar-CH}_2, \text{CH(\text{CH}_3)_2}), 7.30, 7.31 (2 \text{ s, } 1 \text{ H each, Ar-H of p-(polyphenylene)s}), 7.36-7.38 (m, 15 \text{ H}, \text{Ar-H of p-(polyphenylene)s}), 7.43 (s, 1 \text{ H}, \text{Ar-H of p-(polyphenylene)s}), 7.49 (s, 2 \text{ H}, \text{Ar-H ortho to CH(\text{CH}_3)_2}), 7.67 (t, J = 7.8 \text{ Hz}, 2 \text{ H}, \text{H-8, H-11}), 7.95 (d, J = 8.2 \text{ Hz}, 2 \text{ H}, \text{H-9, H-10/H-7, H-12}), 8.50 and 8.51 (2 \text{ d, } J_1 = 8.4 \text{ Hz}, J_2 = 8.1 \text{ Hz}, 2 \text{ H each, H-1, H-2, H-5, and H-6}), 8.68 (d, J = 7.8 \text{ Hz}, 2 \text{ H}, \text{H-7, H-12/H-9, H-10}); \text{MS (MALDI TOP, 22 KV)} \text{ m/z} = 3077.84.

7.9 Free acetylene\textbf{18}_n (n =5, 7, and 9)

7.9.1 Free acetylene \textbf{18}_5

\begin{figure}
\includegraphics{18_5}
\end{figure}

Following the general procedure B, 1 M TBAF in THF (120 \text{ µL, 2 equiv.}) was added to a solution of \textbf{17}_5 (120 \text{ mg, 0.06 mmol}) in THF (4 \text{ mL}) and stirred for 2 h at room temperature. Flash chromatography (4 x 20 cm\(^2\) silica gel, 1:1 CHCl\(_3\) and \text{n-hexane}) afforded \textbf{18}_5 as a red solid (89 mg, 80 \%), \(R_f = 0.15\).

\[^1\text{H} \text{NMR} (500 MHz): \delta = 0.86-0.91 (m, 30 \text{ H}, \text{CH}_2\text{CH}_3), 1.20 (d, J = 6.8 \text{ Hz}, 12 \text{ H}, \text{CH(\text{CH}_3)_2}, 1.30-1.41 (m, 60 \text{ H}, \text{CH}_2), 1.64-1.76 (m, 20 \text{ H}, \text{ArCH}_2-\text{CH}_2), 2.72-2.84 (m, 22 \text{ H}, \text{Ar-CH}_2, \text{CH(\text{CH}_3)_2}), 3.30 (s, 1 \text{ H}, \text{C=CH}), 7.33 (s, 2 \text{ H}, \text{Ar-H of p-(polyphenylene)s), 7.36-7.38 (m, 7 \text{ H}, \text{Ar-H of p-(polyphenylene)s), 7.42 (s, 1 \text{ H}, \text{Ar-H of p-(polyphenylene)s), 7.49 (s, 2 \text{ H}, \text{Ar-H ortho to CH(\text{CH}_3)_2}), 7.67 (t, J = 7.8 \text{ Hz}, 2 \text{ H}, \text{H-8, H-11}),}
7.95 (d, \( J = 8.2 \) Hz, 2 H, H-7, H-12/ H-9, H-10), 8.50 and 8.51 (2 d, \( J_1 = 8.4 \) Hz, \( J_2 = 8.2 \) Hz, 2 H each, H-1, H-2, H-5, and H-6), 8.68 (d, \( J = 8.0 \) Hz, 2 H, H-9, H-10/H-7, H-12). MS (MALDI TOP, 22 KV) \( m/z = 1847.9 \).

7.9.2 Free acetylene \( 18_7 \)

Following the general procedure B, 1 M TBAF in THF (87 \( \mu \)L, 2 equiv.) was added to a solution of \( 17_7 \) (110 mg, 0.04 mmol) in THF (5 mL) and stirred for 2 h at room temperature. Flash chromatography (4 x 20 cm² silica gel, 1:1 CHCl₃ and n-hexane) afforded \( 18_7 \) as a red solid (69 mg, 80 %, \( R_f = 0.46 \)).

\(^1\)H NMR (500 MHz): \( \delta = 0.86-0.92 \) (m, 42 H, CH₂CH₃), 1.22 (d, \( J = 6.8 \) Hz, 12 H, CH(CH₃)₂), 1.32-1.43 (m, 84 H, CH₂), 1.68-1.76 (m, 28 H, ArCH₂-CH₂), 2.72-2.84 (m, 30 H, Ar-CH₂, CH(CH₃)₂), 3.30 (s, 1 H, C=CH), 7.33 (s, 2 H, Ar-H of p-(polyphenylene)s), 7.36-7.38 (m, 11 H, Ar-H of p-(polyphenylene)s), 7.43 (s, 1 H, Ar-H of p-(polyphenylene)s), 7.50 (s, 2 H, Ar-H ortho to CH(CH₃)₂), 7.65 (t, \( J = 7.8 \) Hz, 2 H, H-8, H-11), 7.92 (d, \( J = 8.2 \) Hz, 2 H, H-7, H-12/ H-9, H-10), 8.47 and 8.48 (2 d, \( J_1 = 8.3 \) Hz, \( J_2 = 7.5 \) Hz, 2 H each, H-1, H-2, H-5, and H-6), 8.67 (d, \( J = 7.9 \) Hz, 2 H, H-9, H-10/H-7, H-12) MS (MALDI TOP, 22 KV) \( m/z = 2385.0 \).
7.9.3 Free acetylene 189

Following the general procedure B, 1M TBAF in THF (20 µL, 2 equiv.) was added to a solution of 179 (21 mg, 0.01 mmol) in THF (3 mL) and stirred for 2 h at room temperature. Flash chromatography (4 x 20 cm² silica gel, 1:1 CHCl₃ and n-hexane) afforded 189 as a red solid (22 mg, 74 %, Rf = 0.21).

¹H NMR (500 MHz): δ = 0.86-0.90 (m, 54 H, CH₂CH₃), 1.20 (d, J = 6.8 Hz, 12 H, CH(CH₃)₂), 1.33-1.47 (m, 108 H, CH₂), 1.64-1.73 (m, 36 H, ArCH₂-CH₂), 2.72-2.83 (m, 38 H, Ar-CH₂, CH(CH₃)₂), 3.30 (s, 1 H, C≡CH), 7.33 (s, 2 H, Ar-H of p-(polyphenylene)s), 7.36-7.38 (m, 15 H, Ar-H of p-(polyphenylene)s), 7.43 (s, 1 H, Ar-H of p-(polyphenylene)s), 7.49 (s, 2 H, Ar-H ortho to CH(CH₃)₂), 7.67 (t, J = 7.8 Hz, 2 H, H-8, H-11), 7.95 (d, J = 8.2 Hz, 2 H, H-7, H-12/ H-9, H-10), 8.50 and 8.51 (2 d, J₁ = 8.5 Hz, J₂ = 8.1 Hz, 2 H each, H-1, H-2, H-5, and H-6), 8.68 (d, J = 7.8 Hz, 2 H, H-9, H-10/H-7, H-12); MS (MALDI TOP, 22 KV) m/z = 2919.84.
7.10 PMI-(PPE)$_n$-PMI(OAr)$_3$ dyads 19$_n$ (n = 2, 5, 7, and 9)

7.10.1 Linear PMI-(PPE)$_2$-PMI(OAr)$_3$ dyad 19$_2$

Following the general procedure D, PMI 3a (12 mg, 0.02 mmol) was coupled with the free acetylene 16$_2$ (35 mg, 0.02 mmol) in toluene (4 mL) and Et$_3$N (0.8 mL). Column chromatography (4 × 15 cm$^2$ silica gel, 1:1 mixture of CHCl$_3$ and n-hexane) afforded 19$_2$ as red solid (34 mg, 80%, $R_f$ = 0.36).

$^1$H NMR (500 MHz): δ = 0.88-0.90 (m, CH$_2$CH$_3$, 12 H), 1.17 (d, $J = 5.2$ Hz, 12 H, CH(CH$_3$)$_2$), 1.20-1.22 (12 H, CH(CH$_3$)$_2$), 1.32-1.46 (m, 51 H, t-butyl, CH$_2$), 1.74 (m, 8 H, ArCH$_2$-CH$_2$), 2.72-2.84 (m, 12 H, Ar-CH$_2$, CH(CH$_3$)$_2$), 6.89 (d, $J = 8.8$ Hz, 1 H, H-8'/7'), 7.02, 7.08, and 7.10 (6 H, 3 halves of 3 AA'XX' spin systems, OAr-H meta to t-butyl), 7.36-7.45 (m, 12 H, Ar-H of $p$-(polyphenylene)s, OAr-H ortho to t-butyl, Ar-H ortho to CH(CH$_3$)$_2$), 7.50 (s, 2 H, Ar-H ortho to CH(CH$_3$)$_2$), 7.59-7.65 (m, 3 H, H-8, H-11, and H-11'), 7.91 (d, $J = 8.0$ Hz, 2 H, H-9, H-10/H-7, H-12), 8.31 and 8.34 (2 s, 1 H each, H-2', H-5'), 8.43-8.49 (m, 5 H, H-1, 2, 5, and 6, H-10'), 8.65-8.66 (m, 2 H, H-7, H-12/ H-9, H-
10), 9.24 (d, $J = 8.8$ Hz, 1 H, $H-7'/8'$), 9.44 (d, $J = 7.9$ Hz, 1 H, $H-12'/10'$); MS (MALDI TOP, 22 KV) m/z = 1967.98.

7.10.2 Linear PMI-(PPE)$_2$-PMI(OAr)$_3$ dyad 19$_5$

Following the general procedure D, PMI 3a (11 mg, 0.02 mmol) was coupled with free acetylene 16$_5$ (48 mg, 0.02 mmol) in toluene (5 mL) and Et$_3$N (1 mL). Column chromatography (4 × 20 cm$^2$ silica gel, a 1:1 mixture of CHCl$_3$ and $n$-hexane) afforded 19$_5$ as a red solid (28 mg, 51%, $R_f = 0.08$).

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta = 0.84$-0.91 (m, CH$_2$CH$_3$, 30 H), 1.12-1.14 (12 H, CH(CH$_3$)$_2$), 1.17 (d, $J = 6.8$ Hz, 12 H, CH(CH$_3$)$_2$), 1.30-1.44 (m, 87 H, t-butyl, CH$_2$), 1.71-1.79 (m, 20 H, ArCH$_2$-CH$_2$), 2.69-2.85 (m, 24 H, Ar-CH$_2$, CH(CH$_3$)$_2$), 6.88 (d, $J = 8.8$ Hz, 1 H, $H-8'/7'$), 7.03 (2 H, half of AA'XX' spin system, OAr-H meta to t-butyl), 7.08-7.11 (m, 4 H, OAr-H meta to t-butyl), 7.39-7.46 (m, 18 H, Ar-H of p-(polyphenylene)s), OAr-H ortho to t-butyl, Ar-H ortho to CH(CH$_3$)$_2$, 7.50 (s, 2 H, Ar-H ortho to CH(CH$_3$)$_2$), 7.63-7.67 (m, 3 H, H-8, H-11, and H-11'), 7.94 (d, $J = 8.2$ Hz, 2 H, H-9, H-10/H-7, H-12), 8.23
and 8.26 (2 s, 1 H each, H-2’, H-5’), 8.46-8.50 (m, 5 H, H-1, 2, 5, and 6, H-10’), 8.63 (d, J = 7.9 Hz, 2 H, H-7, H-12/ H-9, H-10), 9.25 (d, J = 8.8 Hz, 1 H, H-7’/8’), 9.45 (d, J = 7.6 Hz, 1 H, H-12’/10’); MS (MALDI TOP, 22 KV) m/z = 2770.10.

7.10.3 Linear PMI-(PPE)_2-PMI(OAr)_3 dyad 19b

Following the general procedure D, a 97:3 the mixture of 5a and 5b (13 mg, 0.01 mmol) was coupled with free acetylene 18 (32 mg, 0.01 mmol) in toluene (5 mL) and Et₃N (1 mL). The crude material purified by chromatography silica gel, 4 × 20 cm², (1:1 CHCl₃ and n-hexane) afforded 19b as a red solid (24 mg, 56%, Rᵢ =0.13).

¹H NMR (500 MHz, CD₂Cl₂): δ = 0.87-0.90 (m, CH₂CH₃, 42 H), 1.12-1.13 (12 H, CH(CH₃)₂), 1.17 (d, J = 6.8 Hz, 12 H, CH(CH₃)₂), 1.31-1.44 (m, 111 H, t-butyl, CH), 1.70-1.73 (m, 28 H, ArCH₂-CH₂), 2.69-2.85 (m, 32 H, Ar-CH₂, CH(CH₃)₂), 6.89 (d, J = 8.8 Hz, 1 H, H-8’/7’), 7.03 (2 H, half of AA’XX’ spinsystem, OAr-H meta to t-butyl), 7.08-7.10 (m, 4 H, OAr-H meta to t-butyl), 7.39-7.45 (m, 22 H, Ar-H of p-(polyphenylene)s, OAr-H ortho to t-butyl, Ar-H ortho to CH(CH₃)₂), 7.50 (s, 2 H, Ar-H ortho to CH(CH₃)₂), 7.64-7.68 (m, 3 H, H-8, H-11, and H-11’), 7.95 (d, J = 8.3 Hz, 2 H, H-9, H-10/H-7, H-12),
8.23 and 8.26 (2 s, 1 H each, H-2', H-5'), 8.46-8.52 (m, 5 H, H-1, 2, 5, and 6, H-10'),
8.64 (d, J = 7.9 Hz, 2 H, H-7, H-12/ H-9, H-10), 9.25 (d, J = 8.7 Hz, 1 H, H-7'/8'), 9.46
(d, J = 7.3 Hz, 1 H, H-12'/10'); MS (MALDI TOP, 22 KV) m/z = 3308.95.

7.10.4 Linear PMI-(PPE)_2-PMI(OAr)_3 dyad 19_g

Following the general procedure D, PMI 3a (7.4 mg, 0.01 mmol) was coupled
with free acetylene 16_g (46 mg, 0.01 mmol) the in toluene (5 mL) and Et_3N (1 mL).
Column chromatography (4 × 25 cm^2 silica gel, 3:7 mixture of CHCl_3 and n-hexane)
afforded 19_g as a red solid (31 mg, 67%, R_f = 0.14).

^1^H NMR (500 MHz, CD_2Cl_2): δ = 0.84-0.91 (m, CH_2CH_3, 54 H), 1.12-1.14 (12 H,
CH(CH_3)_2), 1.17 (d, J = 6.8 Hz, 12 H, CH(CH_3)_2), 1.30-1.44 (m, 135 H, t-butyl, CH_2),
1.69-1.73 (m, 36 H, ArCH_2-CH_2), 2.70-2.86 (m, 40 H, Ar-CH_2, CH(CH_3)_2), 6.89 (d, J =
8.7 Hz, 1 H, H-8'/7'), 7.03 (2 H, half of AA'XX' spinsystem, OAr-H meta to t-butyl), 7.08-
7.11 (m, 4 H, OAr-H meta to t-butyl), 7.40-7.46 (m, 26 H, Ar-H of p-(polyphenylene)s,
OAr-H meta to t-butyl, Ar-H ortho to CH(CH_3)_2), 7.50 (s, 2 H, Ar-H ortho to CH(CH_3)_2),
7.65-7.68 (m, 3 H, H-8, H-11, and H-11'), 7.95 (d, J = 8.2 Hz, 2 H, H-9, H-10/H-7, H-12),
8.23 and 8.26 (2 s, 1 H each, H-2', H-5'), 8.47-8.51 (m, 5 H, H-1, 2, 5, and 6, H-10'), 8.64 (d, J = 7.8 Hz, 2 H, H-7, H-12/ H-9, H-10), 9.26 (d, J = 8.8 Hz, 1 H, H-7'/8'), 9.46 (d, J = 7.5 Hz, 1 H, H-12'/10'); MS (MALDI TOP, 22 KV) m/z = 3844.15.

7.11 21

![Structure of 21](image)

Following the general procedure A, a sample of 3-bromiodobenzene (20) (1g, 3.54 mmol) was coupled with 2-propyn-1-ol (220 µL, 1.05 equiv.) in THF (15 mL, dry), piperidine (5 mL, dry) under Ar. Column chromatography (4 x 20 cm² silica gel, 1:1 mixture of Et₂O/n-pentane) afforded 21 as a light yellow solid (670 mg, 89% yield, R_f = 0.46).

¹H NMR (500 MHz): δ (ppm) = 1.78 (broad singlet, 1 H, OH), 4.48 (d, J = 5.8 Hz, 2 H, CH₂OH), 7.17 (t, J = 7.9 Hz, 1 H, H-5), 7.35 (d, J = 7.7 Hz, 1 H, H-6), 7.45 (d, J = 8.0 Hz, 1 H, H-4), 7.57 (s, 1 H, H-2).

7.12 PMI labeled oligoPPE 22s
Following the general procedure D, the bromo compound 21 (9.9 mg, 0.05 mmol) was coupled with the free acetylene 18 (87 mg, 0.05 mmol) in toluene (6 mL) and Et₃N (1.5 mL). Column chromatography (4 × 30 cm² silica gel, CHCl₃) afforded 22 as a red solid (32 mg, 34%, Rᵣ = 0.19).

1H NMR (500 MHz): δ = 0.88-0.91 (m, 30 H, CH₂CH₃), 1.20 (d, J = 6.8 Hz, 12 H, CH(CH₃)₂), 1.23-1.47 (m, 60 H, CH₂), 1.70-1.75 (m, 20 H, ArCH₂-CH₂), 2.76-2.83 (m, 22 H, Ar-CH₂, CH(CH₃)₂), 4.51 (d, J = 6.3 Hz, 2 H, CH₂OH). 7.31 (t, J = 7.8 Hz, 1 H, H-5, m-phenylene), 7.36-7.42 (m, 11 H, Ar-H of p-(polyphenylene)s, H-6/4 of m-phenylene), 7.47 (d, J = 7.8 Hz, 1 H, H-4/6, m-phenylene), 7.49 (s, 2 H, Ar-H ortho to CH(CH₃)₂), 7.60 (s, 1 H, H-2, m-phenylene), 7.67 (t, J = 7.8 Hz, 2 H, H-8, H-11), 7.95 (d, J = 8.2 Hz, 2 H, H-9, H-10/7, H-12), 8.49 and 8.51 (2 d, J₁ = 8.5 Hz, J₂ = 8.1 Hz, 2 H each, H-1, H-2, H-5, and H-6), 8.68 (d, J = 7.9 Hz, 2 H, H-7, H-12/H-9, H-10); MS (MALDI TOP, 22 KV) m/z = 1976.1.

7.13 Free acetylene 23

Following the general procedure C, to a solution of 22 (32 mg, 0.02 mmol) in CH₂Cl₂ (5 ml), γ-Mn₂O (85 mg, 0.98 mmol) and powdered KOH (25 mg, 0.45 mmol) were added in two portion in an interval of 1 h to afford 23 as a red solid (21 mg, 67 %, Rᵣ = 0.69 in CHCl₃). The material was used as such for next reaction.
1H NMR (500 MHz): δ = 0.88-0.91 (m, 30 H, CH₂CH₃), 1.21 (d, J = 6.9 Hz, 12 H, CH(CH₃)₂), 1.33-1.48 (m, 60 H, CH₂), 1.67-1.76 (m, 20 H, ArCH₂-CH₂), 2.75-2.84 (m, 22 H, Ar-CH₂, CH(CH₃)₂), 3.10 (s, 1 H, C≡CH), 7.32 (t, J = 7.7 Hz, 1 H, H-5, m-phenylene), 7.37-7.38 (m, 7 H, Ar-H of p-(polyphenylene)s), 7.43 (s, 1 H, Ar-H of p-(polyphenylene)s), 7.46 (d, J = 7.7 Hz, 1 H, H-6/4 of m-phenylene), 7.49-7.50 (m, 3 H, H-4/6 of m-phenylene, Ar-H ortho to CH(CH₃)₂), 7.65 (m, 3 H, H-8, H-11 and H-2 of m-phenylene), 7.93 (d, J = 8.2 Hz, 2 H, H-7, H-12/H-9, H-10), 8.47 and 8.48 (2 d, J₁ = 8.3 Hz, J₂ = 7.7 Hz, 2 H each, H-1, H-2, H-5, and H-6), 8.67 (d, J = 7.9 Hz, 2 H, H-9, H-10/H-7, H-12).

7.14 Kinked PMI-(PPE)ₙ-PMI(OAr)₃ dyads 24ₙ (n = 5, 7, and 9)

7.14.1 Kinked PMI-(PPE)₅-PMI(OAr)₃ dyad 24₅

Following the general procedure D, a 97:3 mixture of 5a and 5b (9.9 mg, 0.01 mmol) was coupled with the compound 23₅ (20 mg, 0.01 mmol) in toluene (3.5 mL) and
Et$_3$N (0.7 mL). Column chromatography (4 × 25 cm$^2$ silica gel, 1:1 mixture of CHCl$_3$ and $n$-hexane) afforded $24_5$ as a red solid (20 mg, 70%, $R_f = 0.27$).

$^1$H NMR (500 MHz): $\delta = 0.88-0.91$ (m, CH$_2$CH$_3$, 30 H), 1.15-1.16 (12 H, CH(CH$_3$)$_2$), 1.20 (d, $J = 6.8$ Hz, 12 H, CH(CH$_3$)$_2$), 1.31-1.42 (m, 87 H, $t$-butyl, CH$_2$), 1.71-1.73 (m, 20 H, ArCH$_2$-CH$_2$), 2.70-2.83 (m, 24 H, Ar-CH$_2$, CH(CH$_3$)$_2$), 6.90 (d, $J = 8.8$ Hz, 1 H, H-8'/7'), 7.02, 7.07, and 7.09 (6 H, 3 halves of 3 AA'XX' spinsystems, OAr-H meta to $t$-butyl), 7.35-7.49 (m, 22 H, OAr-H ortho to $t$-butyl, Ar-H ortho to CH(CH$_3$)$_2$, Ar-H of $p$-(polyphenylen)s, H-5, H-6/4 of m-phenylene), 7.53 (d, $J = 7.7$ Hz, 1 H, H-4/6 of m-phenylene), 7.64-7.69 (m, 3 H, H-8, H-11, and H-11'), 7.73 (s, 1 H, H-2 of m-phenylene), 7.95 (d, $J = 8.2$ Hz, 2 H, H-9, H-10/ H-7, H-12), 8.30 and 8.33 (2 s, 1 H each, H-2', H-5'), 8.48-8.52 (m, 5 H, H-1, 2, 5, and 6, H-10'), 8.68 (d, $J = 7.9$ Hz, 2 H, H-7, H-12/H-9, H-10), 9.25 (d, $J = 8.8$ Hz, 1 H, H-7'/8'), 9.45 (d, $J = 7.6$ Hz, 1 H, H-12'/10'); MS (MALDI TOP, 22 KV) m/z = 2871.46.
7.14.2 Kinked PMI-(PPE)$_7$-PMI(OAr)$_3$ dyad 24$_7$

Following the general procedure D, the bromo compound 26 (12 mg, 0.01 mmol) was coupled with free acetylene 18$_7$ (28 mg, 0.01 mmol) in toluene (3.5 mL) and Et$_3$N (0.8 mL). Column chromatography (4 × 25 cm$^2$ silica gel, 1:1 mixture of CHCl$_3$ and n-hexane) afforded 24$_7$ as a red solid (22 mg, 59%, $R_f = 0.27$).

$^1$H NMR (500 MHz): $\delta = 0.88-0.91$ (m, 42 H, CH$_2$CH$_3$), 1.15-1.17 (12 H, CH(CH$_3$)$_2$), 1.21 (d, $J = 6.8$ Hz, 12 H, CH(CH$_3$)$_2$), 1.32-1.43 (m, 111 H, t-butyl, CH$_2$), 1.72-1.73 (m, 28 H, ArCH$_2$-CH$_2$), 2.70-2.84 (m, 32 H, Ar-CH$_2$, CH(CH$_3$)$_2$), 6.90 (d, $J = 8.8$ Hz, 1 H, H-8'/7'), 7.02, 7.08, and 7.09 (6 H, 3 halves of AA'XX' spin systems, OAr-H meta to t-butyl), 7.36-7.50 (m, 26 H, OAr-H ortho to t-butyl, Ar-H ortho to CH(CH$_3$)$_2$, Ar-H of p-(polyphenylene)s, H-5, H-6/4 of m-phenylene), 7.53 (d, $J = 7.6$ Hz, 1 H, H-4/6 of m-phenylene), 7.63-7.68 (m, 3 H, H-8, H-11, and H-11'), 7.74 (s, 1 H, H-2 of m-phenylene), 7.94 (d, $J = 8.3$ Hz, 2 H, H-9, H-10/ H-7, H-12), 8.30 and 8.34 (2 s, 1 H each, H-2', H-5'), 8.47-8.51 (m, 5 H, H-1, 2, 5, and 6, H-10'), 8.68 (d, $J = 7.8$ Hz, 2 H, H-7, H-12/H-9, H-
Following the general procedure D, the bromo compound 26 (6.2 mg, 5.61 x 10⁻³ mmol) was coupled with free acetylene 18₉ (17 mg, 5.82 x 10⁻³ mmol) in toluene (5 mL) and Et₃N (1 mL). Column chromatography (4 x 20 cm² silica gel, 3:7 mixture of CHCl₃ and n-hexane) afforded 2₄₉ as a red solid (19 mg, 85%, Rᵣ = 0.09 in 1:1 CHCl₃ and n-hexane).

¹H NMR (500 MHz): δ = 0.89-0.90 (m, 54 H, CH₂CH₃), 1.16 (d, J = 6.5 Hz, 12 H, CH(CH₃)₂), 1.21 (d, J = 6.7 Hz, 12 H, CH(CH₃)₂), 1.32-1.43 (m, 135 H, t-butyl, CH₂), 1.72 (m, 36 H, ArCH₂-CH₂), 2.70-2.84 (m, 24 H, Ar-CH₂, CH(CH₃)₂), 6.90 (d, J = 8.8 Hz, 1 H, H-8'/7'), 7.02, 7.08, and 7.09 (6 H, 3 halves of AA'XX' spin systems, OAr-H meta to
t-butyl), 7.36-7.50 (m, 30 H, OAr-H ortho to t-butyl, Ar-H ortho to CH(CH₃)₂, Ar-H of p-(polyphenylen)s, H-5, H-6/4 of m-phenylene), 7.53 (d, J = 7.6 Hz, 1 H, H-4/6 of m-phenylene), 7.64-7.68 (m, 3 H, H-8, H-11, and H-11'), 7.74 (s, 1 H, H-2 of m-phenylene), 7.93-7.95 (m, 2 H, H-9, H-10/H-7, H-12), 8.30 and 8.34 (2 s, 1 H each, H-2', H-5'), 8.48-8.52 (m, 5 H, H-1, 2, 5, and 6, H-10'), 8.68 (d, J = 7.7 Hz, 2 H, H-7, H-12/H-9, H-10), 9.26 (d, J = 8.9 Hz, 1 H, H-7'/8'), 9.45 (d, J = 7.9 Hz, 1 H, H-12'/10'); MS (MALDI TOP, 22 KV) m/z = 3943.97.

7.15 Free acetylene 25

Following the general procedure D, Pd₂(db₃)₃ (13.7 mg, 0.01 mmol, 10 mol%), P(o-tolyl)₃ (29.4 mg, 0.09 mmol, 60 mol%) were added to the degassed reaction mixture of 5 (150 mg, 0.15 mmol), TMS acetylene (27 µL, 1.3 equiv.) and heated to 65 °C. After 18 h, Et₂O (20 mL) was added to the reaction mixture followed by 2N HCl (10 mL) and stirred for five minute. The aqueous phase was separated and extracted with Et₂O (3 x 20 mL). The combined organic phases were washed with distilled water 20 mL. The
organic phase was dried with Na₂SO₄ and the solvent was evaporated to get crude product TMS protected product (185 mg). Subsequently, 5N NaOH solution (1 mL) was added to the TMS protected acetylene dissolved in a mixture of THF/MeOH (6 mL and 5 mL) at room temperature. After 2 h the reaction was stopped by adding distilled water (50 mL). Red solid tops out from the solution. The solid was filtered and washed with water and dried to get the crude product. The product was purified by chromatography (4 x 25 cm² silica-gel, 1:1 CHCl₃ and n-hexane) afforded 8a as a magenta solid (100 mg, 70 % yield, $R_f = 0.43$).

$^1$H NMR (500 MHz): $\delta$ (ppm) = 0.86-0.88 (m, 10 H, unknown), $^*$1.12 (d-d, $J_1 = 6.9$ Hz, $J_2 = 1.2$ Hz, 12 H, CH(CH₃)₂), 1.31, $^*$1.33, and $^*$1.34 (3 s, 9 H each, t-butyl), $^*$2.63-2.72 (m, 2 H, CH(CH₃)₂), 3.09 (s, 1 H, C≡CH), 6.89 (d, $J = 8.8$ Hz, 1 H, H-8/7), 7.01, 7.06, and 7.09 (6 H, 3 halves of 3 AA′XX′ spinsystems, OAr-H meta to t-butyl), 7.36 (2 H, half of AA′XX′ spinsystem, OAr-H ortho to t-butyl), $^*$7.39-7.42 (m, 6 H, Ar-H ortho to CH(CH₃)₂, OAr-H ortho to t-butyl), 7.64 (t, $J = 8.1$ Hz, 1 H, H-11), 8.28, 8.32 (2 s, 1 H each, H-2 and H-5), 8.48 (d, $J = 8.1$ Hz, 1 H, H-10/12), 9.24 (d, $J = 8.8$ Hz, 1 H, H-7/8), 9.44 (d, $J = 7.5$ Hz, 1 H, H-12/10).

$^*$These signals have higher intensity than expected and this higher intensity is due to the additional signal for the PMI(OAr)₂ (5b) coupled product. The remaining signals are: $\delta = 7.59$ (t, $J = 8.1$ Hz, 2 H, H-8 and H-11), 7.91 (d, $J = 7.8$ Hz, 2 H, H-7, H-12/ H-9, H-10), 9.36 (d, $J = 8.0$ Hz, 2 H, H-9, H-10/H-7, H-12).
7.16 Synthesis of bromo compound 26

Following general procedure A, Pd(PPh₃)Cl₂ (1.4 mg, 2 mol%), Cul (1.1 mg, 5.8 mol%) were added to the degassed reaction mixture of 3-bromiodobenzene (20) (28 mg, 0.10 mmol) and 25 (100 mg, 1.06 equiv.) and stirred at room temperature. After 18 h, Et₂O (20 mL) and 2N HCl (20 mL) were added to the reaction mixture and stirred for 5 minute. The aqueous phase was separated and extracted with Et₂O (3 x 20 mL). The combined organic phases were washed with water (2 x 20 mL). After drying from Na₂SO₄, the solvent was evaporated to obtain the crude material. Column chromatography (4 x 20 cm² silica gel, 1:1 mixture of CHCl₃ and n-hexane) afforded 26 as a red solid (80 mg, 73% yield, Rᵣ = 0.53).

¹H NMR (500 MHz): δ (ppm) = 1.15 (dd, J₁ = 6.9 Hz, J₂ = 1.2 Hz, 12 H, CH(CH₃)₂), 1.31, 1.33, and 1.34 (3 s, 9 H each, t-butyl), 2.69-2.71 (m, 2 H, CH(CH₃)₂), 6.89 (d, J = 8.8 Hz, 1 H, H-8/7), 7.01. 7.07, and 7.09 (6 H, 3 halves of 3 AA’XX’ spinsystems, OAr-H meta to t-butyl), 7.21 (t, J = 7.9 Hz, 1 H, H-5, bromo phenylene), 7.36, 7.40, and 7.42 (6
H, 3 halves of 3 AA′XX′ spin-systems, OAr-H ortho to t-butyl), 7.41 (2 d, $J_1 = 8.5$ Hz, $J_2 = 8.4$ Hz, 4 H, OAr-H ortho to t-butyl) 7.43 (s, 2 H, Ar-H ortho to CH($CH_3)_2$), 7.46 (d, H-6 of bromo phenylene with fine structure due to coupling with H-2 and H-4), 7.48 (d, H-4 of bromo phenylene with fine structure due to coupling with H-2 and H-6) 7.64 (t, $J = 8.1$ Hz, 1 H, H-11), 7.71 (t, 1 H, H-2 of bromo phenylene with insufficiently resolved fine structure due to coupling with H-4 and H-6 and a coupling constant of about 2 Hz), 8.29, and 8.33 (2 s, 1 H each, H-2, H-5), 8.48 (d, $J = 8.2$ Hz, 1 H, H-10/12), 9.24 (d, $J = 8.8$ Hz,1 H, H-7/8), 9.45 (d, $J = 7.8$ Hz, 1 H, H-12/10); MS (MALDI TOP, 22 KV) m/z = 1105.5.

### 7.17 Synthesis of tribromo perylenemonoimide 27

Following the procedure described by Lindsey et al.$^{56,57}$ a solution of 3b (600 mg, 1.25 mmol) in CHCl$_3$ (70 mL) was treated with Br$_2$ (1.3 mL, 24.89 mmol) to afford bromoperylenemonoimide 27. Column chromatography (silica gel, 4 x 15 cm$^2$, CHCl$_3$/n-hexane (3:1)), afforded a mixture of 27a and 27b as red solid (567 mg, 52%) in a raton of 94:6.

$^1$H NMR (500 MHz) of 27a: $\delta = 1.16$ (d, $J = 6.9$ Hz, 12 H, CH($CH_3)_2$), 2.69 (m, 2 H, CH($CH_3)_2$), 7.33 (d, $J = 7.8$ Hz, 2 H, Ar-H ortho to CH($CH_3)_2$), 7.47 (t, $J = 7.8$ Hz, 1 H, Ar-H meta to CH($CH_3)_2$), 7.81 (t, $J = 8.1$ Hz, 1 H, H-11), 7.99 (d, $J = 8.2$ Hz, 1 H, H-
7. 8.45 (d, $J = 8.2$ Hz, 1 H, $H_{-12}$), 8.90 and 8.92 (2s, 1 H each, $H_{-2}, H_{-5}$), 9.11 (d, $J = 8.2$ Hz, 1 H, $H_{-8}$), 9.33 (d, $J = 7.6$ Hz, 1 H, $H_{-10}$).

These signals have higher intensity than expected and this higher intensity is due to the additional signal for the phenyl group at the imides moiety of 27b. The signals due to the compound 27b are $\delta = 8.12$ (d, $J = 8.2$ Hz, 2 H, $H_{-7}, H_{-12}$), 8.89 (s, 2 H, $H_{-2}, H_{-5}$), 8.95 (d, 2 H, $H_{-8}, H_{-11}$).

7.18 Synthesis of alkynyl-substituted perylenemonoimide 28

Following the general procedure D, the mixture of 4a and 4b (60 mg, 0.08 mmol) was treated with 3-(4-methoxyphenyl)ethyn-1-yl (35.4 mg, 3.15 mmol) in toluene (5 mL) and Et$_3$N (1 mL) to afford 28. Column chromatography (silica gel, 4 x 25 cm$^2$, CHCl$_3$) afforded 27 as pink solid (25 mg, 34%).

$^1$H NMR (500 MHz): $\delta = 1.19$ (d, $J = 6.9$ Hz, 12 H, CH(CH$_3)_2$), 2.78 (m, 2 H, CH(CH$_3)_2$), 3.86 (s, 6 H, OMe at 1 and 6), 3.88 (s, 3 H, OMe at 9), 6.93-6.97 (m, 6 H, C≡CAr-H meta to OMe), 7.37 (d, $J = 7.9$ Hz, 2 H, Ar-H ortho to CH(CH$_3)_2$), 7.50 (t, 1 H,
Ar-H meta to CH(CH$_3$)$_2$, 7.55-7.58 (m, 4H, C≡CAr-H ortho to OMe at 1 and 6), 7.64 (d, $J = 8.7$ Hz, 2H, C≡CAr-H ortho to OMe at 9), 7.84 (t, $J = 8.0$ Hz, 1H, H-11), 7.94 (d, $J = 8.1$ Hz, 1H, H-8), 8.66 (d, $J = 8.1$ Hz, 1H, H-10), 8.78 and 8.89 (2s, 1H each, H-2, H-5), 9.87 (d, $J = 8.1$ Hz, 1H, H-7), 9.97 (d, $J = 7.5$ Hz, 1H, H-12).
Chapter 8

References


56. Loewe, R. S.; Tomizaki, K.-Y.; Chevalier, F.; Lindsey, J. S. J. Porphyrins Phthalocyanines, **2002**, *6*, 626-642.


Curriculum Vitae

Mr. Dhananjaya Sahoo

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**Personal Information**

Date of birth: 23rd Jan. 1978
Gender: Male
Nationality: Indian
Occupation: Chemist

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**Scientific Curriculum**

Apr. 05-expected time Oct. 09
Ph.D. Chemistry
Bielefeld University, Bielefeld, Germany
Title of Thesis: “Synthesis of Molecular Rulers to Study Distance and Orientation Dependent Förster Resonance Energy Transfer”
Advisor: Prof. Dr. Adelheid Godt

Sept. 04-Mar. 05
Graduate Program in Nanomolecular Science (Discontinued)
Jacobs University Bremen, Germany
Advisor: Prof. Dr. Thomas Nugent

Nov. 02-Mar. 03
Junior Research Fellow
Indian Institute of Technology Madras (IITM), India
Project: Synthesis of Newkome-type dendrimer (up to 2nd gen.)
Advisor: Prof. Dr. Sundarbabu Bhaskaran

Sept. 99-Oct. 01
M.Sc. Chemistry
Berhampur University, Orissa, India
Specialization: Applied Organic Chemistry
Aug. 96-Jul. 99  B.Sc. Chemistry (Honors)  
Salipur College Salipur, Utkal University, Orissa, India  
Other Subjects: Physics and Mathematics

---

**Work Experience**

Apr. 03-Aug. 04  Senior Project Assistant  
Chembiotek Research International Pvt. Ltd. India  
Main activities and responsibilities: Research and development

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**Distinctions and Awards**

Sep. 04-Mar. 05  Graduate Student Fellowship, Jacobs University Bremen, Germany for Graduate Program in Nanomolecular Science

Jun. 04  Lectureship Qualification Examination, Successfully Passed the “Lectureship Qualification Examination (for all the Indian Universities in Chemical Sciences) Conducted by the Council of Scientific and Industrial Research (CSIR)”, Delhi, India

2002 & 2003  Qualified all India level Graduate Aptitude Test in Engineering (GATE), Category: Chemical Sciences.

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**Publications (in preparation)**

1. **D. Sahoo**, M. Schulte, A. Godt; “A Update on the Synthesis of Monodisperse oligo(phenyleneethynylene)s using Orthogonally Pro-protecting Groups with Different Polarity”.


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