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# Symmetrical and unsymmetrical ferrocenyl perylenediimides: Design, synthesis and properties



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#### A R T I C L E I N F O

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#### ABSTRACT

Symmetrical and unsymmetrical ferrocenyl perylenediimides (PDIs) **1–6** were designed and synthesized by the Sonogashira cross-coupling and nucleophilic aromatic substitution ( $S_NAr$ ) reactions. The PDIs were functionalized with ferrocenyl moiety through varying spacers to study the effect of one and two ferrocenyl units on their photophysical and electrochemical properties. The ferrocenyl unit and PDI were coupled through 3-phenylacetylene, 4-phenylacetylene and 4-phenoxy linkages to tune the electronic properties. The ferrocenyl PDIs show red shift in the absorption with the increasing conjugation. The efficient electronic communication between the ferrocenyl unit and PDI leads to the strong charge-transfer from donor ferrocene to the acceptor PDI core and quenching of fluorescence. The electronic energy levels. The oxidation of ferrocenyl PDIs **1–6** are harder than free ferrocene indicating the considerable delocalization of ferrocenyl electrons on the PDI moiety. The experimental observations were adequately supported by theoretical calculations.

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#### 1. Introduction

The Perylene dyes are one of the promising candidate for organic electronics [1]. Perylene dyes belong to the class of rylene family, a well-known industrial colorant [2]. The perylenediimide (PDI) and its derivatives exhibit spectacular photonic and electrochemical properties, and high n-channel mobility [3]. The well communicating and highly planar  $\pi$ -aromatic framework of PDI gives them high electron mobility. The high electron affinity of two imide groups leads to low lying LUMOs, which makes PDI a strong electron acceptor for Donor-Acceptor (D-A) systems [4]. The  $\pi$ -conjugated Donor-Acceptor (D-A) molecular systems exhibit strong photovoltaic performance, information storage, charge separation, lower HOMO-LUMO gap, red shifted absorption and strong Non-linear Optical (NLO) response [5].

Another important component of D-A system is the donor. Ferrocene is a promising donor among the wide range of electron rich moieties. It is highly reversible redox active centre with the well-established optical and electrochemical properties [6]. The strong NLO response of ferrocene leads to extensive use in wide variety of photonic applications [7].

The PDIs can be functionalized at imide as well as at the bay position. The node on the nitrogen atom of imide position obstructs the electronic communication between the substituent and the PDI core. Therefore the imide substituents have negligible effect on the optical properties of the PDI. On the other hand, the bay position can be substituted through wide range of spacers to tune the properties of PDIs substantially [8].

The major problem associated with the perylene dye is the poor solubility due to extensive  $\pi$ - $\pi$  staking interactions. This hurdle can be overcome by introducing the long, branched alkyl chains at imide position which eliminates the  $\pi$ - $\pi$  staking and improves the solubility without affecting the electronic properties of PDIs.

Neil Champness group have explored the di-substituted ferrocenyl PDI as multistate redox architectures for promising 3-D memory storage applications [9]. The PDIs were decorated with ferrocenyl moiety at the imide positions and studied for redox or photoinduced electron transfer molecular fluorescent switches [10]. The non-fluorescent neutral ferrocenyl PDIs were reversibly switched to highly fluorescent entity by ferric perchlorate chemically or by electrochemical oxidation. In our previous report we have explored the optical and electrochemical properties of unsymmetrical mono-substituted ferrocenyl PDIs [11]. We were further interested to explore the effect of substituting one and two





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ferrocenyl unit on the PDI core through different spacers. Herein we have designed and synthesized unsymmetrical (1-3) and symmetrical (4-6) ferrocenyl PDIs by incorporating one and two ferrocenyl units on PDI respectively (Scheme 1). We chose the spacers 3-phenylacetylene, 4-phenylacetylene and 4-phenoxy linkage which can offer the systematic tuning of the electronic communication between the ferrocenyl units and the PDI core.

#### 2. Results and discussion

The ferrocenyl PDIs 1-6 were synthesized by the Sonogashira cross-coupling and nucleophilic aromatic substitution ( $S_NAr$ ) reaction of bromo PDIs with respective ferrocenyl counterparts. The mono and di-bromo PDIs 7-8 were obtained by the bromination reaction of perylenediimide **9**, which in turn was obtained from the



Scheme 1. Synthesis of symmetrical and unsymmetrical ferrocenyl PDIs 1-6.

imidation reaction of perylenedianhydride **10** in molten imidazole as solvent (Scheme 1). The bromination reaction of imidated PDI **9** with bromine in chloroform yielded the mixture of mono-bromo and di-bromo PDIs (**7** and **8**). The mono-bromo and di-bromo PDIs were separated by column chromatography. The di-bromo PDI was mixture of 1,6- and 1,7-isomers and used as mixture throughout the studies.

The Pd-catalyzed Sonogashira cross-coupling reaction of monobromo PDI **7** with respective ferrocenyl alkyne resulted ferrocenyl PDIs **1** and **2** in 65 and 61% yields respectively. Similarly, the Sonogashira coupling reaction of di-bromo PDI **8** with respective ferrocenyl alkynes resulted the ferrocenyl PDIs **4** and **5** in 59 and 62% yields respectively.

The nucleophilic aromatic substitution reaction of 4-ferrocenyl phenol with mono-bromo and di-bromo PDIs (**7** and **8**) in the presence of K<sub>2</sub>CO<sub>3</sub> resulted ferrocenyl PDIs **3** and **6** in 68 and 70% yields respectively. All the ferrocenyl PDIs were well characterized by <sup>1</sup>H, <sup>13</sup>C NMR and HRMS techniques.

#### 2.1. Photophysical properties

The photophysical properties of ferrocenyl PDIs **1–6** and PDI **9** were recorded in dichloromethane (Fig. 1) and the corresponding data are shown in Table 1. The PDI **9** show intense absorption band at 524 nm with distinct bands in higher energy region corresponding to the characteristic vibronic pattern of PDI. The

incorporation of ferrocenyl unit on the PDI, red shifts the absorption band with increasing  $\pi$ -conjugation. The characteristic vibronic pattern of PDI was weakened in the ferrocenyl PDIs to a shoulder in higher energy region due to the extended conjugation and substituent induced non-planarity of the PDI core [12]. The unsymmetrical mono-substituted ferrocenyl PDIs absorb in 530–545 nm region whereas the symmetrical di-substituted ferrocenyl PDIs absorb in 538–570 nm region. The redshift in the absorption spectra of symmetrical di-substituted ferrocenyl PDIs compared to the unsymmetrical mono-substituted ferrocenyl PDIs can be assigned to enhanced conjugation. The phenoxy linked ferrocenyl PDIs **3** and **6** show absorption at 530 and 538 nm respectively, which is blue shifted than the alkynylated ferrocenyl PDIs.

The 4-phenylacetylene linked symmetrical mono-substituted ferrocenyl PDI **2** and unsymmetrical di-substituted ferrocenyl PDI **5** show CT band as a shoulder at lower energy region indicating the presence of charge transfer interaction (Fig. 1(B)). Such charge transfer band was not observed in ferrocenyl PDIs **1**, **3**, **4** and **6** indicating that, the 4-phenylacetylene show superior electronic communication compared to the 3-phenylacetylene and 4-phenoxy linkage. The solvatochromism studies were performed on the PDIs **2** and **5** (Fig. S6). The 3-phenylacetylene linked symmetrical and unsymmetrical ferrocenyl PDIs show red shifted absorption than the 4-phenylacetylene linked ferrocenyl PDIs.





Fig. 1. Comparison of normalized electronic absorption spectra of parent PDI 9 with symmetrical and unsymmetrical ferrocenyl PDIs 1 and 4 (A); 2 and 5 (B); 3 and 6 (C) and their emission spectra at 0.1 absorption, exited at 487 nm in dichloromethane (D).

PDI	$\lambda_{max}$ (nm)	$\epsilon/10^4 \ (M^{-1} \ cm^{-1})^b$	$\lambda_{em} (nm)^c$	$\boldsymbol{\phi}^d$	HOMO-LUMO gap (eV) <sup>e</sup>
9	524	4.4	532, 573	0.89	2.53
1	546	4.9	536, 573	0.05	2.11
2	541	4.6	533, 577	0.05	2.14
3	529	4.5	554, 596	0.12	2.26
4	571	4.2	_	-	2.16
5	563	4.7	_	-	2.04
6	540	4.9	_	_	2.34

 Table 1

 Photophysical properties of ferrocenyl PDIs 1–6 and parent PDI 9.<sup>a</sup>

<sup>a</sup> Recorded in DCM.

<sup>b</sup> Determined at  $\lambda_{max}$ .

<sup>c</sup> Excited at  $\lambda_{max}$ .

<sup>d</sup> Determined using Rhodamine 6G as standard.

<sup>e</sup> From DFT calculation.

charge transfer interaction the representative TD-DFT calculations were performed on unsymmetrical ferrocenyl PDIs **1–3** (ESI and Fig. S7). The simulated absorption spectra resemble with the experimental absorption with deviation by only 10–15 nm, and the trend in  $\lambda_{max}$  matches well with experimental data (Table 1). The both simulated and experimental  $\lambda_{max}$  values of the unsymmetrical ferrocenyl PDIs follow the order **1** > **2** > **3**. The TD-DFT calculations also support the strength of charge transfer band. The oscillator strengths of the first electronic transition from HOMO to LUMO are predicted to be 0.0080, 0.1619 and 0.0265 for PDIs **1**, **2** and **3** respectively, which indicates that the charge transfer interaction in PDI **2** is most prominent, in **3** it is minor, whereas in **1** it's almost absent. This is in good agreement with the existence or absence of the CT band observed in the absorption spectra, which show charge transfer band in PDI **2** and not in PDI **3**.

The emission behaviour of ferrocenyl PDIs **1–6** and PDI **9** was recorded in dichloromethane (Fig. 1)(D). The incorporation of one ferrocenyl unit decreases the fluorescence quantum yield of PDI, whereas the incorporation of two ferrocenyl units completely quenches the fluorescence of PDIs. The quenching of fluorescence is attributed to the fast non-radiative deactivation of the excited state through the charge transfer from donor ferrocene to the acceptor PDI [13]. The nature of spacers plays an important role in tuning the electronic communication between the ferrocene and PDI. The superior electronic communication shows stronger charge transfer interaction, and leads to quenching of fluorescence, whereas the weak electronic communication hinders the charge transfer interaction and retains the fluorescence quantum yield. The strongly communicating phenylacetylene spacer (in ferrocenyl PDI **1** and **2**)

prominently decreases the fluorescence quantum yield compared to the weakly communicating 4-phenoxy spacer (in ferrocenyl PDI **3**).

The absorption spectra of ferrocenyl PDIs **1–6** in solid state was recorded (Fig. S5). The absorption spectra suggest the different packing behaviour depending on the nature of linkage. The effect of symmetrical and unsymmetrical substitution on the solid state absorption of the PDIs **1–6** is minor.

#### 2.2. Electrochemical properties

The electrochemical properties of ferrocenyl PDIs 1–6 and PDI 9 were recorded in dichloromethane using Glassy carbon as working electrode, Platinum wire as counter electrode and Ag/AgCl as reference electrode in 0.1 M tetrabutylammoniumhexafluorophosphate as supporting electrolyte (Figs. 2 and S1–S4). The potentials were referenced against the Fc/Fc<sup>+</sup> couple. The electrochemical potentials are displayed in Table 2. The parent PDI show two reduction waves and the free ferrocene shows one oxidation wave only. The ferrocenyl PDIs 1–6 show two reduction waves and one oxidation wave, which indicates that the reduction waves correspond to the reduction of PDI unit whereas the oxidation wave corresponds to the oxidation of ferrocenyl moiety. The higher oxidation potential of ferrocenyl PDIs compared to free ferrocene, indicates the considerable delocalization of donor ferrocenyl electrons to the acceptor PDI moiety. This reveals the strong D-A interaction between ferrocene and the PDI moiety.

There is slight variation in the oxidation and reduction potentials of 3-phenylacetylene and 4-phenylacetylene linked ferrocenyl



Fig. 2. Comparison of electrochemical behaviour of ferrocenyl PDIs 1 and 4.

## Table 2Electrochemical properties of parent PDI 9 and ferrocenyl PDI 1–6.ª

PDI	E <sub>oxid</sub> (V)	$E^{1}_{red}(V)$	$E_{red}^{2}(V)$
9	_	-1.07	-1.28
1	0.06	-1.02	-1.22
2	0.06	-1.02	-1.22
3	0.01	-1.10	-1.30
4	0.07	-0.97	-1.16
5	0.05	-0.98	-1.17
6	0.01	-1.14	-1.32

 $^a$  Determined by electrochemical analysis in 0.1 M solution of Bu\_4NPF\_6 in CH\_2Cl\_2 (1.0  $\times$  10<sup>-4</sup> M) at 100 mV S^{-1} Scan rate, Vs Fc/Fc^+.

PDIs, which suggest the minor effect of *meta* or *para* linkage on the HOMO and LUMO energy levels of PDI but, slightly easier oxidation of 4-phenylacetylene linked ferrocenyl PDIs **2** and **5** than 3-phenylacetylene linked ferrocenyl PDIs supports the observed charge transfer band in absorption studies and TD-DFT calculations. There is much difference in the oxidation and reduction potentials of phenylacetylene and phenoxy linked ferrocenyl PDIs indicating the poor electronic communication of phenoxy linkage than phenylacetylene linkages.

The comparison of voltammetric analysis of mono and disubstituted ferrocenyl PDIs show that ferrocenyl oxidation current in symmetrical di-substituted ferrocenyl PDIs is much higher than in unsymmetrical mono-substituted ferrocenyl PDIs. This indicates the simultaneous two electron oxidation of two ferrocenyl units in symmetrical ferrocenyl PDIs **4–6** and single electron oxidation of single ferrocenyl unit in unsymmetrical ferrocenyl PDIs **1–3**.

#### 2.3. DFT calculations

The density functional theory (DFT) calculations on the ferrocenyl PDIs **1–6** were performed to understand the electronic energy levels and orbital distribution using Gaussian 09 programme at B3LYP/6-31G(d) level for C, H, N, O and the Lanl2DZ level for Fe (the B3 exchange functional [14] and LYP correlation functional [15]). The calculated electronic energy levels and the frontier molecular orbitals are shown in Fig. 3. The energy level diagram shows that the HOMO-LUMO gap steadily decreases with the increasing conjugation and is in agreement with the observed absorption spectrum. The frontier molecular orbital plots reveal that the LUMOs are localized on the PDI core indicating the strong electron acceptor nature of PDI. In ferrocenyl PDIs **1**, **3**, **4** and **6** the HOMO is localized on donor ferrocenyl moiety whereas in 4-phenylacetylene linked ferrocenyl PDIs **2** and **5** the HOMO is distributed over the ferrocene unit and PDI moiety indicating efficient distribution of electron density. The HOMO-LUMO distribution reveals the strong D-A interaction in ferrocenyl PDIs.

#### 3. Conclusions

The symmetrical and unsymmetrical ferrocenyl PDIs were designed and synthesized by Sonogashira cross coupling and nucleophilic aromatic substitution (S<sub>N</sub>Ar) reactions. The ferrocenyl PDIs show strong D-A interactions and the strength of D-A interaction depend on the nature of the spacer. The symmetrical disubstituted ferrocenyl PDIs show red shifted absorption than the unsymmetrical mono substituted ferrocenyl PDIs due to the extended  $\pi$ -conjugation. The 4-phenylacetylene linked ferrocenyl PDIs 2 and 5 show charge transfer band as a shoulder at lower energy region indicating the presence of strong charge transfer interaction. The strong D-A interactions were also evident from the electrochemical studies. The higher ferrocenvl oxidation potential in ferrocenvl PDIs than free ferrocene reveals the considerable delocalization of donor ferrocenyl electrons to the acceptor PDI moiety. The frontier molecular orbital distribution indicates the strong D-A interaction and efficient  $\pi$ -electron delocalization.

The broad absorption in visible region, low HOMO-LUMO gap and strong D-A interaction in ferrocenyl PDIs **1–6** make them a potential candidate for photovoltaic and NLO applications. The results presented here will be useful in the design and synthesis of new molecular systems for efficient optoelectronic applications.



Fig. 3. The frontier molecular orbital distribution and electronic energy levels in ferrocenyl PDIs 1–6.

#### 4. Experimental section

#### 4.1. General methods

Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere using standard schlenk method. Triethylamine (TEA) was received from commercial source and distilled on KOH prior to use. <sup>1</sup>H NMR (400 MHz), and <sup>13</sup>C NMR (100 MHz) spectra were recorded on the Bruker Avance (III) 400 by using CDCl<sub>3</sub> as solvent. <sup>1</sup>H NMR chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl<sub>3</sub>, 7.26 ppm and Acetone-d<sub>6</sub> 2.05 ppm). Multiplicities are given as: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublets), m (multiplet), and the coupling constants, *J*, are given in Hz. <sup>13</sup>C NMR chemical shifts are reported relative to the solvent residual peak (CDCl<sub>3</sub>, 77.36 ppm). UV-visible absorption spectra of all compounds were recorded on a PerkinElmer's LAMBDA 35 UV/Vis Spectrophotometer. Fluorescence spectra of all the compounds were recorded on a Horiba Jobin Yvon Floromax 4P spectrophotometer. HRMS were recorded on Brucker-Daltonics, micrOTOF-Q II mass spectrometer. The voltammograms were recorded on CHI620D electrochemical analyzer in dichloromethane solvent and 0.1 M TBAF<sub>6</sub> as supporting electrolyte. The electrodes used were glassy carbon as working electrode, Pt wire as counter electrode and the saturated calomel electrode as reference electrode. The potentials were referenced against Fc/Fc<sup>+</sup> as per IUPAC guidelines [16].

#### 4.2. Synthetic procedures

#### 4.2.1. Generalized procedure for the Sonogashira reaction of 1bromo-perylenediimide and ferrocenyl alkynes

N,N'-Di-(2-ethyl-1-hexyl)-1-bromoperylene-3,4:9,10-

tetracarboxylic acid bisimide (**7**) (100 mg, 0.14 mmol) was dissolved in a mixture of dry toluene (13 mL) and dry triethylamine (6.5 mL) in an Ar atmosphere. PdCl<sub>2</sub>-(PPh<sub>3</sub>)<sub>2</sub> (10 mg, 0.014 mmol), Cul (3 mg, 0.015 mmol), and ferrocenyl alkyne (0.1582 mmol) were added, and the reaction mixture was stirred at 70 °C for 8 h. Following cooling to room temperature, the reaction mixture was evaporated to dryness on rotary evaporator and dissolved in CH<sub>2</sub>Cl<sub>2</sub> and filtered through a small pad of silica. The crude product was purified by column chromatography on 230–400 mesh size silica in 4:1 mixture of chloroform: hexane, and recrystallized in chloroform methanol mixture to yield desired product.

4.2.1.1. Ferrocenyl PDI **1**. Red-purple solid. Yield: 65% (84 mg); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  10.19 (d, J = 8 Hz), 8.67–8.52 (m, 6H), 7.57–7.52 (m, 4H), 4.75 (s, 2H), 4.44 (s, 2H), 4.2–4.14 (m, 9H), 1.94 (m, 2H), 1.42–1.33 (m, 16H), 0.97–0.88 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 163.2, 163.0, 162.9, 162.5, 140.8, 137.8, 133.3, 132.8, 132.5, 130.2, 129.0, 128.94, 128.86, 128.3, 127.6, 127.5, 162.2, 162.1, 125.6, 123.0, 122.93, 122.86, 122.5, 122.4, 121.8, 121.6, 119.6, 101.4, 90.7, 83.7, 69.8, 69.6, 66.7, 44.25, 44.22, 38.0, 30.8, 28.7, 26.9, 24.1, 23.18, 23.16, 14.2, 10.61, 10.57. TOF HRMS *m/z* = 898.3452 (calculated for C<sub>58</sub>H<sub>54</sub>FeN<sub>2</sub>O<sub>4</sub> = 898.3433). UV–Vis (in CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$  [M<sup>-1</sup> cm<sup>-1</sup>]): 546 nm (49000). Fluorescence (in CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{ex}$  = 487 nm): 573 nm  $\varphi_{\rm F}$ : 0.0119.

#### 4.2.2. Generalized procedure for the Sonogashira reaction of 1, 7-dibromo-perylenediimide and ferrocenyl alkynes

*N*,*N*<sup>′</sup>-Di-(2-ethyl-1-hexyl)-1, 7-di-bromoperylene-3,4:9,10tetracarboxylic acid bisimide (**8**) (300 mg, 0.39 mmol) was dissolved in a mixture of dry toluene (13 mL) and dry triethylamine (6.5 mL) in an Ar atmosphere. PdCl<sub>2</sub>-(PPh<sub>3</sub>)<sub>2</sub> (27.3 mg, 0.039 mmol), Cul (7.4 mg, 0.039 mmol), and ferrocenyl alkyne (0.97 mmol) were added, and the reaction mixture was stirred at 70 °C for 8 h. Following cooling to room temperature, the reaction mixture was evaporated to dryness on rotary evaporator and dissolved in  $CH_2Cl_2$  and filtered through a small pad of silica. The crude product was purified by Column chromatography on 230–400 mesh size silica in 5:1 mixture of chloroform: hexane, and recrystallized in chloroform methanol mixture to yield desired product.

4.2.2.1. *Ferrocenyl PDI* **4.** Red-purple solid. Yield: 59% (271 mg); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  10.12 (d, J = 8 Hz, 2H), 8.87–8.70 (m, 4H), 7.72 (s, 8H), 4.57–7.35 (m, 8H), 4.73 (s, 4H), 4.40 (s, 4H), 4.19–4.10 (m, 14H), 1.98 (m, 2H), 1.42–1.32 (m, 16H), 0.99–0.90 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 163.4, 163.1, 140.6, 137.7, 135.5, 133.8, 130.2, 129.3, 129.1, 128.9, 127.5, 127.4, 127.2, 127.1, 126.8, 123.0, 122.2, 121.9, 120.0, 99.8, 90.8, 83.8, 69.9, 69.6, 66.8, 44.4, 38.1, 31.0, 28.9, 24.3, 23.3, 14.3, 10.8. TOF HRMS m/z = 1182.3993 (calculated for C<sub>76</sub>H<sub>66</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>4</sub> = 1182.3721). UV–Vis (in CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$  [M<sup>-1</sup> cm<sup>-1</sup>]): 571 nm (42000).

4.2.2.2. Ferrocenyl PDI 5. Red-purple solid. Yield: 62% (285 mg); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  10.12 (d, J = 8 Hz, 2H), 8.84–8.70 (m, 4H), 7.54 (s, 8H), 4.73 (s, 4H), 4.42 (s, 4H), 4.21-4.09 (m, 14H), 1.98 (m, 2H), 1.43–1.34 (m, 16H), 0.99–0.91 (m, 12H).  $^{13}\mathrm{C}$  NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 163.9, 163.5, 153.1, 152.9, 142.2, 140.7, 137.7, 132.1, 130.5, 128.1, 127.8, 126.4, 123.1, 122.0, 120.8, 119.3, 91.4, 85.8, 84.1, 83.8, 70.0, 69.9, 66.9, 38.2, 31.0, 29.9, 28.9, 24.3, 23.3, 14.3, 10.8. TOF HRMS m/z1182.3706 (calculated for =  $C_{76}H_{66}Fe_2N_2O_4 = 1182.3721$ ). UV–Vis (in  $CH_2Cl_2$ ):  $\lambda_{max}$  ( $\epsilon$  $[M^{-1} cm^{-1}]$ : 563 nm (47).

# 4.2.3. Procedure for the nucleophilic aromatic substitution reaction of 1-bromo-perylenediimide (7) and 4-ferrocenylphenol

N,N'-Di-(2-ethyl-1-hexyl)-1-bromoperylene-3,4:9,10tetracarboxylic acid bisimide (7) (100 mg, 0.14 mmol) was dissolved in a mixture of dry toluene (10 mL) in an Ar atmosphere. To this, 4ferrocenyl phenol (44.2 mg, 0.16 mmol), 18-crown-6 ether (152.6 mg, 0.58 mmol), and K<sub>2</sub>CO<sub>3</sub> (39.88 mg, 0.29 mmol), was added and the reaction mixture was heated at 100 °C for two hours. After completion of the reaction the reaction mixture was cooled to room temperature and washed with water. The organic layer was concentrated on rotary evaporator and the crude product was purified by column chromatography on silica gel in chloroform:hexane (1:1) mixture followed by precipitation in chloroform diethyl ether mixture to yield desired product.

4.2.3.1. *Ferrocenyl PDI* **3**. Red-purple solid. Yield: 68% (87 mg); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  9.39 (d, J = 8 Hz, 1H), 8.55–8.41 (m, 6H), 8.21 (s, 1H), 7.56 (d, J = 8 Hz, 2H), 7.10 (d, J = 8 Hz, 2H), 4.62 (s, 2H), 4.34 (s, 2H), 4.11–4.02 (m, 9H), 1.91 (m, 2H), 1.39–1.29 (m, 16H), 0.94–0.86 (m, 12H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): 163.8, 163.6, 163.5, 163.0, 156.1, 152.7, 137.2, 134.0, 133.9, 133.4, 131.8, 130.6, 129.5, 128.8, 128.5, 128.2, 126.5, 125.4, 124.2, 124.1, 123.4, 123.0, 122.9, 122.8, 122.3, 122.1, 119.9, 84.8, 69.8, 69.2, 66.8, 44.5, 44.3, 38.1, 38.0, 30.9, 28.8, 24.2, 23.23, 23.22, 14.3, 10.8, 10.7. TOF HRMS *m*/*z* = 890.3408 (calculated for C<sub>56</sub>H<sub>54</sub>FeN<sub>2</sub>O<sub>5</sub> = 890.3378). UV–Vis (in CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\epsilon$  [M<sup>-1</sup> cm<sup>-1</sup>]): 529 nm (45000). Fluorescence (in CH<sub>2</sub>Cl<sub>2</sub>,  $\lambda_{ex}$  = 538 nm): 554 nm  $\varphi_{\rm F}$ : 0.12.

### 4.2.4. Procedure for the nucleophilic aromatic substitution reaction of 1-bromo-perylenediimide (7) and 4-ferrocenylphenol

*N*,*N*<sup>'</sup>-Di-(2-ethyl-1-hexyl)-1, 7-di-bromoperylene-3,4:9,10tetracarboxylic acid bisimide (**8**) (100 mg, 0.13 mmol) was dissolved in a mixture of dry toluene (10 mL) in an Ar atmosphere. To this, 4-ferrocenyl phenol (79.4 mg, 0.28 mmol), 18-crown-6 ether (118.8 mg, 0.78 mmol), and  $K_2CO_3$  (71.8 mg, 0.52 mmol), was added and the reaction mixture was heated at 100 °C for two hours. After completion of the reaction the reaction mixture was cooled to room temperature and washed with water. The organic layer was concentrated on rotary evaporator and the crude product was purified by column chromatography on silica gel in chloroform:hexane (1:1) mixture followed by precipitation in chloroform diethyl ether mixture to yield desired product.

4.2.4.1. *Ferrocenyl PDI* **6**. Red-purple solid. Yield: 68% (87 mg); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  9.58 (d, J = 8 Hz, 2H), 8.62 (d, J = 8 Hz, 2H), 8.38 (s, 2H), 7.51 (d, J = 8 Hz, 4H), 7.09 (d, J = 8 Hz, 4H), 4.65 (s, 4H), 4.36 (s, 4H), 4.13–4.06 (m, 14H), 1.91 (m, 2H), 1.35–1.34 (m, 16H), 0.90–0.85 (m, 12H). <sup>13</sup>C NMR(CDCl<sub>3</sub>, 100 MHz, ppm): 163.9, 163.5, 155.4, 154.5, 153.3, 148.1, 136.8, 133.6, 132.2, 130.5, 129.5, 129.0, 128.4, 127.6, 125.3, 124.2, 124.05, 123.99, 122.4, 119.7, 69.9, 69.3, 69.2, 66.9, 53.6, 44.5, 38.1, 30.9, 28.9, 24.2, 23.2, 14.2, 108. TOF HRMS *m*/*z* = 1166.3625 (calculated for C<sub>72</sub>H<sub>66</sub>Fe<sub>2</sub>N<sub>2</sub>O<sub>6</sub> = 1166.3619). UV–Vis (in CH<sub>2</sub>Cl<sub>2</sub>):  $\lambda_{max}$  ( $\varepsilon$  [M<sup>-1</sup> cm<sup>-1</sup>]): 540 nm (49000).

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.07.006.

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