β -pyrrole substituted porphyrin–pyrene dyads using vinylene spacer: Synthesis, characterization and photophysical properties

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Abstract. We have designed and synthesized donor–acceptor conjugates having donor pyrene at the pyrrole- β position of either free-base porphyrin or Zn(II) porphyrin using vinylene spacer. Both the dyads have been completely characterized by elemental analysis, MALDI-MS, UV-Vis., and fluorescence (steady state and time-resolved) spectroscopies as well as cyclic voltammetry. The absorption maxima of both dyads are red-shifted by 8–12 nm. The ground state properties showed that there exist minimum π – π interaction between the aromatic subunits of these D–A systems. Quenched emission was observed in both the dyads when excited at 290 nm. The quenched emission explained in terms of intramolecular excitation energy transfer competes with the photo-induced electron transfer reaction in these D–A system.

Keywords. Porphyrin; pyrene; hydrocarbon; π – π interactions; energy.

1. Introduction

Excitation energy transfer (EET) and photo-induced electron transfer (PET) reactions are essential processes for mimicking natural photosynthesis,^{1–4} opto-electronic applications,^{5,6} biological system,^{7,8} excitonic solar cells and medicinal application such as photodynamic therapy.^{9–11} Intramolecular EET and PET systems between two chromophores involving the porphyrin chromophore have received much attention in elucidation of the natural photosynthetic system.^{12–14} A great variety of porphyrin-based donor–acceptor systems in which a porphyrin or a metalloporphyrin is covalently/non-covalently linked to either an energy donor or an acceptor were reported in order to study the intramolecular EET and PET reactions. Majority of these porphyrin based donor–acceptor systems are having either a donor or an acceptor at *meso* phenyl position of tetraphenyl porphyrins and a few systems at the axial position/s of resident metallo/metalloid ion of porphyrin.^{15–18} In contrast, energy or electron acceptors such as fullerenes at pyrrole- β position of a porphyrin were also reported in the literature.^{19–21} However, energy or electron donor at pyrrole- β position of a porphyrin is not reported in the literature to the best of our knowledge. Here, we have designed a porphyrin-based donor–acceptor system having a pyrene donor at pyrrole- β position

of either free-base or Zn(II) porphyrin using vinylene spacer for the first time. Both free-base and Zn(II) dyads are completely characterized by using CHN analysis, MALDI-MS, UV-Vis., fluorescence (both steady state and time-resolved) spectroscopies as well as cyclic voltammetry. The structure of the dyads is shown in scheme 1.

2. Experimental

All chemicals and reagents were purchased from Aldrich and used as such. The solvents are of commercial grade and purified prior to use.²² ACME silica gel (100–200 mesh) was used for column chromatography and thin-layer chromatography was performed on Merck-precoated silica gel 60-F₂₅₄ plates. Either gravity or flash chromatography was used for compound purification. Where as a dual solvent system was used, gradient elution was employed, and the major band was collected. All porphyrin reactions were carried out under nitrogen or argon atmosphere using dry degassed solvents, and the apparatus was shielded from ambient light.

2.1 Synthesis

The compounds 5,10,15,20-tetraphenyl porphyrin (H_2L^1), 5,10,15,20-tetraphenyl porphyrinato zinc(II) (ZnL^1), and triphenyl[(5,10,15,20-tetraphenyl porphyrin-

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Scheme 1. Synthetic scheme of porphyrin-pyrene dyads.

2-yl]methyl] phosphonium chloride (**H₂L^{1a}**) were synthesized according to the reported procedures in the literature.^{23,24}

2.1a Synthesis of 5,10,15,20-tetraphenyl-2-(2-pyren-1-yl-vinyl)-porphyrin (H₂L²**):** This compound was synthesized by using Wittig-Horner reaction.²⁵ **H₂L^{1a}** (0.100 g, 0.108 mmol), 1-pyrenecarboxaldehyde (0.0028 g, 0.118 mmol) and DBU (0.090 g, 0.592 mmol) were dissolved in 20 ml of CH₂Cl₂ and stirred magnetically at RT for 5 min. The reaction mixture was subjected to flash chromatography using CH₂Cl₂/Hexane 1:1 as eluant and the solvent was evaporated to dryness. The obtained solid material was redissolved in 20 ml of CH₂Cl₂. To this, about 0.002 g of I₂ was added for *cis-trans* isomerization and the reaction mixture was stirred at RT for 16 h. After completion of the reaction, the reaction mixture was washed with 1M Na₂S₂O₃ solution in water and extracted with CH₂Cl₂. The solvent was removed and the obtained solid material was subjected to silica gel chromatography using CH₂Cl₂/hexane (1:1) as eluant to get the desired product in 80% yield. Anal. Calcd. for C₆₀H₄₂N₄, % (842.34): Calculated C, 88.33; H, 5.02; N, 6.65. Found C, 88.35; H, 5.01; N, 6.63. MALDI-MS (*m/z*): C₆₀H₄₂N₄ [842]: 842 (100%). ¹H NMR (CDCl₃, δppm): 9.20 (s, 1H); 8.75 (m, 6H); 8.55 (d, 2H, *J* = 8.0 Hz); 8.30 (m, 2H); 8.20 (m, 8H); 8.15 (m, 5H); 7.75 (m, 12H), 7.35 (d, 1H, *J* = 6.2 Hz), 7.15 (d, 1H, *J* = 6.2 Hz) and -2.72 (b, 2H).

2.1b Synthesis of 5,10,15,20-tetraphenyl-2-(2-pyren-1-yl-vinyl)-porphyrinato zinc(II) (ZnL²**):** **H₂L²** (0.100 g, 0.12 mmol) and ZnO(Ac)₂·2H₂O were dissolved in 25 ml of CHCl₃/CH₃OH mixture. The resultant reaction mixture was refluxed until there is a change in Q-band absorption. The solvent was removed and washed with water. The obtained solid material was subjected to silica gel column chromatography using CH₂Cl₂ as eluent. The solvent front running band was collected and recrystallized with CH₂Cl₂/hexane

mixture to get **ZnL²** in 95% yield. Anal. Calcd. for C₆₂H₃₈N₄Zn, % (902.24): Calculated C, 82.34; H, 4.24; N, 6.20. Found C, 82.30; H, 4.20; N, 6.20. ¹H NMR (CDCl₃, δppm): 9.30 (s, 1H); 8.90 (m, 6H); 8.55 (d, 2H, *J* = 8.0 Hz); 8.35 (m, 2H); 8.25 (m, 8H); 8.15 (m, 5H); 7.80 (m, 12H), 7.35 (d, 1H, *J* = 6.2 Hz), 7.15 (d, 1H, *J* = 6.2 Hz).

2.2 Methods

The UV-Visible spectra were recorded with Ocean Optics spectrophotometer for 1×10^{-6} M (porphyrin Soret band) and 5×10^{-5} M (porphyrin Q bands) solutions. Steady state fluorescence spectra were recorded using a Spex model Fluorlog-3 spectrofluorimeter for solutions having optical density at the wavelength of excitation (λ_{ex}) $\approx$ 0.11. The fluorescence quantum yields (ϕ) were estimated by integrating the fluorescence bands and by using either 5,10,15,20-tetraphenyl porphyrin (**H₂TPP**) (ϕ = 0.13 in CH₂Cl₂), or 5,10,15,20-tetraphenyl porphyrinato zinc(II) (**[ZnTPP]**) (ϕ = 0.036 in CH₂Cl₂) as the standards.²⁶ Time-resolved fluorescence measurements have been carried out using HORIBA jobin yvon spectrofluorometer. Briefly, the samples were excited at 405 nm and the emission was monitored at 655 nm, in case of porphyrin. Whereas in case of pyrene it was excited at 290 nm and the emission was monitored at 375 nm. The count rates employed were typically 10^3 – 10^4 s⁻¹. Deconvolution of the data was carried out by the method of iterative reconvolution of the instrument response function and the assumed decay function using DAS-6 software. The goodness of the fit of the experimental data to the assumed decay function was judged by the standard statistical tests (i.e., random distribution of weighed residuals, the autocorrelation function and the values of reduced χ^2). MALDI-MS spectra were recorded on a TO-4X KOMPACT SEQ, KARTOS, UK, mass spectrometer. Major fragmentations are given as percentages relative to the base peak

intensity. ^1H NMR spectra were obtained at 300 MHz using a Bruker 300 Avance NMR spectrometer running X-WIN NMR software. The chemical shifts are relative to tetramethylsilane (TMS). Differential pulse voltammetric measurements were performed on a PC-controlled CH instruments model CHI 620C electrochemical analyzer. The electrochemical experiments were performed on 1 mM porphyrin dyads solution in dichloromethane solvent using 0.1 M tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. The working electrode is glassy carbon, standard calomel electrode (SCE) is reference electrode and platinum wire is an auxiliary electrode.

3. Results and discussion

3.1 Ground state properties

Scheme 1 illustrates the synthesis of both the dyads. The free-base dyad was synthesized by adopting Wittig–Horner reaction and followed by zinc metal insertion into the porphyrin cavity to get the corresponding zinc dyad. Preliminary characterization was done by using elemental analysis and MALDI-MS spectroscopy. The MALDI-MS spectrum H_2L^2 is shown in figure 1 and it consists of molecular ion peak 842, which ascribe to the presence of corresponding dyad molecule. ^1H NMR spectra data of H_2L^2 and ZnL^2 and **Py-CHO** are displayed in figure 2. A comparison of these spectra with those of H_2L^1 , ZnL^1 and **Py-CHO**

reveals that the resonance positions of the various protons present either on the porphyrin macrocycle or the pyrene subunit are not shifted considerably upon linking the two chromophores via the vinylene spacer. This is reasonable if one considers that the two aromatic rings are at ‘*trans*’ configuration with respect to the $\text{C}=\text{C}$ spacer, avoiding the steric interaction. The two doublets appeared at 7.15 and 7.35 ppm belongs to the vinylene protons, which indicates the formation of the dyad.

Figure 3 illustrates the differential pulse voltammograms of the dyads investigated in this study and the corresponding data summarized along with their individual constituents are presented in table 1. As can be seen from the figure 3 and table 1, each investigated new dyad shows up to two reductions and three oxidation peaks under the experimental conditions employed in this study. Wave analysis suggested that, in general, while the first two reduction steps and first two oxidation steps are reversible, one-electron transfer reactions, the subsequent steps are, in general, either quasi-reversible or totally irreversible. While the first reduction peak in both dyads corresponds to the reduction of the porphyrin ring, the remaining extensively overlapping peaks are assigned to electron addition to the porphyrin/pyrene moiety in each case. Similarly, the peaks occurring at potentials that are less anodic than 1.25 V are ascribed to successive one-electron oxidations of the porphyrin parts of dyads; the peak occurring at more anodic potential represents the oxidation of the appended pyrene moiety. The electrochemical data suggests that the redox potentials of the dyads are close to those of the corresponding reference compounds.

Figure 1. MALDI-MS spectrum of H_2L^2 .

Figure 2. ^1H NMR spectra of **Py-CHO**, **ZnL²** and **H₂L²** in CDCl_3 .

Figure 4 displays the absorption spectrum of **H₂L²** measured in dichloromethane solvent. The wavelength of maximum absorbance (λ_{max}) and molar extinction coefficients ($\log \epsilon$) values of the both the dyads and their constituent individual components (i.e., **H₂L¹**, **ZnL¹** and **Py-CHO**) as obtained from the UV-Vis. studies are summarized in table 1. Comparison of the spectrum in figure 4 and data in table 1 suggests that the appended pyrene chromophore in these dyads absorbs dominantly between ca. 230 and 350 nm region in which porphyrin part of each molecule show

its so-called N and L bands. Nonetheless, the peak at ~ 287 nm for each dyad corresponds largely to the absorbance of the pyrene moiety because the N and L bands are quite weak compared to the pyrene absorbance in this wavelength region. Analogously, porphyrin part of these dyads shows either four (**H₂L²**) or two (**ZnL²**) Q-bands in the wavelength region (500–700 nm) where the pyrene moiety of the dyad molecules does not absorb. The peak at around 420 nm is Soret band of porphyrin part of the dyads. Spectral data given in the table 1 further reveal that the absorption maxima of both dyads are red-shifted by 8–12 nm in comparison with the corresponding absorption bands in **H₂L¹** and **ZnL¹**. Similar red-shifted bands are also observed in other pyrrole- β substituted porphyrins.^{20,24} Finally, it was observed that the λ_{max} and spectral shapes of the bands of both the dyads are more or less similar to those of solutions containing one equivalent of each **H₂L¹/ZnL¹** and **Py-CHO**.

The ground state properties and electrochemical features described above suggested that electronic communication between porphyrin and pyrene chromophores is quite negligible in these new D–A systems. More importantly, the absorption data suggests that it is possible to individually address photophysical behaviour of the porphyrin and pyrene subunits in these bichromophoric systems. This situation is unlike in previously reported porphyrin–pyrene conjugates, where pyrene subunit/s is directly connected to the porphyrin macrocycle, but is quite similar to the porphyrin–pyrene systems wherein the two chromophores are linked via C=N spacer at the *meso* phenyl ring of tetraphenyl porphyrin as well as in P(V) porphyrin–pyrene wherein the

Figure 3. Differential Pulse Voltammogrammes in CH_2Cl_2 and 0.1 M TBAP.

Table 1. UV-visible and electrochemical data.

Compound	Absorption, $\lambda_{\max}$, nm ($\log \epsilon$, $M^{-1} \text{ cm}^{-1}$) ^a					Potential V vs. SCE ^b		
	Porphyrin bands					Pyrene bands		
H₂L¹	417 (5.18)	515 (4.15)	545 (3.90)	590 (3.60)	646 (3.70)	-	-1.21, -1.51	1.01, 1.39
ZnL¹	417 (5.60)	547 (4.13)	586 (3.64)			-	-1.40, -1.71	0.74, 1.09
Py-CHO		-				290 (4.55)	372 (4.39)	398 (4.34)
H₂L²	425 (5.10)	523 (4.20)	569 (4.00)	602 (3.80)	658 (3.30)	287 (4.30)	350 (4.39)	372 (4.42)
ZnL²	429 (5.10)	559 (4.30)	598 (4.04)			287 (4.40)	349 (4.42)	
							-1.44,	1.53
							-1.13, -1.36,	1.07, 1.23, 1.52
							-1.49, -1.60,	0.74, 1.25, 1.55

^aSolvent CH₂Cl₂, error limits: $\lambda_{\max}$, ± 1 nm, $\log \epsilon$, $\pm 10\%$

^bCH₂Cl₂, 0.1 M TBAP; glassy carbon working electrode, standard calomel electrode is reference electrode, Pt electrode is auxiliary electrode. Error limits, $E_{1/2} \pm 0.03$ V

two chromophores are linked, via alkoxy spacer at axial sites.^{27–30} In fact, the whole entity functions as a modified porphyrin in the former system, the spectroscopic signatures of the porphyrin and pyrene subunits are easily identifiable in later ones. Despite the presence of a short C=C bond separating two subunits, the D–A systems investigated in this study seem to belong to the latter class of compounds as suggested by spectroscopic data presented above.

3.2 Singlet state properties

Figure 5 illustrates the steady state fluorescence spectra of the dyads along with the individual constituents measured in CH₂Cl₂ solvent and the corresponding

data presented in table 2. When excited at 290 nm ($\lambda_{\max}$, where pyrene absorbs predominantly), resulted quenched emission spectra in both the dyads in comparison with the fluorescence due to pyrene (Py) (figure 5a). However, when excited at 550 nm (porphyrin absorption), the resulted spectra are seen to be similar to those in the spectrum of either **H₂L¹** or **ZnL¹** (figure 5b) except in emission maxima. The emission maxima is red-shifted, when compared to its individual constituents. A similar red-shift in emission maxima was also observed in other pyrrole- β substituted porphyrins.^{20,31} The E_{0-0} (0–0 spectroscopic transition energy) values of the pyrene (3.56 ± 0.05 eV) and the porphyrin (1.90 ± 0.05 eV for **H₂L²** and 2.07 ± 0.05 eV for **ZnL²**) moieties of the dyads, as estimated from an overlap of their absorption and emission spectra, were found to be in the same range as the E_{0-0} values of pyrene, **H₂L¹** and **ZnL¹**, respectively.

A major difference is noticed between the fluorescence data of these dyads and those of individual constituents. The fluorescence quantum yield (ϕ) was similar in both the dyads when excited into the porphyrin part of each dyad in comparison with that of unlinked porphyrin (i.e., **H₂L²/ZnL²**, $\phi = 0.13 \pm 0.01$ and 0.036 ± 0.001 , respectively). In contrast, quenched emission intensity was observed in both the dyads, when excited at 290 nm in comparison with **Py**. The quenching efficiency values (Q),

$$Q = \frac{\phi(\text{Py}) - \phi(\text{H}_2\text{L}^2/\text{ZnL}^2)}{\phi(\text{Py})}, \quad (1)$$

where $\phi(\text{Py})$ and $\phi(\text{H}_2\text{L}^2/\text{ZnL}^2)$ refer to the fluorescence quantum yields for **Py** and the D–A systems

Figure 4. UV-Visible absorption spectra in CH₂Cl₂.

Figure 5. Fluorescence spectra of equiabsorbing solutions ($OD \lambda_{ex} = 0.11$) in CH_2Cl_2 . (a) $\lambda_{ex} = 290$ nm, **Py** (—), **H₂L²** (-----) and **ZnL²** (·····) and (b) $\lambda_{ex} = 420$ nm **H₂L¹** (—), **H₂L²** (·····), **ZnL¹** (-----) and **ZnL²** (-.-.-).

H₂L²/ZnL², respectively; ($\lambda_{ex} = 290$ nm) have been calculated for these systems in three different solvents. The quenching is more than 90% for both the dyads in all three investigated solvents. Figure 6 illustrates excited state fluorescence decay profile of both dyads collected in CH_2Cl_2 solvent, by selectively exciting the sample with two different excitation sources ($\lambda_{ex} = 290$ and 405 nm), where the individual subunits (pyrene and porphyrin) absorb predominantly at one wavelength. As expected, when we monitored the porphyrin emission ($\lambda_{em} = 655$ nm), the fluorescence lifetime (τ) of

both the dyads **H₂L²** and **ZnL²** (7.8 and 1.7 ns, respectively) was not quenched much compared to **H₂L¹** and **ZnL¹** (8.9 and 2.05 ns, respectively). However, on the other hand, when the pyrene emission is monitored ($\lambda_{em} = 375$ nm), the fluorescence lifetime of the **H₂L²** is found to be 1.81 ns while **ZnL²** is about 1.55 ns. It is known from the literature that the fluorescence lifetime of simple pyrene in medium polar solvents is ≥ 250 ns.³⁰ The dramatic fluorescence quenching can be perhaps understood based on the excited state electron or energy transfer from pyrene to porphyrin subunit.

Table 2. Fluorescence data.^a

Compound	λ_{em} , nm (ϕ , %Q) ^b					
	Toluene		CH_2Cl_2		CH_3CN	
	$\lambda_{ex} = 290$ nm	$\lambda_{ex} = 420$ nm	$\lambda_{ex} = 290$ nm	$\lambda_{ex} = 420$ nm	$\lambda_{ex} = 290$ nm	$\lambda_{ex} = 420$ nm
H₂L¹	-	649, 715 (0.110)	-	648, 715 (0.110)	-	649, 715 (0.120)
ZnL¹	-	603, 655 (0.032)	-	601, 647 (0.036)	-	603, 655 (0.033)
Py	374, 394 (0.069)	-	374, 394 (0.090)	-	373, 393 (0.070)	-
H₂L²	390 (0.004, 94)	667, 736 (0.011)	380 (0.003, 97)	661, 734 (0.120)	385 (0.002, 97)	664, 733 (0.012)
ZnL²	394 (0.006, 91)	628, 673 (0.037)	381 (0.004, 96)	611, 768 (0.039)	394 (0.002, 97)	628, 673 (0.037)

^aError limits: λ_{ex} , ± 2 nm; ϕ , $\pm 10\%$. ^bQ is defined in equation 2

Figure 6. Fluorescence decay of H_2L^2 (o) and ZnL^2 (∇) in CH_2Cl_2 .

There exists a strong overlap between the emission of pyrene and the absorption of porphyrin in these D–A conjugated systems; this suggests that fluorescence quenching of these dyads may be due to an intramolecular EET from singlet state of pyrene to the porphyrin. Indeed, excitation of *ca.* 10^{-7} M solution of both the dyads at 290 nm results in appearance of well-defined porphyrin emission bands. Furthermore, overlap of the corrected and normalized excitation spectra (emission collected at the porphyrin emission maximum, 650 nm) with the corresponding absorption spectra (figure 7) reveals that the fluorescence quenching is due to the intramolecular energy transfer in these dyad systems. The efficiency of energy transfer was found to be $90 \pm$

Figure 7. Overlay of excitation (-----) and absorption (—) spectra of H_2L^2 in CH_2Cl_2 ($\lambda_{\text{em}} = 765$ nm). The excitation spectra were corrected for the instrument response function and were normalized with respect to the absorption spectra as described in ref. 32.

10% in both the dyads. However, a photo-induced electron transfer reaction cannot be ruled out in these dyad systems when excited at 290 nm based on thermodynamic consideration. The change in free energy when PET occurs from the ground state of porphyrin part of the dyads to the singlet state of pyrene is calculated by equation (2),

$$\begin{aligned} \Delta G (^1\text{Py} \rightarrow \text{H}_2\text{L}^2/\text{ZnL}^2) \\ = E_{\text{CT}} \left(\text{Py}^+ (\text{H}_2\text{L}^2/\text{ZnL}^2)^- \right) \\ - E_{0-0} (\text{H}_2\text{L}^2/\text{ZnL}^2). \end{aligned} \quad (2)$$

ΔG was found to be -1.04 and -1.09 eV for H_2L^2 and ZnL^2 , respectively. Thus, the low ϕ values observed upon excitation of these systems at 290 nm can be rationalized in terms of intramolecular EET reaction competing with PET reaction from ground state of porphyrin to the excited state of pyrene in these dyad systems.

In comparison of photophysical properties of these D–A conjugates with those of literature reported porphyrin–pyrene conjugates reveal that the energy transfer is the major pathway when pyrene is either directly connected to porphyrin macrocycle^{29,30} or separated from porphyrin by a short C=N bridge.²⁷ In contrast, photo-induced electron transfer is the major pathway when pyrene is connected at the axial position/s of P(V) porphyrin via alkoxy bridge.²⁸ In the present D–A systems, the energy transfer is the major pathway but one cannot neglect the electron transfer reaction also on thermodynamic consideration.

In conclusion, we have designed and synthesized D–A conjugates having pyrene hydrocarbon at the pyrrole- β position of either free-base or Zn(II) porphyrin through C=C bridge. Ground state properties indicate that there is a minimum electron interaction between donor pyrene subunit and acceptor porphyrin subunit. However, excited state properties showed that there is an energy transfer reaction competing with electron transfer reaction from pyrene to porphyrin when excited at pyrene absorption maxima.

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