Ethynyl thiophene-appended unsymmetrical zinc porphyrin sensitizers for dye-sensitized solar cells**

P. Silviya Reeta, L. Giribabu, S. Senthilarasu, Min-Hung Hsu, D. Kishore Kumar, Hari M. Upadhyaya, Neil Robertson and Tracy Hewat

[1] Inorganic & Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology, Uppal Road, Tarnaka, Hyderabad 500007, India.

[2] Energy Conversion Laboratory (ECL), Institute of Mechanical, Process and Energy Engineering (IMPEE), School of Engineering and Physical Sciences, Heriot-Watt University, Riccarton, Edinburgh, UK.

[3] Environment and Sustainability Institute (ESI), University of Exeter, Penryn, Cornwall, UK.

[4] EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3FJ, UK.

[*] Corresponding author; e-mail: giribabu@iict.res.in; fax: +91-40-27160921; tel: +91-40-27193186

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Graphical abstract:
The increasing global energy crisis has demanded the search for new alternative energy conversion materials as competitors of silicon photovoltaic devices. In this regard, dye-sensitized solar cells (DSSCs) are found to display low-cost, ease of fabrication, short-energy pay-back time, low sensitivity to temperature changes and environmental friendliness compared with the conventional solid-state p–n photovoltaic devices. Typical DSSC consists of a dye-sensitized nanocrystalline semiconductor sandwiched between the platinum-coated counter electrode within which is the redox electrolyte of the type I/III. The sensitizer is one of the key components in achieving high efficiency and durability of the device. The most widely studied sensitizers employed so far are Ru(II) polypyrrolidyl complexes (N719, N3, N945, Z-907) which produced solar-energy-to-electricity conversion efficiencies (η) more than 11%. In spite of this high conversion efficiency, the main drawbacks of Ru(II) polypyrrolidyl complexes are the expense due to the rarity of the metal in earth’s crust and lack of absorption in near-IR region of the visible spectrum, where the solar flux of photons is still significant, thus limiting the realization and usability of highly-efficient devices. For this reason, dyes with large π-conjugated systems such as porphyrins and phthalocyanines are receiving considerable attention as sensitizers for DSSC applications.

A great variety of porphyrin sensitizers used for DSSC applications comprise the anchoring group either at the pyrole-β (η up to 7.1%) or –meso position/s (η up to 12.3%). Consistent with recent reports, unsymmetrical porphyrin sensitizers designed with unique directionality have proven to be promising alternatives and competitive with conventional Ru(II) polypyrrolidyl complexes. Enormous effort has been put forth in recent years to advance the existing highest power conversion efficiency by various structural modifications at –meso positions of porphyrin macrocycles by adopting donor-π-acceptor approach (D–π–A). Recently, Yella et al. a porphyrin sensitizer (1D-o-CA) having N,N’-diphenyl amine as donor, porphyrin macrocycle as acceptor and aryl benzoxy group as acceptor, with highest η value of 12.3% using a Co(II)/Co(III) based redox electrolyte. This has stimulated further investigations of porphyrin based sensitizers in order to enhance the photovoltaic performance of DSSC devices.

The performance of porphyrin sensitizers can be significantly improved by grafting the molecule with precisely chosen donor, π-linker and acceptor/anchoring groups (D–π–A approach). According to previous reports, combination of a wide-range of donor moieties, mainly such as functionalized arylamines, polyaromatic or heterocyclic donors, with ethylbenzoic acid anchoring group at the -meso position of the porphyrin has revealed significantly-improved cell performance. In contrast to many available porphyrin sensitizers reported with ethylbenzoic acid anchoring group, in the present scheme, we have attempted to introduce an ethynyl thiophene π-conjugated linker with either cyanoacrylic or malonic acid anchoring groups and study its influence on solar cell performance. Herein in the present article, we report four new unsymmetrical zinc metallated porphyrin sensitizers (PYR-Por-CA, PYR-Por-MA, FLU-Por-CA and FLU-Por-MA), as shown in Figure 1, appended with ethynyl thiophene linker between porphyrin and anchoring group to facilitate shift in the absorption towards the red region, and either cyanoacrylic or malonic acid anchoring group and a polycyclic aromatic hydrocarbon (PAH) such as either pyrene or fluorene as the donor moiety.
5-pyryl-15-ethyl-10,20-Bis[4-(hexyloxy)-3,5-dimethylphenyl]porphyrin zinc(II) (9a): Porphyrin (8a) (65 mg, 0.057 mmol) and K₂CO₃ (0.59 g) were dissolved in 30 ml of CH₂Cl₂/MeOH mixture and allowed to stir at RT for 5 h. The crude mixture was filtered to remove K₂CO₃, washed with water and extracted with CHCl₃. Purification by silica gel column using CHCl₃/Hexane (4:1 v/v) afforded a more polar green product (90% yield). Elemental analysis of Anal. Calcd. For C₅₆H₄₈N₈O₈Zn: calculated: 1202.90, found: 1204 [(M+2H)⁺].

5-fluorenyl-15-ethyl-10,20-Bis[4-(hexyloxy)-3,5-dimethylphenyl]porphyrin zinc(II) (9b): This compound was synthesized by adopting a similar procedure that was used to prepare 9a in 91% yield. ¹H NMR (CDCl₃, 300 MHz): δ = 8.06 (m, 12H), 0.99 (m, 8H), 1.44 (m, 8H), 1.50 (m, 10H), 1.60 (m, 4H), 1.99 (m, 4H), 2.11 (m, 4H), 2.39 (m, 4H), 3.82 (m, 4H), 4.28 (m, 4H), 5.92 (m, 12H), 7.34 (m, 12H), 9.13 (d, 2H), 9.35 (s, 2H). ESI-MS: m/z C₁₁₂H₈₈N₈O₈Zn calculated: 1230.20, found: 1231 [(M+H)⁺]. UV-Vis (CH₂Cl₂) λₘₐₓ (nm) (log ε) : 267 (4.3), 304 (4.4), 413 (5.0), 553 (4.3), 663 (4.0).

5-pyryl-15-(5-formylthiophene-2-yl)-10,20-Bis[4-(hexyloxy)-3,5-dimethylphenyl]porphyrin zinc(II) (10a): Porphyrin 9a (50 mg, 0.047 mmol) and Pd(PPh₃)₄Cl₂ (5.75 mg, 0.005 mmol) were dissolved in 10 ml of dry triethylamine to which 5-bromothiophene-2-carboxaldehyde (44.16 mg, 0.25 ml, 0.23 mmol) and CuI (0.95 mg, 0.005 mmol) were added and the solution was heated to 50 °C for 8 h. After cooling to RT the crude mixture was washed with water and extracted with CHCl₃. The green product was purified using silica gel column with CHCl₃/Hexane (3:1 v/v) as the eluant to afford the desired product (85% yield). Elemental analysis of Anal. Calcd. For C₁₁₀H₇₄N₄O₈S-Zn [1180.72]: 1182 [M+2H]⁺ (100%). ¹H NMR (CDCl₃, δ ppm): 10.11 (s, 1H), 9.90 (d, 1H), 9.77 (s, 1H), 9.20 (d, 2H), 8.77 (m, 3H), 8.50 (m, 6H), 8.21 (m, 2H), 7.83 (m, 4H), 7.45 (m, 7H), 6.90 (s, 1H), 4.22 (m, 4H), 3.93 (s, 12H), 1.93 (m, 4H), 1.44 (m, 12H), 0.97 (m, 6H). UV-Vis (CH₂Cl₂) λₘₐₓ (nm) (log ε) : 426 (5.83), 454 (4.83), 566 (3.82), 623 (4.00).

5-fluorenyl-15-(5-formylthiophene-2-yl)-10,20-Bis[4-(hexyloxy)-3,5-dimethylphenyl]porphyrin zinc(II) (10b): This compound was synthesized by adopting a similar procedure that was used to prepare 10a in 83% yield. ¹H NMR(CDCl₃, 300 MHz): δ = 0.87 (m, 12H), 0.98 (m, 8H), 1.25 (m, 8H), 1.45 (m, 10H), 1.60 (m, 4H), 2.1 (m, 8H), 3.95 (s, 12H), 8.29 (m, 4H), 9.03 (m, 4H), 9.48 (d, 2H), 9.54 (s, 2H), 9.64 (s, 1H). ESI-MS: m/z C₁₁₀H₇₄N₄O₈S-Zn calculated: 1313.04, found: 1315 [M+2H]⁺. UV-Vis (CH₂Cl₂) λₘₐₓ (nm) (log ε) : 267 (4.5), 308 (4.5), 423 (5.6), 453 (sh, 5.1), 551 (4.2), 621(4.0).
5-pyrenyl-1-[5-(formylthiophene-2-yl)-2-cyanoacrylicacid]-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin zinc(II) (PYR-Por:CA)  

This compound was synthesized by adopting a similar procedure that was used to prepare 11a.  

\[ \text{MALDI-TOF MS: m/z C_{46}H_{27}N_{10}O_{10}Szn: 1380.08, found: 1381 [M+H]^+}. \]  

UV-Vis (CHCl\textsubscript{3}) \( \lambda_{\text{max}} \) (nm) (log \( e \)) : 266(4.6), 308(4.5), 444(5.2), 575(4.2), 638(4.5).  

5-fluorenyl-15-[5-(formylthiophene-2-yl)methylene malonic acid]-10,20-Bis[4-(hexyloxy)-3,5-dimethoxyphenyl]porphyrin zinc(II) (FLU-Por:CA) This compound was synthesized by adopting a similar procedure that was used to prepare 12a.  

\[ \text{MALDI-TOF MS: m/z C_{47}H_{27}N_{10}O_{10}Szn: 1399.08, found: 1398 [M+H]^+}. \]  

UV-Vis (CHCl\textsubscript{3}) \( \lambda_{\text{max}} \) (nm) (log \( e \)) : 474(5.32), 575(4.04), 639(4.36).  

Cell Fabrication  

The commercially available TiO\textsubscript{2} pastes (Dyesol) of 18 nm in diameter were used to prepare nanocrystalline TiO\textsubscript{2} electrodes. DSSCs were prepared on 3 mm thick float glass substrates coated with FTO (TEC-8 from Pilkington Group Limited). These FTO thin films have a sheet resistance of \( \sim 8 \) \( \Omega \)/sq and an average transmission of \( \sim 80\% \) in the Visible and NIR spectral region. The TiO\textsubscript{2} electrodes were made by the screen printing method to prepare transparent layers. Subsequently, a second scattering layer made up of a paste containing 400 nm anatase TiO\textsubscript{2} nanoparticles. As a post deposition treatment the TiO\textsubscript{2} electrodes were annealed at 450°C for 30 min on a hotplate. The dye molecules were dissolved in ethanol at a concentration of 0.1 \( \times 10^{-3} \) M. The TiO\textsubscript{2} thin films were soaked in the dye solution and then kept at room temperature for 16 h so that the dye was adsorbed onto TiO\textsubscript{2} films. The TiO\textsubscript{2} electrodes were soaked overnight in dye solution, sandwiched with a platinised conducting counter electrode using a Surlon frame (Solaronix SA), filled with the electrolyte through a hole in the counter electrode and sealed. The iodide/tri-iodide electrolyte comprising 0.4 M LiI, 0.4 M tetrabutylammonium iodide (TBAI), and 0.04 M I\textsubscript{3} dissolved in 0.3 M N-methylbenzimidazole (NMB) in acetonitrile (ACN) and 3-methoxypropionitrile (MPN) solvent mixture at volume ratio of 3:1 was used. The area of the cells was 0.25 cm\textsuperscript{2}.  

Results and Discussions  

The synthetic scheme of all porphyrin sensitizers is illustrated in Figure 2 (for detailed synthetic scheme of each compound,
D = Pyrene = 9a
D = Fluorene = 9b

(i) DMF, K$_2$CO$_3$, reflux 4h (ii)(b) Dipyromethane, CH$_2$Cl$_2$, TFA, RT (iiib) DDQ, TEA, RT (iii) NBS, CH$_2$Cl$_2$, RT (iv)(a,b) Pd(PPh$_3$)$_4$, Cs(CO$_3$)$_3$, Toluene, reflux, 12h (va) NBS, CH$_2$Cl$_2$, RT (vb) Zn(OAc)$_2$, CHCl$_3$/CH$_2$OH, reflux, 2h (vi) TMSA, TEA, Pd(PPh$_3$)$_2$Cl$_2$, CuI, 50 °C, 8h (vii) K$_3$CO$_3$, CH$_2$OH/CH$_2$Cl$_2$, RT, 3h (viii) 5-bromothiophene-2-carboxaldehyde, TEA, Pd(PPh$_3$)$_2$Cl$_2$, CuI, 50 °C, 8h (ix) Cyanoacetic acid (PYR-Por-CA or FLU-Por-CA) or malonic acid (PYR-Por-MA or FLU-Por-MA), CHCl$_3$/CH$_3$CN (3:1), piperidine, reflux, 8h.

(iii) 2
(iv) $\text{(H)}$
(v)
(vi) 6a or 6b
(vii) 7a or 7b
(viii) 8a or 8b

Figure 2: Synthetic scheme.

Experimental procedure and analytical data See Supporting information. We have adopted the Lindsey method for the synthesis of the unsymmetrical porphyrin (3). The donors, poly cyclic aromatic hydrocarbons such as either pyrene or fluorene, were introduced at the –meso position via Suzuki-Miyura cross-coupling with the corresponding donor boronic acid pinacol ester and mono brominated porphyrin (3). Thiophene moiety with rigid ethynyl linker was introduced via Sonogashira cross-coupling reaction of the corresponding TMS(Trimethysilylacetylene) deprotected porphyrin (either 9a or 9b) with 5-bromo thiophene carboxaldehyde. Finally, presence of hexyloxy substituents on 10- and 20-meso phenyl rings of the porphyrin macrocycle is to increase the solubility of the porphyrin and was also expected to minimise charge recombination. The presence of the thiophene group is to enhance the molar absorption coefficient, bathochromically shift the absorption and increase the excited state life time. Moreover, some of the thiophene based organic D-π-A sensitizers are shown to improve the open circuit voltage and enhance the efficiency up to 7%. All new unsymmetrical porphyrins are characterized by various spectroscopic techniques. The MALDI-TOF MS mass spectra of each compound displays peaks at PYR-Por-CA: 1246 [(M-H)$^-$], PYR-Por-MA: 1264 [(M-2H)$^-$], FLU-Por-CA: 1381
The electronic absorption spectra of typical metalloporphyrins are having an intense Soret band at around 420 nm, which is which is an $a_{1u}(\pi)/e_{g}(\pi^*)$ electronic transition, assigned to the second excited state ($S_2$) and two less-intense Q bands (500-700 nm) originating from $a_{1u}(\pi)/e_{g}(\pi^*)$ electronic transition, attributed to the first excited state ($S_1$). The absorption spectra of all four sensitizers have been measured in dichloromethane solvent and representative absorption spectra of PYR-Por-CA depicted in Figure 3 and the corresponding absorption maxima and molar extinction coefficients are given in Table 1. Figure 3 and Table 1 suggests that the absorption peaks in the ultra violet region i.e., between 230-380 nm region belong to the absorption of donor PAH group in all four sensitizers and it is not much altered, when compared to its isolated donor molecules. In contrast, a split in the Soret band was observed in both fluorene derivatives i.e., FLU-Por-CA and FLU-Por-MA (See supporting information). Both Soret and Q bands of four sensitizers are broadened and red-shifted in comparison with ZnTTP, which could be attributed to the reduced molecular symmetry, extended-$\pi$ conjugation via ethynyl linker and also due to electronic communication via the aromatic hydrocarbon donors/thiophene with the porphyrin macrocycle. The broadening of absorption bands is more pronounced in sensitizers with malonic acid anchoring group sensitizers (PYR-Por-MA & FLU-Por-MA) than the corresponding cyanoacrylic acid derivatives (PYR-Por-CA & FLU-Por-CA) (See Supporting information). Similarly, the sensitizers having pyrene derivatives are more bathochromically shifted when compared to their fluorene derivatives, which may be due to more electron releasing nature of the pyrene moiety.\textsuperscript{23,25} Figure 3 also displays the absorption spectrum of PYR-Por-CA adsorbed onto 2 $\mu$m thick TiO$_2$ electrode which is similar to that of the solution spectra but exhibits a small red shift. This may be due to the anchoring of carboxylic protons of porphyrin on TiO$_2$ which releases the proton upon binding to Ti\textsuperscript{4+}.\textsuperscript{30}

The emission spectra of all four porphyrin sensitizers were measured at room temperature in dichloromethane solvent and the representative spectrum of PYR-Por-CA is illustrated in Figure 4 with the corresponding emission maxima with quantum yields reported in Table 2. From Figure 4 and Table 2, it is clear that the quantum yields of all four sensitizers is enhanced in comparison with reference compound 5,10,15,20-tetraphenyl zinc porphyrin (ZnTPP). The singlet state energies ($E_{0,0}$) of all four sensitizers, estimated from excitation and emission spectra are presented in Table 2. No emission spectra are observed for the porphyrin sensitizers adsorbed

**Figure 3**: UV–Vis absorption spectra of PYR-Por-CA (---) in CH$_2$Cl$_2$ and (-----) adsorbed onto a 2 $\mu$m thick TiO$_2$ film.

**Figure 4**: Fluorescence spectra of PYR-Por-CA (---) in CH$_2$Cl$_2$ and (-----) adsorbed onto a 2 $\mu$m thick TiO$_2$ film. The excitation wavelength $\lambda_{ex}$ = 440 nm.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Absorption, $\lambda_{max}$ (nm, $g$, M$^{-1}$ cm$^{-1}$)$^a$</th>
<th>Porphyrin Bands</th>
<th>Donor PAH Bands$^c$</th>
<th>Reduction</th>
<th>Oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td>PYR-Por-CA</td>
<td>447, 575 (4.13) (4.40)</td>
<td>339</td>
<td>326, 275, 234</td>
<td>-1.05, -1.34, 0.76, 1.12,</td>
<td>-1.62</td>
</tr>
<tr>
<td>PYR-Por-MA</td>
<td>468, 580 (4.13) (4.40)</td>
<td>339</td>
<td>326, 275, 234</td>
<td>-1.26, -1.50, 0.64, 1.06,</td>
<td>-1.60</td>
</tr>
<tr>
<td>FLU-Por-CA</td>
<td>444, 569 (4.13) (4.40)</td>
<td>267</td>
<td>308</td>
<td>-1.14, -1.47, 0.79, 1.09,</td>
<td>-1.70</td>
</tr>
<tr>
<td>FLU-Por-MA</td>
<td>448, 572 (4.13) (4.40)</td>
<td>266</td>
<td>309</td>
<td>-0.98, -1.35, 0.66, 1.27,</td>
<td>-1.51</td>
</tr>
</tbody>
</table>

$^a$Solvent CH$_2$Cl$_2$. Error limits: $\lambda_{max}$ ± 1 nm, log $g$, ± 10%. $^b$D = Pyrene or Fluorene. $^c$CH$_2$Cl$_2$, 0.1 M TBAP; Glassy carbon working
onto 6 µm thick TiO$_2$ layer as a consequence of electron injection from excited singlet state of porphyrin into the conduction band of TiO$_2$. The singlet excited-state life-times of all four unsymmetrical porphyrins were measured in DCM solvent ($\lambda_{ex} = 440$ nm & $\lambda_{em} = 650$ nm) and were found to be 0.82, 0.97 & 0.97 ns for PYR-Por-CA, PYR-Por-MA, FLU-Por-CA & FLU-Por-MA, respectively (See Supporting information). In all four cases the excited state life-time was quenched when adsorbed onto 2 µm thick TiO$_2$ layer.

With a view to evaluate the HOMO-LUMO levels of the porphyrin sensitizers, we have performed the electrochemistry by using cyclic and differential pulse voltammetric techniques in dichloromethane solvent. The redox potentials were determined from half-wave potentials ($E_{1/2}$) ($E_{ox}$-$E_{red}/2$) by cyclic voltammetry (CV) or peak potentials ($E_{p}$) by differential pulse voltammetry (DPV). The redox potential data are presented in Table 1. Each new porphyrin sensitizer undergoes three reductions and either two or three oxidations under the experimental conditions employed. Wave analysis suggested that, both oxidation and reduction reactions are either quasi-reversible or totally irreversible. The first two oxidation processes belongs to the porphyrin macrocycle that generates radical and the dication and the third oxidation belongs to the polycyclic aromatic hydrocarbon moiety in all four investigated sensitizers. The data presented in Table 1, suggest that the sensitizers with cyanoacrylic acid group are more difficult to oxidize than the corresponding sensitizers with malonic acid group. This is due to the more electron withdrawing nature of cyanoacrylic acid group. The excited state oxidation potential of all four porphyrin sensitizers (Table 1) was found to be more negative than the energy level of conduction band edge of TiO$_2$ (-0.8 V vs. SCE) and $E_{ox}$ energy level is more positive than the redox potential of iodine/iodide system (0.2 V vs. SCE) for these dyes.

Quantum Mechanical Calculations
In order to obtain insight on the effect of differing donor (pyrene or fluorene) and acceptor (CA or MA) groups on the electrochemical, optical and geometrical properties of these new porphyrin...
sensitizers, we have performed TD-DFT calculations using B3LYP/6-31G(d) level indichloromethane polarisable-continuum model solvent phase. The molecular orbital analysis of the frontier orbitals of PYR-Por-CA is illustrated in Figure 6 while their energy levels are summarized in Table 3. The electron distribution pattern in Figure 6 suggests that the first two HOMOs are essentially porphyrin ring centred with a slight electron delocalization onto the donor pyrene and on the thiophene part of the anchoring group whereas in the HOMO-2, the delocalization was mainly on the donor pyrene along with a contribution from the macrocyclic ring. In contrast the electron density of the LUMO level was mainly localized on the thiophene-cyanoacrylic acid moiety, anchoring group and on the ethynyl linker with a considerable contribution from the porphyrin ring as well. In contrast, for LUMO+1 the electron density was exclusively distributed on the porphyrin ring and for LUMO+2 there was delocalization of electron density on both porphyrin and the ethynyl thiophene linker. The above discussion suggests that the porphyrin unit is mainly responsible for the first oxidation process, although with a noticeable contribution from

Figure 6: Frontier orbitals of PYR-Por-MA calculated using B3LYP/6-31G(d) within dichloromethane PCM.

Figure 7: Energy level diagram of D-π-A dyes.
the thiophene adjacent to the anchoring group. Similarly, the first reduction process in each of the reported porphyrins was contributed by charge delocalization on both the ethynyl thiophene acrylic acid groups and the porphyrin macrocyclic ring. The pyrene unit plays a negligible role in the frontier orbitals suggesting its potential role as an electron donating unit is not realised in practice, consistent with little change in redox potential between fluorene and pyrene analogues. This may be detrimental in terms of charge separation following electron transfer to the TiO$_2$, since a noticeable component of the positive charge density on the dye will be distributed close to the TiO$_2$ which can promote charge recombination.

Figure 7 depicts the energy level diagram of D-$\pi$-A porphyrins with the conduction band (CB) of TiO$_2$ as well as redox energy of I$_3^-$/I$^-$. As suggested in the Figure 7, all four new porphyrin sensitizers should be capable of injecting electrons to the CB of TiO$_2$ upon excitation. More importantly, electron injection from the sensitizers to TiO$_2$ should be more favourable for PYR-Por-MA than the other sensitizers owing to the higher LUMO levels.

In Figure 8 we report the calculated absorption spectra of PYR-Por-CA in dichloromethane solvent. All calculated electronic transitions energies, along with their oscillator strengths and molecular orbital compositions of dyes are summarized in supporting information. In general, the calculations show excellent agreement with the experimental spectra, although the Q-band, assigned to the HOMO-LUMO transition (>80%), shows a higher than expected intensity.

### Photovoltaic Measurements

![Figure 9: J−V characteristics of DSSCs constructed with different porphyrin sensitizers under 1 sun illumination](image)

Figure 9 shows the performance of the DSSCs of different sensitizers on the basis of their steady-state current–voltage characteristics. Table 4 summarizes the key cell parameters for DSSCs as a function of different porphyrin sensitizers. DSSC parameters are significantly influenced by the porphyrin sensitizers. The maximum conversion efficiency has been achieved for the cells sensitized with PYA-Por-MA. It shows increased $J_{sc}$ and $V_{oc}$ effects.

### Table 3: Percentage contributions from component parts of PYR-Por-CA to selected molecular orbitals. Also quoted are the calculated energies for these molecular orbitals (Ar-based = trimethoxyaryl unit; S-based = thiophene-cyanoacetic acid unit)

<table>
<thead>
<tr>
<th>MO</th>
<th>MO energy / eV</th>
<th>Zn-based</th>
<th>Porphyrin-based</th>
<th>Pyrene-based</th>
<th>S-based</th>
<th>Ar-based</th>
</tr>
</thead>
<tbody>
<tr>
<td>HOMO-2</td>
<td>-5.52</td>
<td>0.01</td>
<td>15.66</td>
<td>82.80</td>
<td>0.16</td>
<td>1.37</td>
</tr>
<tr>
<td>HOMO-1</td>
<td>-5.47</td>
<td>0</td>
<td>79.93</td>
<td>12.91</td>
<td>0.04</td>
<td>7.12</td>
</tr>
<tr>
<td>HOMO</td>
<td>-5.22</td>
<td>0.84</td>
<td>62.12</td>
<td>3.17</td>
<td>23.46</td>
<td>10.41</td>
</tr>
<tr>
<td>LUMO</td>
<td>-3.09</td>
<td>0.16</td>
<td>32.48</td>
<td>1.86</td>
<td>63.91</td>
<td>1.59</td>
</tr>
<tr>
<td>LUMO+1</td>
<td>-2.44</td>
<td>0.23</td>
<td>88.60</td>
<td>1.42</td>
<td>0</td>
<td>9.75</td>
</tr>
<tr>
<td>LUMO+2</td>
<td>-2.37</td>
<td>0.14</td>
<td>53.27</td>
<td>3.21</td>
<td>41.23</td>
<td>2.15</td>
</tr>
</tbody>
</table>
in the frontier orbitals. However, the overall conversion efficiency is less than the controlled cells made with standard N719 sensitizer. The reason for the decreased efficiency compared to the previously reported acene modified dyes can be deduced as follows. The flaccidity of the acrylic bond causes the dye molecule anchored on TiO₂ to be inclined with respect to the adjacent dye molecule, consequently reducing the extent of dye adsorption on TiO₂ (FF) and henceforth results in a decreased IPCE and current density values.³² Moreover there is also a chance of increased recombination rate at the TiO₂/ electrolyte interface, due to the possibility of halogen bonding between iodine in the electrolyte and some electron rich segments like the sulfur atom in the thiophene moiety.³³ The presence of long side chains may be an added advantage to minimize dye aggregation but still they may lead to surface blocking, resulting in low dye uptake.⁴⁴,⁴⁵ The reduced Vₘₚ values of certain zinc porphyrin dyes may be due to faster recombination rate between TiO₂ electrons and the acceptor species in the 1/2 redox electrolyte and also by means of other deactivation pathways which competes and lowers the electron injection efficiency.⁴⁶ The introduction of twisted spacer as an alternative to rigid benzoic acid anchoring group may interrupt the overall conjugation in the dye molecule and hence weakens the ICT interaction and also replacing a phenyl spacer with a thiophene moiety may also lead to decrease in the total absorption cross-section by half which will consequently lead to poor photovoltaic performance.⁴³,⁴⁶

### Thermal Stability

Finally, we have studied the thermal stability of these porphyrin sensitizers by using thermogravimetric analysis. This thermal stability is essential for roof top applications of DSSC devices. It is well known in the literature that tetraphenyl porphyrin and its metallo derivatives are thermally stable up to 400 °C. Figure 10 shows the thermal behaviour of PYR-POR-CA. From the figure it is clear that the sensitizer PYR-POR-CA is stable up to 250 °C. The initial weight loss (~2%) observed between 200 to 250 °C is attributed to the removal of the carboxyl group. A similar trend in thermal stability was also obtained in other sensitizers of this series.

![Figure 10: TG/DTG curves of PYR-POR-CA with heating rate of 10 °C min⁻¹ under Nitrogen atmosphere.](Image)

(Note: See Supporting Information). It is clear from the thermal data that these dyads are highly durable for longstanding outdoor applications.

### Conclusions

In conclusion, we have designed four unsymmetrical zinc porphyrins based on D-π-A approach for DSSC applications. Both Soret and Q band absorption of all four sensitizers are broadened and red-shifted. The emission maxima and excited state life-time were quenched, when adsorbed onto nanocrystalline TiO₂. Electrochemical and spectro-electrochemical properties suggest that first oxidation is localized on the porphyrin centre. Up on photosensitization of nanocrystalline TiO₂, the pyrene substituted sensitizers have shown efficiency of up to 3.14%. The reason may be due to more electron releasing nature of pyrene derivatives than the corresponding fluorrine derivatives. This result the Soret band absorption is more red-shifted in case of pyrene derivatives as it can harvest more sunlight and more favorable conditions for injection of electron from excited state of sensitizer to the TiO₂ conduction band. However for exact reason, one has to do the dynamic studies of these sensitizers in detail and also impedance spectroscopy. Such studies are currently in progress.

### Notes and references

† Electronic Supplementary Information (ESI) available: [Detailed experimental procedure, absorption and emission spectra, fluorescence decay curves, spectro-electrochemical, HOMO-LUMO energy levels information available]. See DOI: 10.1039/b000000x/
