Sensitizers

Synthesis and Characterization of Donor– π -Acceptor-Based Porphyrin Sensitizers: Potential Application of Dye-Sensitized Solar Cells

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Abstract: New porphyrin sensitizers based on donor- π -acceptor (D- π -A) approach have been designed, synthesized, characterized by various spectroscopic techniques and their photovoltaic properties explored. N,N'-Diphenylamine acts as donor, the porphyrin is the π -spacer, and either carboxylic acid or cyanoacryclic acid acts as acceptor. All compounds were characterized by using ¹H NMR spectroscopy, ESI-MS, UV-visible emission spectroscopies as well as electrochemical methods. The presence of aromatic groups between porphyrin π -plane and acceptor group push the absorption of both Soret and Q-bands of porphyrin towards the red region. The electrochemical properties suggests that LUMO of these sensitizers above the TiO₂ conduction band. Finally, the device was fabricated using liquid redox electrolyte (I-/ I_3^{-}) and its efficiency was compared with that of a leading sensitizer.

Introduction

Nanocrystalline dye-sensitized solar cells (DSSCs) are currently attracting widespread interest for the conversion of sunlight into electricity because of their low cost and high conversion efficiency^[1] in these cells; the dye sensitizer is one of the key components for high power conversion efficiencies. The most successful charge-transfer sensitizers employed so far in such bis(tetrabutylammonium)-cis-di(thiocyanato)-N,N'cells are bis(4-carboxylato-4'-carboxylic acid-2,2'-bipyridine) ruthenium(II) (the N719 dye) and trithiocyanato 4,4',4"-tricarboxy-2,2':6',2"-terpyridine ruthenium(II) (the "black dye"), produced solar-energy-to-electricity conversion efficiencies (η) of more than 11% under AM 1.5 irradiation and stable operation for millions of turnovers.^[2] Although Ru^{II} polypyridyl complexes have shown very good efficiency, there are certain limitations in the practical application of these complexes for DSSC. They are relatively low molar extinction coefficient above 600 nm,

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rarity of the ruthenium metal in the earth's crust, and tedious synthesis and tricky purification steps.

For a light-harvesting system, the essential requirements are that the sensitizing dye absorbs light over a wide wavelength range, preferably one that encompasses the visible spectrum, bind strongly to the semiconductor surface, have a suitably high redox potential for regeneration following excitation and be stable over many years of exposure to sunlight. Based on chemical, thermal, photophysical and redox properties, porphyrins are found to be suitable, low-cost alternative sensitizers for DSSC applications even though the synthetic protocols of the porphyrin are tedious.^[3]

Given their primary role in photosynthesis, the use of porphyrin as light harvesters on semiconductors is particularly attractive. Owing to the delocalized macrocyclic structure and very strong absorption in the 400-450 nm region (Soret band) as well as two/four less intense absorption bands in the 500-700 nm region (Q-bands), porphyrins have been studied extensively and have proved to be promising components of molecular electronic and photonic devices.^[4] The first porphyrin that was used for the sensitization of nanocrystaline TiO₂ is [tetrakis(4-carboxyphenyl) porphyrinato] zinc(II) with an overall conversion efficiency of 3.5%.^[5] Later, Officer, Nazeeruddin, and coworkers have reported porphyrin-based sensitizers by using the β -pyrrole position with an overall conversion efficiency of up to 7%.^[6] These efficiencies are relatively less when compared with ruthenium(II) polypyridyl complexes. To further improve the efficiency of DSSC device based on a porphyrin sensitizer, the design strategy has to change. Porphyrin is has a minimum absorption in 450-500 nm regions; one has to improve the absorption capability of porphyrin in 450-500 nm

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region and/or redshift of both Soret as well as Q-bands for further improvement of efficiency of DSSC device. For this reason, Grätzel, Eric, and co-workers adopted the donor– π -acceptor (D– π -A) approach and reported the "**YD**" series of sensitizers in which an organic molecule such as *N*,*N*'-diphenyl amine acts as the donor, porphyrin macrocycle as the π spacer, and the ethynylbenzoic acid moiety serves as an acceptor as well as anchoring onto nanocrystalline TiO₂.^[7] With this strategy, DSSCs based on porphyrin sensitizers have crossed an efficiency of 11%. However, the recent record performance of **YD2-OC8** dye with highest η value of 12.3% using a Co^{II}/Co^{III}-based redox electrolyte has triggered a new hope for further deeper exploration of the purple pigment through varied structural modifications.^[7c]

Here, in the present manuscript, we further extend this strategy and report a series of porphyrin sensitizers by using either thiophene or furan as an acceptor link in place of ethynylbenzoic acid moiety and we have compared their efficiencies with that of **YD2-OC8** and **YD2**. The structure of the new sensitizers are shown in Figure 1. The incorporation of a thiophene moiety is to increase the conjugation of porphyrin-ring system and more importantly the injection property of the sensitizing dye.





Molecular structures of D- π -A porphyrins.

We have designed new porphyrin sensitizers based on the donor– π -acceptor concept. In this design, the donor is bis(4-hexylphenyl)amine moiety, the acceptor is either thiophene or furan moiety, and the porphyrin ring acts as π -spacer. Cyano acrylic acid or carboxyl group acts as the anchoring group. The synthesis of all newly designed porphyrin sensitizers is illustrated in Schemes 1–4. Both compounds 1 and 2 were synthesized by adopting literature-reported procedures.^[8]

We have adopted two different procedures for the coupling of donor group bis(4-hexylphenyl)amine to porphyrin π -spacer. The first method involves coupling of bis(4-hexylphenyl)amine with compound **2** (Buchwald–Hartwig N–C cross-coupling^[9]). This method involves an additional one-step synthesis of bromo-porphyrin (**2**) from compound **1**. The second method is



Scheme 1.

facile and efficient.^[10] Compound 3 is directly synthesized by the NaAuCl₄·2H₂O/(diacetoxyiodo)benzene (PIDA), hypervalentiodine(III)-mediated, single-electron transfer (SET) driven nucleophilic substitution reaction for convenient synthesis of a wide range of Zn-meso-amino porphyrins (Scheme 1). The compound 3 is the key intermediates for the most of the abovelisted porphyrin compounds (Scheme 2) and was achieved by this diversity-oriented synthetic approach in open air with good yields (65.85%). Another requirement for having such type of required N-C coupling is that compound 1 exactly fits into the three-sided meso-blocked porphyrin. Next, the mesoamino porphyrin 3 was treated with tetrabutylammonium fluoride (TBAF) to deprotect the silvl group^[7] to obtain common intermediate compound 4, which was coupled (Sonogashira) with various halo aryl acids to have different targeted molecules (YD-2, HYD-2A, HYD-4, HYD-4T, HYD-8, HYD-8T, and HYD-FA) as shown Scheme 2.^[11]

The sensitizers **HYD1** and **HYD3** were synthesized by corresponding heteroaromatic aldehydes with compound **5** through Suzuki coupling followed by N–C coupling as shown in Scheme 3. Compound **10** was synthesized as per the procedure reported in the literature.^[7c] By adopting similar Aureate coupling procedure, **HYD4-OC8** and **YD2-OC8** were synthesized as shown in Scheme 4. All these new porphyrin sensitizers were fully characterized by using ¹H/¹³C NMR spectroscopy, ESI-MS, IR, UV–visible, and fluorescence spectroscopies, as well as electrochemical methods.

The mass spectral data of all new sensitizers have molecular ion peaks to their corresponding molecular weight (see the Supporting Information).

The electronic absorption spectra of these sensitizers were measured in ethanol solvent and representative absorption spectra of **YD-2**, **YD2-OC8**, and **HYD4-OC8** were illustrated in Figure 2. The corresponding wavelength of absorption maxima (λ_{max}) and the molar extinction coefficients $(\log \varepsilon)$ of all sensitiz-

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Scheme 2. Reaction conditions employed for synthesis of new porphyrin photosensitizers: i) TBAF, THF; ii) [Pd₂(dba)₃], [AsPh₃], THF/Et₃N, 4-iodobenzoic acid; iii) 5-bromoisophthalic acid; iv) 5-bromothiophene-2-carboxylic acid; v) 5'-bromo-2,2'-bithiophene-5-carboxylic acid; vi) 1-3-(5-bromothiophen-2yl)-2-cyanoprop-2-eneperoxoic acid; vii) 1-3-(5'-bromo-2,2'-bithiophen-5-yl)-2cyanoprop-2-eneperoxoic acid; viii) 5-bromofuran-2-carboxylic acid.



Scheme 3. Synthetic route for preparation of **HYD-1** and **HYD-3**:) [Pd(PPh₃)₄], Cul, aq. NaHCO₃, THF, (5-formylthiophen-2-yl)boronic acid for **6** and (5'-formyl-2,2'-bithiophen-5-yl)boronic acid for **7**; ii) bis(4-hexylphenyl)amine, NaAuCl₄-2H₂O, (diacetoxyiodo)benzene, CH₂Cl₂; iii), iv) cyanoacetic acid, piperidine, CHCl₃.



Scheme 4. i) Bis(4-hexylphenyl)amine, (diacetoxyiodo)benzene, and sodium tetrachloroaurate dihydrate, CH₂Cl₂; ii) TBAF, THF, and with [AsPh₃], [Pd₂(dba)₃], THF/Et₃N and either 5-bromothiophene-2-carboxylic acid (for iii), or 4-iodobenzoic acid (for iv).

ers are given in Table 1. All these porphyrins exhibit characteristic intense Soret bands (\approx 440 nm), which is an $a_{1u}(\pi)/eg(\pi^*)$ electronic transition, assigned to the second excited state (S_2) and Q-bands (500–700 nm) originated from $a_{2u}(\pi)/eg(\pi^*)$ electronic transition, attributed to the first excited state (S_1). From the Figure 2 and Table 1, it is clear that both the Soret and Qbands are redshifted, when compared with the parent compound **ZnTPP** except in case of **HYD-1**. This is probably due to the lack of extended π -conjugation. We have replaced the ethenyl benzoic acid group in **YD2-OC8** with ethenyl thiophene carboxylic acid group (**HYD4-OC8**) to investigate the electronic effects and resulting efficiency of the device.



Figure 2. Absorption spectra of YD-2, YD2-OC8, and HYD4-OC8 in EtOH.

Both the Soret and Q-bands of **HYD4-OC8** are redshifted by 2–5 nm compared with **YD2-OC8**. This is probably due to more electron-withdrawing nature of thiophene group rather than benzene group. Figure 3 displays the absorption spectrum of **HYD4-OC8** and **YD2-OC8** adsorbed onto 2 μ m thick TiO₂ electrode, which is similar to that of the solution spectra but exhibits a small redshift. This may be due to the anchoring of carboxylic protons of porphyrin on TiO₂, which releases the proton upon binding to Ti⁴⁺.^[12] Similar redshifts in absorption spectra were also observed in other sensitizers when adsorbed on TiO₂.

The emission spectra of all newly synthesized D- π -A porphyrin sensitizers were measured at room temperature in dichloromethane solvent and the representative spectra of HYD4-OC8, YD2-OC8, and YD-2 are illustrated in Figure 4 with the corresponding emission maxima reported in Table 1. From Figure 4 and Table 1, it is clear that the guantum yields of all porphyrin sensitizers are enhanced compared with the reference compound 5,10,15,20-tetraphenyl zinc porphyrin (ZnTPP). The singlet state energies (E_{0-0}) of all porphyrin sensitizers, estimated from excitation and emission spectra are presented in Table 1; they are in the range of (1.90 ± 0.05) eV, which is slightly less, when compared with its reference compound, ZnTPP. No emission spectra are observed for all porphyrin sensitizers adsorbed onto 6 µm thick TiO2 layer as a consequence of electron injection from excited singlet state of porphyrin into the conduction band of TiO₂.

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Table 1. Absorption, fluorescence, and electrochemical data for porphyrin dyes.								
Dye	Absorption ^[a] λ_{\max} [nm] (log ε [M^{-1} cm ⁻¹])	Emission ^(b) λ_{\max} [nm] (ϕ)	Q _f	E ₀₋₀ [eV]	E [*] _{ox}	Potential V versu oxidation	us SCE ^[c] reduction	
YD-2	442 (5.25), 587 (3.92), 649 (4.43)	682	0.074	1.93	-1.37	$+0.56, +0.84, +1.47^{[d]}$	-1.04, ^[d] -1.62	
HYD-2A	438 (5.33), 585 (4.03), 647 (4.49)	676	0.073	1.93	-1.4	$+0.53, +0.77, +1.45^{[d]}$	-1.31, ^[d] -1.68	
HYD-4	448 (5.24), 590 (3.95), 652 (4.49)	683	0.088	1.92	-1.36	$+0.56, +0.83, +1.46^{[d]}$	-1.28, -1.72	
HYD-4T	462 (5.12), 582 (3.78), 657 (4.45)	688	0.065	1.89	-1.37	$+0.52$, $+0.79$, $+1.46^{[d]}$	-1.28, -1.66	
HYD-8	466 (5.11), 589 (3.82), 664 (4.56)	703	0.08	1.85	-1.28	$+0.57, +0.83, +1.45^{[d]}$	-0.88, -1.43	
HYD-8T	466 (5.21), 590 (4.04), 664 (4.75)	697	0.098	1.86	-1.33	$+0.53, +0.81, +1.48^{[d]}$	-1.25, ^[d] -1.5	
HYD-FA	444 (5.18), 585 (3.92), 651 (4.41)	680	0.077	1.93	-1.38	$+0.55$, $+0.82$, $+1.46^{[d]}$	-1.27, ^[d] -1.7	
HYD-1	422 (5.15), 571 (4.03), 628 (4.11)	673	0.072	1.99	-1.45	$+0.54$, $+0.8$, $+1.48^{[d]}$	-1.34, -1.85	
HYD-3	426 (5.18), 569 (4.36), 626 (4.34)	670	0.044	1.99	-1.4	$+0.59, +0.77, +1.47^{[d]}$	-1.37, -1.78	
HYD4-OC8	453 (5.29), 586 (4.04), 646 (4.48)	670	0.081	1.94	-1.36	$+0.58, +0.79, +1.46^{[d]}$	$-1.44^{[d]}$	
YD2-OC8	447 (5.28), 584 (4.05), 644 (4.45)	670	0.083	1.95	-1.37	$+0.59, +0.79, +1.45^{[d]}$	-1.43 ^[d]	
[3] All dives measured in EtOH (0.01 mu) error limits: (1 ± 1) nm (c ± 10)% [b] Solvent: CH CL (1 ± 1) nm E values were estimated from the 5% in								

[a] All dyes measured in EtOH (0.01 mm), error limits: $(\lambda_{max} \pm 1)$ nm, ($\epsilon \pm 10$)%. [b] Solvent: CH₂Cl₂, $(\lambda_{max} \pm 1)$ nm, $E_{0.0}$ values were estimated from the 5% intensity level of the emission spectra at 77 K. [c] Solvent: CHCl₂, 0.1 M TBAP, glassy carbon working electrode, standard calomel electrode, Pt electrode is the auxiliary electrode. Error limits: $E_{1/2} \pm 0.03$ V. [d] Irreversible process E_{pa} .



Figure 3. UV–visible absorption spectra of HYD4-OC8 and YD2-OC8; solid lines in solution (0.01 $mM \times 10$) and dotted lines on TiO₂ (0.1 mM) in EtOH.



Figure 4. Emission spectrum of YD-2, YD2-OC8, and HYD4-OC8 in CH₂Cl₂.

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). Representative CV and DPV of HYD4-OC8 are depicted in Figure 5. The corresponding redox potential data of all sensitizers are presented in Table 1. Wave analysis suggested that, in general, whereas the first reduction step and first two oxidation steps are reversible ($i_{pc}/i_{pa} = 0.9-1.0$) and diffusion-controlled $(i_{pc}/v^{1/2} = \text{constant} \text{ in the scan rate } (v)$ range 50–500 mV s⁻¹) one-electron transfer ($\triangle E_p = 60-70$ mV; $\triangle E_p =$ (65 ± 3) mV for ferrocenium/ferrocene couple) reactions, the subsequent steps are, in general, either quasi-reversible $(E_{pa}-E_{pc}=90-200 \text{ mV} \text{ and } i_{pc}/i_{pa}=0.5-0.8 \text{ in the scan rate } (v)$ range 100-500 mV s⁻¹) or totally irreversible. The oxidation potential of all porphyrin sensitizers is anodically shifted when compared with the reference compound ZnTPP. 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 TiO₂ (-0.8 V vs. SCE)^[13] and E_{ox} energy level is more positive than the redox potential of iodine/iodide system (0.2 V vs. SCE)^[14] for these dyes.



Figure 5. CV and DPV plots of HYD4-OC8, TBAP (0.1 M) in CH₂Cl₂ at 23 °C.

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Photovoltaic measurements

The performance of the newly synthesized porphyrin molecules as a sensitizer^[1c] with a sandwich-type nanocrystalline TiO₂ electrodes $(8+4 \,\mu m \text{ composed of transparent layer and}$ scattering layer) was determined from measurements on photovoltaic cells using E01 as redox electrolyte, which consists of 0.05 м I₂, 0.1 м Lil, 0.6 м 1,2-dimethyl-3-propylimidazolium iodide (DMPII), and 0.5 M tert-butylpyridine (TBP) in acetonitrile. We added 3α , 7α -dihydroxy- 5β -cholic acid (CDCA; 0.4 mm) into the dye solution to minimize the aggregation of the porphyrin. The representative photocurrent action spectrum of HYD4-OC8, YD2-OC8, YD-2, and N-719 are shown in Figure 6, in which the photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. The photocurrent action spectrum resembles the absorption spectra except for a slight redshift by about 5 nm. The photoresponse of thin films extends up to 750 nm. The IPCE was calculated according to the following Equation:

$$\mathsf{IPCE}\ [\%] = \frac{1240[\mathsf{eVnm}] \cdot J_{\mathsf{sc}}[\mathsf{mAcm}^{-2}]}{\lambda[\mathsf{nm}] \cdot \phi[\mathsf{WM}^{-2}]} \times 100 \tag{1}$$

in which J_{sc} is the short-circuit photocurrent density for monochromatic irradiation, λ and ϕ are the wavelength and the intensity, respectively, of the monochromatic light. We have observed an IPCE value of 80% at 680 nm in case of HYD4-OC8 and YD2-OC8 sensitizers. Under similar conditions, an IPCE of 80% was observed at 550 nm in the case of N719. Figure 7 shows the performance of the DSSCs of sensitizers HYD4-OC8, YD2-OC8, YD2, and N719 on the basis of their steady-state current/voltage characteristics. Table 2 summarizes the key cell-parameters for DSSCs (open-circuit potential (Voc), current density (J_{sc}) , fill factor (ff) and efficiency (η)) as a function of different porphyrin sensitizers. The sensitizer YD2-OC8 has shown overall conversion efficiency of 12.3% using Co"/Co" redox couple. However, in the present test cell conditions using the I^-/I_3^- redox couple, it has shown an efficiency of 9.4%. Under similar test cell conditions, the redesigned sensitizer HYD4-OC8 has shown $V_{\rm OC}$ 740 mV and $J_{\rm SC}$ 17.70 mA cm⁻² with an overall conversion of efficiency of 9.25%. In HYD4-OC8 we replaced phenyl group with thiophene because of its better electron conduction,^[15] however, we observed almost similar physical properties in HYD4-OC8, that is, absorption, highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/LUMO) levels, and so on, (Table 1) compared with YD2-OC8 and it reflects even in the efficiency of the device. A comparison of YD-2 with HYD-2A shows a decrease in efficiency, because of two carboxylic acid groups present in phenyl ring of HYD-2A.^[16] The furan derivative, that is, HYD-FA, has shown an efficiency of 2.78%, whereas under similar test cell conditions its corresponding thiophene derivative (HYD4) shown an overall conversion efficiency of 5.68%. This is due to more electron-withdrawing nature of thiophene group compared with the furan group.^[17] Similarly, YD2 has an efficiency of 6.96%, whereas under similar conditions, HYD1

has shown only 4.56%. The reason may be that when we replaced phenyl acetylene carboxylic acid group with thiophene cyanoacetic acid, there was a blueshift in the absorption, change in HOMO-LUMO levels, and an influence in efficiency. From the literature, use of the acetylenic group in sensitizers has led to better efficiency. To confirm, we have replaced the acetylinic group with thiophene cyanoacetic acid group; consequently, we observed reduced efficiency. The reason to replace the acetylenic group is to enhance the durability of the device.^[18]



Figure 6. IPCE [%] spectrum of YD-2, YD2-OC8, HYD4-OC8, and N-719.



Figure 7. Current–voltage spectrum of YD-2, YD2-OC8, HYD4-OC8, and N-719.

Finally, we studied the thermal stability of these porphyrin sensitizers by using thermogravimetric analysis. This thermal stability is essential for rooftop applications of DSSC devices. It is well known in the literature that tetraphenylporphyrin and its metallo-derivative are thermally stable up to $400 \,^{\circ}C.^{(19)}$ Figure 8 shows the thermal behavior of **HYD4-OC8**. From the Figure it is clear that the sensitizer **HYD4-OC8** is stable up to $200 \,^{\circ}C$. The initial weight loss ($\approx 2\%$) observed in between 200 to $250 \,^{\circ}C$ is attributed to the removal of the carboxyl group. A

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Table 2.	Photovolta	c parameters	of por	phyrin-based	dye-sensitized	solar	cells	und
illumination (power 100 mW cm ⁻²) and an active area of 0.16 cm ² .								

Dye ^[a,b]	CDCA ^[c] [тм]	Solvent	J _{sc} [mA cm ⁻²] ^[d]	V _{oc} [mV] ^[d]	ff ^[d]	η [%]		
YD-2	0.4	CH₃CN/tBuOH	15.20	0.64	0.71	6.96		
HYD-2A	0.4	CH₃CN/tBuOH	11.50	0.65	0.71	5.31		
HYD-4	0.4	CH₃CN/tBuOH	13.10	0.59	0.72	5.68		
HYD-4T	0.4	EtOH	3.40	0.56	0.71	1.39		
HYD-8	0.4	EtOH	5.48	0.58	0.71	2.27		
HYD-8T	0.4	EtOH	8.74	0.62	0.72	3.90		
HYD-FA	0.4	CH₃CN/tBuOH	6.70	0.56	0.74	2.78		
HYD-1	0.4	EtOH	9.40	0.65	0.74	4.56		
HYD-3	0.4	EtOH	3.16	0.55	0.73	1.28		
HYD4-OC8	0.4	CH₃CN/tBuOH	17.70	0.74	0.70	9.25		
YD2-OC8	0.4	CH₃CN/tBuOH	17.30	0.76	0.71	9.40		
N-719	-	CH ₃ CN/tBuOH	14.66	0.73	0.74	7.99		
[] Due concentration of 0.2 mark N.710 (0.2 mark) [] [] Electrolytic (E01)								

[a] Dye concentration of 0.2 mM except **N-719** (0.3 mM). [b] Electrolyte (E01): I₂: 0.05 M, Lil: 0.1 M, 1,2-dimethyl-3-propylimidazolium iodide (DMPII):0.6 M, *tert*-butylpyridine (TBP):0.5 M in acetonitrile. [c] Co-adsorption (CDCA): 0.4 mM. [d] Error limits: J_{SC} : \pm 0.20 mA cm⁻², $V_{OC} = \pm$ 30 mV, ff = \pm 0.03, immersion time for all dyes: 17–18 h at T = 22 °C.

similar trend in thermal stability was also obtained in other sensitizers of this series. It is clear from the thermal data that these dyads are highly durable for longstanding outdoor applications.



Figure 8. TG/DTG curves of HYD4-OC8.

Conclusion

We have designed new unsymmetrical zinc porphyrins based on D- π -A approach for DSSC applications. Both Soret and Qbands of all the porphyrin sensitizers are redshifted and also quantum yields of all sensitizers are enhanced in comparison with the reference compound, **ZnTPP**. Electrochemical properties suggest that first oxidation is localized on the porphyrin center. Upon photosensitization of nanocrystalline TiO₂, the sensitizer **HYD4-OC8** has shown an overall conversion efficiency of 9.25%, whereas the standard sensitizer **YD2-O-C8** has shown 9.40% efficiency under similar test cell conditions by using a liquid redox electrolyte. Finally, thermal studies indicate that these sensitizers are stable up to 200°C and indicate their suitability in rooftop applications.

Experimental Section

Materials

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3,5-Di-*tert*-butyl-benzaldehyde, (triisopropyl)silylacetylene, (siacetoxyiodo)benzene, NaAuCl₄·2 H₂O, TFA, TBAF, [Pd^{II}Cl₂(PPh₃)₂], Cul, [Pd₂(dba)₃] (dba = dibenzylideneacetone), triphenylarsine, 4-iodobenzoic acid, 5-bromo-2thiophene carboxylic acid, [Pd(PPh₃)₄], (5-formylthiophen-2-yl)boronic acid, (5'-formyl-2,2'-bithiophen-5-yl)boronic acid were purchased from Sigma Aldrich and were used as received. Dipyrromethane^[20] and 2,6-bis-(octyloxy)benzaldehyde^[7c] were prepared according to the literature-reported procedures. All the solvents (dichloromethane, tetrahydrofuran (THF), toluene, methanol, chloroform, and *n*-hexane) were obtained from MERCK chemicals Limited, India and were dried before

further use. Zinc acetate was purchased from FINAR Chemicals Ltd, India. Chemical reagents and catalysts used in the reactions were of Analytical reagent grade (AR), purchased from Sigma-Aldrich (India) and were used without further purification. All the reactions were performed using dried and distilled solvents of laboratory reagent (LR) grade. The solvents CHCl₃, CH₂Cl₂, and triethylamine (Et₃N) were dried over CaH₂. Toluene was dried over sodium chunks overnight and distilled under nitrogen atmosphere. Purification of compounds by column chromatography was performed on ACME Silica Gel (100–200 mesh).

Syntheses

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Synthesis of 3: Two different methods were adopted for the synthesis of this compound. Compounds 1 and 2 were prepared according to the literature reported procedure.^[8]

Method 1: Compound **3** was prepared according to reported procedure. $^{\scriptscriptstyle [8]}$ (48% yield).

Method 2: A stirred solution of compound 1 (2.0 g, 2.15 mmol) and bis(4-hexylphenyl)amine (2.17 g, 6.45 mmol) in CH₂Cl₂ (200 mL) was added to (diacetoxyiodo)benzene (0.69 g, 2.15 mmol) and sodium tetrachloroaurate dihydrate (1.03 g, 2.58 mmol) at 0 °C and stirred for 30 min at room temperature under open atmosphere. The reaction was monitored by TLC examination, the reaction mixture was quenched with saturated aqueous solution of sodium thiosulfate and separated the organic layer, extracted the aqueous layer with CH_2CI_2 (2×60 mL), the combined organic phases were washed with brine (1 \times 30 mL), and dried over on Na₂SO₄. The solvent was evaporated by using a rotary evaporator. The crude reaction mixture was purified by silica gel column chromatography by using CH₂Cl₂/Hexane (2:9) as an eluent, to give the title compound 3 (1.79 g, 65.85% yield) as a dark-green powder. ¹H NMR (CDCl₃, 400 MHz): $\delta = 9.75$ (d, J = 4.6 Hz, 2 H), 9.28 (d, J = 4.6 Hz, 2 H), 8.95 (d, J=4.6 Hz, 2 H), 8.81 (d, J=4.6 Hz, 2 H), 8.00 (d, J=1.8 Hz, 4 H), 7.77 (t, J=1.8 Hz, 2 H), 7.21 (d, J=8.6 Hz, 4 H), 6.96 (d, J=8.6 Hz, 4H), 2.46 (t, J=7.9 Hz, 4H), 1.52 (s, 36H), 1.45 (m, 21H), 1.25 (m, 12 H), 0.82 ppm (t, J=7.5 Hz, 6 H); ESI MS: m/z calcd for C₈₃H₁₀₅N₅SiZn: 1264; found: 1265.2 [*M*+H]⁺.

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Synthesis of 4: TBAF (0.158 mL, 0.158 mmol, 1 mmol solution in THF) was added to a stirred solution of porphyrin **3** (0.20 g, 0.158 mmol) in dry THF (20 mL). The solution was stirred at 0 °C for 30 min under argon atmosphere. The reaction mixture was quenched with water and then extracted with CH₂Cl₂ (3×30 mL). The organic layers were dried over on anhydrous Na₂SO₄ and the solvent was removed under vacuum to afford the residual compound **4**, which was used in the next step without any further purification or analysis.

Note: The above step is common for following porphyrin compounds (**YD-2**, **HYD-2A**, **HYD-4**, **HYD-4T**, **HYD-8**, **HYD-8T**, and **HYD-FA**).

Synthesis of YD-2: The above compound 4 (0.158 mmol) and 4-iodobenzoic acid (0.089 g, 0.36 mmol) were dissolved in dry THF (40 mL), and triethylamine (Et₃N, 8 mL) was then added. The reaction mixture was degassed with argon for 10 min, and [Pd₂(dba)₃] (0.04 g, 0.04 mmol) and $[AsPh_3]$ (0.11 g, 0.36 mmol) were then added to reaction mixture. Then, the reaction mixture was heated at reflux for 5 h under an argon atmosphere. The solvent was removed under vacuum, the crude residue was purified on a silica gel column chromatography by using CH₂Cl₂/CH₃OH (19:1) as an eluent to give the semi-solid, which was further recrystallized from CH₃OH/ether to give the compound YD-2 (0.120 g, 61% yield). ¹H NMR: (CDCl₃, 400 MHz): $\delta = 9.79$ (d, J = 4.6 Hz, 2 H), 9.29 (d, J =4.6 Hz, 2 H), 9.00 (d, J=4.6 Hz, 2 H), 8.83 (d, J=4.6 Hz, 2 H), 8.24 (d, J=8.2 Hz, 2 H), 8.12 (d, J=8.2 Hz, 2 H), 8.03 (d, J=1.7 Hz, 4 H), 7.79 (d, J=1.7 Hz, 2H), 7.22 (d, J=8.6 Hz, 4H), 6.98 (d, J=8.6 Hz, 4H), 2.47 (t, J=7.6 Hz, 4 H), 1.50 (s, 36 H), 1.26 (m, 16 H), 0.86 ppm (t, J= 7.1 Hz, 6H); UV/Vis (0.01 mm): λ_{max} (ε): 442 (1,77,636), 587 (8,293), 649 nm (27155 mol⁻¹cm⁻¹); ESI MS: *m/z* calcd (%) for C₈₁H₈₉N₅O₂Zn: 1230; found: 1229.8 [*M*⁺] (100).

Synthesis of HYD-2A: This compound was synthesized by adopting a similar procedure for the synthesis of compound YD-2 by using the compound 5-bromoisophthalic acid (0.10 g, 0.36 mmol). HYD-2A (0.129 g, 56.16% yield) was obtained as a dark-green solid. ¹H NMR ([D₅]Pyridine, 400 MHz): $\delta = 10.15$ (d, J = 4.5 Hz, 2 H), 9.67 (d, J=4.5 Hz, 2H), 9.56 (s, 1H), 9.40 (s, 2H), 9.27 (d, J=4.5 Hz, 2H), 9.08 (d, J=4.5 Hz, 2H), 8.32 (d, J=1.6 Hz, 4H), 8.05 (d, J= 1.6 Hz, 2 H), 7.22–7.15 (m, 8 H), 2.50 (t, J=7.8 Hz, 4 H), 1.51 (s, 36 H), 1.26 (m, 16H), 0.8 ppm (t, J=6.8 Hz, 6H);¹³C NMR ([D₅]Pyridine, 100 MHz): $\delta = 168.3$, 153.0, 151.4, 151.0, 150.5, 149.2, 142.3, 136.4, 136.0, 135.0, 134.2, 133.9, 133.5, 131.2, 130.4, 130.3, 129.6, 125.2, 123.9, 122.9, 122.6, 121.4, 121.2, 99.3, 95.5, 95.3, 35.3, 35.1, 31.8, 31.7, 31.2, 29.9, 22.7, 14.1 ppm; FTIR (KBr): v=2957, 2923, 2851, 2192, 1698, 1591, 1506, 1462, 1362, 1248, 1064 cm⁻¹; UV/Vis (0.01 mm): λ_{max} (ϵ): 438 (2,17,289), 585 (10,741), 647 nm (31 259 mol^{-1} cm^{-1}); ESI MS: *m/z* calcd for C₈₂H₈₉N₅O₄Zn: 1271.6; found: 1271.5 ([*M*⁺] 100%).

Synthesis of HYD-4: This compound was synthesized by adopting a similar procedure for the synthesis of compound YD-2, using the compound 5-bromo-2-thiophenecarboxylic acid (0.08 q, 0.36 mmol), HYD-4 (0.131 g, 58.5% yield) was obtained as a green solid. ¹H NMR (CDCl₃, 400 MHz): $\delta = 9.70$ (d, J = 4.6 Hz, 2H), 9.27 (d, J=4.6 Hz, 2 H), 8.97 (d, J=4.5 Hz, 2 H), 8.80 (d, J=4.5 Hz, 2 H), 7.99 (s, 5 H), 7.74 (s, 2 H), 7.67 (d, J=3.6 Hz, 1 H), 7.2 (d, J=8.5 Hz, 4 H), 6.96 (d, J=8.5 Hz, 4H), 2.46 (t, J=7.6 Hz, 4H), 1.50 (s, 36H), 1.26 (m, 16H), 0.83 ppm (t, J = 7.1 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): $\delta = 152.5, 152.1, 150.5, 150.4, 150.1, 148.7, 141.0, 135.6, 133.5,$ 133.3, 132.0, 131.0, 130.4, 129.6, 128.9, 124.7, 123.6, 122.1, 121.0, 99.0, 98.6, 88.9, 35.2, 35.0, 31.7, 29.7, 29.0, 22.5, 14.0 ppm; FTIR (KBr): $\tilde{\nu} = 2958$, 2918, 2849, 2187, 1659, 1591, 1461, 1361, 1262, 1078 cm⁻¹; UV/Vis (0.01 mm): λ_{max} (ϵ): 448 (176216), 590 (8932), 652 nm (31304 mol⁻¹ cm⁻¹); ESI MS: m/z calcd (%) for $C_{79}H_{87}N_5O_2SZn$: 1236.0, found: 1236.7 [M^+] (100).

Synthesis of HYD-4T: This compound was synthesized by adopting a similar procedure for the synthesis of compound YD-2. Using the compound 5'-bromo-2,2'-bithiophene-5-carboxylic acid (0.10 g, 0.36 mmol) to give HYD-4T (0.132 g, 55.6% yield) as a dark-green solid. ¹H NMR (CDCl₃, 400 MHz): δ = 9.63 (d, J = 4.6 Hz, 2 H), 9.21 (d, J=4.6 Hz, 2 H), 8.91 (d, J=4.6 Hz, 2 H), 8.75 (d, J=4.6 Hz, 2 H), 7.95 (d, J=1.6 Hz, 4 H), 7.72-7.70 (m, 3 H), 7.54 (d, J=3.6 Hz, 1 H), 7.32 (d, J=3.6 Hz, 1 H), 7.24-7.15 (m, 5 H), 6.91 (d, J=8.6 Hz, 4 H), 2.40 (t, J=7.6 Hz, 4 H), 1.46 (s, 36 H), 1.21 (m, 16 H), 0.80 ppm (t, J= 7.2 Hz, 6 H); $^{13}{\rm C}$ NMR (CDCl_3, 100 MHz): $\delta\!=\!$ 169.0, 152.5, 151.9, 150.4, 150.3, 149.9, 148.7, 141.1, 134.9, 133.3, 132.6, 130.8, 130.3, 129.6, 128.9, 125.5, 124.3, 123.5, 122.0, 121.0, 99.3, 99.0, 89.1, 35.2, 35.0, 31.7, 31.5, 29.7, 29.0, 22.6, 14.1 ppm; FTIR (KBr): v=2957, 2922, 2851, 2180, 1672, 1591, 1506, 1446, 1362, 1288, 1066, 1004 cm $^{-1}$; UV/Vis (0.01 mm): $\lambda_{\rm max}$ (ϵ): 462 (131930), 582 (6048), 657 nm (28 268 mol⁻¹ cm⁻¹); ESI MS: m/z calcd (%) for C₈₃H₈₉N₅O₂S₂Zn: 1315.6; found: 1317.0 [*M*⁺] (100).

Synthesis of HYD-8: This compound was synthesized by adopting a similar procedure for the synthesis of compound YD-2, using the compound (E)-3-(5-bromothiophen-2-yl)-2-cyanoacrylic acid (0.10 g, 0.36 mmol), to give HYD-8 (0.121 g, 52.27%) as a dark-green solid. ¹H NMR (CDCl₃, 400 MHz): $\delta = 9.59$ (d, J = 4.6 Hz, 2 H), 9.20 (d, J =4.6 Hz, 2 H), 8.90 (d, J=4.6 Hz, 2 H), 8.80 (d, J=4.6 Hz, 2 H), 8.0 (d, J=1.7 Hz, 4H), 7.9 (s, 1H), 7.73 (d, J=1.7 Hz, 2H), 7.69 (d, J= 3.6 Hz, 1 H), 7.63 (d, J=3.6 Hz, 1 H), 7.15 (d, J=8.6 Hz, 4 H), 6.90 (d, J=8.6 Hz, 4 H), 2.42 (t, J=7.6 Hz, 4 H), 1.46 (s, 36 H), 1.18 (m, 16 H), 0.80 ppm (t, J = 6.7 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): $\delta = 152.5$, 152.1, 150.5, 150.4, 150.2, 148.8, 140.9, 135.1, 133.8, 133.4, 132.1, 131.1, 130.2, 129.6, 128.9, 124.1, 122.1, 121.1, 111.5, 98.1, 88.9, 77.2, 35.2, 35.0, 31.8, 31.7, 29.7, 29.0, 22.5, 14.1 ppm; FTIR (KBr): $\tilde{\nu} =$ 2954, 2924, 2854, 2217, 2172, 1694, 1582, 1506, 1436, 1361, 1248, 1205, 1066 cm⁻¹; UV/Vis (0.01 mm): λ_{max} (ϵ): 466 (1,29,578), 589 (6,694), 664 nm (36762 mol⁻¹ cm⁻¹); ESI MS: m/z calcd (%) for C₈₂H₈₈N₆O₂SZn: 1287.1; found: 1287.6 [*M*⁺] (100).

Synthesis of HYD-8T: This compound was synthesized by adopting a similar procedure for the synthesis of compound YD-2, using (E)-3-(5'-bromo-2, 2'-bithiophen-5-yl)-2-cyanoacrylic acid (0.12 g, 0.36 mmol), to give HYD-8T (0.134 g, 54.33 % yield) as a dark-green solid. ¹H NMR ([D₈]THF, 400 MHz): $\delta = 10.88$ (s, 1 H), 9.64 (d, J =4.5 Hz, 2 H), 9.20 (d, J=4.3 Hz, 2 H), 8.86 (d, J=4.3 Hz, 2 H), 8.71 (d, J=4.3 Hz, 2 H), 8.34 (s, 1 H), 8.04 (s, 4 H), 7.86-7.75 (m, 4 H), 7.63 (d, J=3.4 Hz, 1 H), 7.53 (d, J=3.4 Hz, 1 H), 7.20 (d, J=7.7 Hz, 4 H) 6.96 (d, J=7.7 Hz, 4H), 2.46 (t, J=7.6 Hz, 4H), 1.53 (s, 36H), 1.29 (m, 16H), 0.85 ppm (t, J = 7.1 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): $\delta =$ 152.5, 152.0, 150.9, 150.3, 150.0, 148.6, 142.0, 134.6, 132.3, 132.8, 132.5, 130.5, 129.8, 129.7, 128.7, 124.8, 124.3, 123.1, 122.0, 120.8, 99.8, 98.5, 88.9, 35.2, 34.8, 31.8, 31.1, 29.7, 29.1, 22.6, 13.5 ppm; FTIR (KBr): $\tilde{\nu} = 2958$, 2923, 2852, 2307, 2214, 2176, 1693, 1590, 1506, 1462, 1362, 1246, 1062 cm⁻¹; UV/Vis (0.01 mм): λ_{max} (ε): 466 (1,62,813), 590 (11,157), 664 nm (57010 mol⁻¹ cm⁻¹); ESI MS: *m/z* calcd (%) for C₈₆H₉₀N₆O₂S₂Zn: 1369.2.0, found: 1370.0 [*M*⁺] (100).

Synthesis of HYD-FA: This compound was synthesized by adopting a similar procedure for the synthesis of compound **YD-2**. Using the compound 5-bromo furan-2-carboxylic acid (0.08 g, 0.36 mmol), **HYD-FA** (0.123 g, 55.98% yield) as a dark-green solid. ¹H NMR (CDCl₃, 400 MHz): δ = 9.69 (d, *J* = 4.3 Hz, 2 H), 9.25 (d, *J* = 4.6 Hz, 2 H), 8.95 (d, *J* = 4.6 Hz, 2 H), 8.79 (d, *J* = 4.6 Hz, 2 H), 8.03 (d, *J* = 1.6 Hz, 4 H), 7.79 (t, *J* = 1.6 Hz, 2 H), 7.50 (d, *J* = 8.4 Hz, 1 H), 7.20 (d, *J* = 8.4 Hz, 4 H), 7.18 (d, *J* = 8.4 Hz, 1 H) 6.96 (d, *J* = 8.4 Hz, 4 H), 2.48 (t, *J* = 7.5 Hz, 4 H), 1.51 (s, 36 H), 1.28 (m, 16 H), 0.86 ppm (t, *J* = 7.2 Hz, 6 H); ¹³C NMR (CDCl₃, 100 MHz): δ = 162.5, 152.3, 152.1,

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150.5, 150.3, 150.1, 148.6, 142.3, 141.2, 134.8, 133.5, 133.2, 130.9, 130.3, 129.7, 128.8, 124.7, 124.3, 123.6, 123.5, 122.0, 120.9, 116.6,98.5, 96.7, 84.8, 35.2, 35.0, 31.7, 31.4, 29.7, 29.0, 22.6, 14.1 ppm; FTIR (KBr): $\tilde{\nu} = 2957$, 2924, 2853, 2192, 1693, 1591, 1462, 1362, 1248, 1097, 1001 cm⁻¹; UV/Vis (0.01 mM): λ_{max} (ε): 444 (1,54,015), 585 (8,440), 651 nm (25 999 mol⁻¹ cm⁻¹); ESI MS: *m/z* calcd (%) for C₇₉H₈₇N₅O₃Zn: 1217.6, found: 1218.6 [*M*+1]⁺ (100).

Synthesis of 6: Compound 5 (0.50 g, 0.60 mmol) in dry THF (5 mL) was added slowly to a solution of (5-formylthiophen-2-yl)boronic acid (0.28 g, 1.81 mmol) in dry THF (5 mL) and degassed with argon for 5 min. Then, [Pd(PPh₃)₄] (0.01 g, 0.005 mmol) followed by aq. Na_2CO_3 (1.25 g, 11.82 mmol) were added to reaction mixture and the mixture was heated at reflux for 12 h. After completion of the reaction, the solvent was evaporated, resulting residue was dissolved in water (30 mL), extracted with CH_2CI_2 (2×20 mL). The combined extracts were washed with brine (20 mL), dried over on $\mathsf{Na}_2\mathsf{SO}_4$ and concentrated in vacuum. The residue was purified by silica gel column chromatography by using hexane/ethyl acetate (98:2) as a mobile phase to obtain the compound 6 (0.340 g, 65.63 % yield), as a dark-red powder. ¹H NMR (CDCl₃, 400 MHz): $\delta =$ 10.32 (s,1 H), 9.89 (s,1 H), 9.43 (d, J=4.6 Hz, 2 H), 9.15 (d, J=4.6 Hz, 2 H), 9.13 (d, J = 4.8 Hz, 2 H), 9.08 (d, J = 4.8 Hz, 2 H), 8.16 (d, J =3.7 Hz, 1 H), 8.10 (d, J=1.7 Hz, 4 H), 8.02 (d, J=3.7 Hz, 1 H), 7.83 (t, J = 1.7 Hz, 2 H), 1.48 ppm (s, 36 H); ESI-MS: m/z calcd for $C_{53}H_{54}N_4OSZn$: 860.5; found: 861.4 $[M+1]^+$.

Synthesis of 7: This compound was synthesized by adopting similar procedure for the synthesis of compound **6** using the compound **5** (0.40 g, 0.60 mmol). The only difference is that we have taken (5'-formyl-2,2'-bithiophen-5-yl)boronic acid (0.23 g, 0.96 mmol) in this reaction to give compound **7** (Yield: 0.25 g, 55%). ¹H NMR (CDCl₃, 400 MHz): $\delta = 10.23$ (s,1H), 9.82 (s,1H), 9.36 (d, J = 4.6 Hz, 2H), 9.21 (d, J = 4.6 Hz, 2H), 9.08 (d, J = 4.4 Hz, 2H), 9.00 (d, J = 4.6 Hz, 2H), 8.03 (d, J = 1.8 Hz, 4H), 7.80 (d, J = 3.5 Hz, 1H), 7.76 (t, J = 1.7 Hz, 2H), 7.68 (dd, J = 3.6 Hz, 2H), 7.36 (d, J = 3.5 Hz, 1H), 1.48 ppm (s, 36H); ESI-MS: m/z calcd (%) for $C_{57}H_{56}N_4OS_2Zn$: 942.6; found: 942.4 [M^+] (100).

Synthesis of 8: This compound was synthesized by adopting a similar procedure of Method 2, using **6** (0.32 g, 0.37 mmol), bis(4-hexylphenyl)amine (0.38 g, 1.11 mmol), (diacetoxyiodo)benzene (0.12 g, 0.37 mmol), and sodium tetrachloroaurate dihydrate (0.22 g, 0.56 mmol). The crude product was purified by silica gel column chromatography by using ethyl acetate/hexane (2:98) as an eluent to afford the compound **8** (0.289 g, 65.0%) as a darkviolet powder. ¹H NMR (CDCl₃, 400 MHz): $\delta = 10.15$ (s, 1H), 9.29 (d, J = 4.6 Hz, 2H), 8.96 (d, J = 4.7 Hz, 2H), 8.87 (d, J = 4.7 Hz, 2H), 8.81 (d, J = 4.6 Hz, 2H), 8.07 (d, J = 3.7 Hz, 1H), 7.95 (d, J = 1.7 Hz, 4H), 7.93 (d, J = 3.7 Hz, 1H), 7.71 (t, J = 1.7 Hz, 2H), 7.16 (d, J = 8.6 Hz, 4H), 6.91 (d, J = 8.6 Hz, 4H), 2.42 (t, J = 7.6 Hz, 4H), 1.46 (s, 36H), 1.21 (m, 16H), 0.81 ppm (t, J = 7.1 Hz, 6H); ESI-MS: *m/z* calcd (%) for $C_{77}H_{87}N_3OSZn$: 1196; found: 1195.9 [*M*⁺] (100).

Synthesis of 9: This compound was synthesized by adopting a similar procedure of compound **8**, using the compound **7** (0.24 g, 0.25 mmol), to obtain compound **9** (0.211 g, 65.2%) as a dark-violet powder. ¹H NMR (CDCl₃, 400 MHz): $\delta = 9.78$ (s, 1H), 9.28 (d, J = 4.6 Hz, 2H), 9.09 (d, J = 4.7 Hz, 2H), 8.87 (d, J = 4.7 Hz, 2H), 8.81 (d, J = 4.6 Hz, 2H), 7.95 (d, J = 1.8 Hz, 4H), 7.78 (d, J = 3.6 Hz, 1H), 7.70 (t, J = 1.8 Hz, 2H), 7.65 (d, J = 3.2 Hz, 1H), 7.63 (d, J = 3.2 Hz, 1H), 7.36 (d, J = 3.2 Hz, 1H), 7.16 (d, J = 8.6 Hz, 4H), 6.91 (d, J = 8.6 Hz, 4H), 2.42 (t, J = 7.6 Hz, 4H), 1.44 (s, 36H), 1.21 (m, 16H), 0.81 (t, J = 6.9 Hz, 6H) ppm; ESI-MS: m/z calcd for $C_{81}H_{89}N_5OS_2Zn$: 1278; found: 1279 $[M + 1]^+$.

Synthesis of HYD-1: A mixture of compound **8** (0.12 g, 0.10 mmol), cyano acrylic acid (0.03 g, 0.30 mmol), and piperidine

(0.06 g, 0.70 mmol) were dissolved in dry CH₂Cl₂ (10 mL), the reaction mixture was heated at reflux for 12 h under argon atmosphere until TLC shows the consumption of starting material. The solvent was removed under vacuum and the resulting residue was purified by silica gel column chromatography by using ethyl acetate/ hexane (8:2) as an eluent to obtained the semi-solid, which was recrystallized from CH₃OH/ether to give the HYD-1 (0.082 g, 65.2% yield) as a dark-green solid. ¹H NMR (CDCl₃, 400 MHz): δ = 9.36 (d, J=4.6 Hz, 2 H), 9.04 (d, J=4.5 Hz, 2 H), 8.94 (d, J=4.5 Hz, 2 H), 8.89 (d, J=4.6 Hz, 2 H), 8.56 (s, 1 H), 8.16 (s, 1 H), 8.03 (d, J=1.5 Hz, 4 H), 7.77 (s, 2H), 7.24 (d, J=8.6 Hz, 4H),6.98 (d, J=8.5 Hz, 4H), 2.48 (t, J = 7.8 Hz, 4H), 1.51 (s, 36H), 1.25 (m, 16H), 0.83 ppm (t, 6H, J =7.8 Hz); ¹³C NMR (CDCl₃, 100 MHz): $\delta = 152.7$, 150.8, 150.5, 150.1, 149.9, 148.7, 141.2, 134.9, 133.5, 133.1, 131.0, 130.9,130.8, 129.6, 128.9, 124.2, 123.4, 123.2, 122.1, 121.0, 35.2, 35.0, 31.7, 31.4, 29.7, 29.0, 22.6, 14.1 ppm; FTIR (KBr): $\tilde{\nu} = 2957$, 2924, 2852, 2359, 2341, 1695, 1590, 1454, 1361, 1287, 1070, 1002 cm⁻¹; UV/Vis (0.01 mм): λ_{max} (ε): 422 (1,41,566), 571 (10,723), 628 nm (13035 mol⁻¹ cm⁻¹); ESI MS: m/z calcd (%) for C₈₀H₈₈N₆O₂SZn: 1263.07, found: 1263.8 $[M+1]^+$ (100).

Synthesis of HYD-3: This compound was synthesized by adopting similar procedure, which is used for the synthesis of HYD-1 by using compound 9 (0.12 g, 0.1 mmol) to give HYD-3 (0.082 g, 65.6% yield) as a dark-green solid. ¹H NMR (CDCl₃, 400 MHz): $\delta =$ 9.28 (d, J=4.4 Hz, 2H), 9.10 (d, J=4.2 Hz, 2H), 8.88 (d, J=4.4 Hz, 2H), 8.82 (d, J=4.4 Hz, 2H), 8.26 (d, J=3.4 Hz, 1H), 7.95 (s, 4H), 7.79 (d, J=3.4 Hz, 1 H), 7.70 (s, 4 H), 7.39 (s, 1 H), 7.16 (d, J=8.5 Hz, 4H), 6.91 (d, J=8.5 Hz, 4H), 2.40 (t, J=7.8 Hz, 4H), 1.48 (s, 36H), 1.21–1.18 (m, 16H), 0.82 ppm (t, J=7.1 Hz, 6H); ¹³C NMR (CDCl₃, 100 MHz): $\delta =$ 152.7, 150.8, 150.5, 150.0, 148.7, 141.3, 137.8, 134.9, 134.5, 133.5, 133.1, 132.9, 131.1, 130.9, 129.6, 128.9, 125.7, 124.5, $123.4,\ 122.9,\ 122.1,\ 120.9,\ 90.2,\ 81.6,\ 35.2,\ 35.0,\ 31.7,\ 31.4,\ 29.7,$ 29.0, 22.6, 14.1 ppm; FTIR (KBr): $\tilde{\nu} = 2956$, 2925, 2857, 2216, 2061, 1694, 1589, 1506, 1459, 1362, 1257, 1068, 1002 cm⁻¹; UV/Vis (0.01 mm): λ_{max} (ϵ): 426 (1,51,309), 569 (23,238) and 626 nm (22367 mol⁻¹ cm⁻¹); ESI MS: *m/z* calcd for C₈₄H₉₀N₆O₂S₂Zn: 1345.1; found: 1344.7 [*M*]⁺.

Synthesis of 11: This compound was synthesized by adopting a similar procedure of method 2. Using the compound **10** (1.5 g, 1.2 mmol), bis(4-hexylphenyl)amine (1.24 g, 3.7 mmol), (diacetox-yiodo)benzene (0.40 g, 1.2 mmol), and sodium tetrachloroaurate di-hydrate (0.59 g, 1.4 mmol) to give compound **11** (1.20 g, 65.0% Yield) as a dark-green powder. ¹H NMR (CDCl₃, 400 MHz): δ = 9.65 (d, *J* = 4.5 Hz, 2H), 9.18 (d, *J* = 4.6 Hz, 2H), 8.85 (d, *J* = 4.6 Hz, 2H), 8.68 (d, *J* = 4.5 Hz, 2H), 7.64 (t, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 8.5 Hz, 4H), 6.94 (m, 8H), 3.82 (t, *J* = 6.4 Hz, 8H), 2.46 (t, *J* = 7.6 Hz, 4H), 1.55–1.52 (m, 4H), 1.49–1.43 (m, 21H), 1.27 (t, 12H), 1.01–0.94 (m, 8H), 0.88–0.76 (m, 22H), 0.65–0.43 ppm (m, 44H); APCI-MS: *m/z* calcd for C₉₉H₁₃₇N₅O₄SiZn: 1554.6; found: 1555.8 [*M*+1]⁺.

Synthesis of 12: This compound was synthesized by adopting a similar procedure of compound **4**, using porphyrin **11** (0.2 g, 0.128 mmol) and TBAF (0.13 mL, 0.128 mmol 1 M in THF). The obtained compound **12** was used in the next step without any further purification.

Note: The above step is common for preparation of **HYD4-OC8** and **YD2-OC8**.

Synthesis of HYD4-OC8: This compound was synthesized by adopting a similar reported procedure,^[7c] using compound **12** (0.128 mmol), 5-bromo-2-thiophene carboxylic acid (0.15 g, 0.7 mmol), [Pd₂(dba)₃] (0.04 g, 0.04 mmol), and AsPh₃ (0.09 g, 0.29 mmol) to give **HYD4-OC8** (0.135 g, 62.56%) as a green solid. ¹H NMR (CDCl₃, 400 MHz): δ = 9.57 (d, *J* = 4.6 Hz, 2 H), 9.17 (d, *J* = 4.5 Hz, 2 H), 8.87 (d, *J* = 4.5 Hz, 2 H), 8.67 (d, *J* = 4.6 Hz, 2 H), 7.83 (d,

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$$\begin{split} J = 3.4 \text{ Hz}), \ 7.63 \ (t, \ 2H, \ J = 8.4 \text{ Hz}), \ 7.59 \ (d, \ 1H, \ J = 3.7 \text{ Hz}), \ 7.19 \ (d, \ 4H, \ J = 8.6 \text{ Hz}, \ 1H), \ 6.94-6.91 \ (m, \ 8H), \ 3.84 \ (t, \ J = 6.6 \text{ Hz}, \ 8H), \ 2.43 \ (t, \ J = 7.7 \text{ Hz}, \ 4H), \ 1.51 \ (s, \ 4H), \ 1.28 \ (s, \ 12H), \ 0.95 \ (t, \ J = 7.1 \text{ Hz}, \ 16H), \ 0.89-0.77 \ (m, \ 14H), \ 0.70-0.40 \ ppm \ (m, \ 36H); \ ^{13}C \ NMR \ (CDCl_3, \ 100 \ MHz): \ \delta = 159.8, \ 152.0, \ 151.8, \ 150.5, \ 150.3, \ 134.7, \ 134.5, \ 132.3, \ 132.1, \ 131.5, \ 130.6, \ 130.0, \ 129.8, \ 128.7, \ 123.6, \ 122.0, \ 120.7, \ 114.7, \ 105.2, \ 100.5, \ 97.2, \ 87.8, \ 68.6, \ 35.2, \ 32.0, \ 31.7, \ 31.4, \ 30.2, \ 29.7, \ 29.4, \ 295.3, \ 292.3, \ 2182, \ 1723, \ 1671, \ 1587, \ 1506, \ 1455, \ 1245, \ 1098 \ cm^{-1}; \ UV/Vis \ (0.01 \ mM): \ \lambda_{max} \ (\varepsilon): \ 453 \ (1,95,758), \ 586 \ (11,105), \ 646 \ nm \ (30771 \ mol^{-1} \ cm^{-1}); \ APCI-MS: \ m/z \ calcd \ for \ C_{95}H_{119}N_5O_6SZn: \ 1522.8; \ found: \ 1523.9 \ [M+1]^+. \end{split}$$

Synthesis of YD2-OC8: This compound was synthesized by adopting a similar reported procedure,^[7c] using compound **12** (0.2 g, 0.14 mmol), 4-iodobenzoic acid (0.174 g, 0.7 mmol), $[Pd_2(dba)_3]$ (0.04 g, 0.04 mmol), and $[AsPh_3]$ (0.09 g, 0.29 mmol) to give **YD2-OC8** (0.144 g, 66.4%) as a green solid. ¹H NMR (CDCl₃, 400 MHz): δ =9.66 (d, *J*=4.5 Hz, 2H), 9.18 (d, *J*=4.6 Hz, 2H), 8.89 (d, *J*=4.5 Hz, 2H), 8.69 (d, *J*=4.6 Hz, 2H), 8.24 (d, *J*=8.3 Hz, 2H), 8.08 (d, *J*=8.4 Hz, 2H), 7.65 (t, *J*=8.4 Hz, 2H), 7.21 (d, *J*=8.6 Hz, 4H), 6.98 (d, *J*=8.5 Hz, 4H), 6.91 (d, *J*=8.5 Hz, 4H), 3.83 (t, *J*=4.8 Hz, 8H), 2.45 (t, *J*=7.6 Hz, 4), 1.52 (s, 4H), 1.25 (s, 12H), 0.98 (t, *J*=7.1 Hz, 16H), 0.81–0.72 (m, 14H), 0.62–0.41 ppm (m, 36H); UV/Vis (0.01 mM): λ_{max} (ε): 447 (1,93,793), 584 (11,297), 644 nm (28553 mol⁻¹ cm⁻¹); APCI-MS: *m/z* calcd for C₉₇H₁₂₁N₅O₆Zn: 1519; found: 1520 [*M*+1]⁺.

Methods

The UV-visible spectra were recorded with a Shimadzu model 1700 spectrophotometer. Concentrations of solutions are about $1 \times$ 10^{-6} M for Soret band and 1×10^{-5} M for Q band absorption. Steady-state fluorescence spectra were recorded using a Spex model Fluoromax-3 spectrofluorometer for solutions having optical density at the wavelength of excitation $(\lambda_{\text{ex}})\!\approx\!0.11.$ The fluorescence quantum yields (ϕ) were estimated by integrating the fluorescence bands of 5,10,15,20-tetraphenyl porphyrinato zinc(II) ([ZnTPP]) (<Gff> = 0.036 in CH₂Cl₂) as the standards.^[21] 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 JEOL-400 MHz (Varian spectrometer) model JNM-400. ¹³C NMR spectra were performed at 100 MHz, on a JNM-400 instrument. The chemical shifts are relative to tetramethylsilane (TMS). The Fourier transforms IR (FTIR) spectra of all the samples were measured using a KBr Pellet, JASCO FTIR-4100.

The photovoltaic performance of the dye-sensitized nanocrystalline TiO_2 cells was determined using the instrument SOLARONIX SA SR-IV unit Type 312. The spectral response was determined by measuring the wavelength dependence of the incident photon-to-current conversion efficiency (IPCE) using light from a 100 W xenon lamp that was focused onto the cell through a double monochromator.

Cyclic- and differential pulse voltammetric measurements were performed on a PC-controlled CH instruments model CHI 620C electrochemical analyzer. Cyclic voltammetric experiments were performed on 1 mm porphyrin dye solution in dichloromethane at scan rate of 100 mV s⁻¹ using 0.1 m tetrabutylammonium 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. After a cyclic voltammogram (CV) had been recorded, ferrocene was added, and a second voltammogram was measured.

Preparation of dye-sensitized nanocrystalline TiO₂ thin films: The TiO₂ photoelectrode (area: ca. 0.16 cm²) was prepared by a similar method reported in the literature. $^{\scriptscriptstyle [2b,22]}\mbox{TiO}_2$ anatase nanoparticles were prepared by hydrolysis of titanium(IV) isopropoxide. Nanocrystalline TiO₂ films of 8 µm thickness were deposited onto transparent conducting glass (Nippon Sheet Glass, which has been coated with a fluorine-doped stannic oxide layer, sheet resistance of 8–10 $\Omega\,m^{-2}\!)$ by screen-printing. These films were dried at 150 $^\circ\text{C}$ for 20 min and then were gradually sintered at 500 °C for 20 min. The heated electrodes were immersed in a freshly prepared 0.05 M aqueous titanium tetrachloride solution for 30 min at 70 °C and then were washed with distilled water. The 0.05 M titanium tetrachloride solution was prepared by adding titanium tetrachloride to ice to make a 2 M solution. This solution was then cooled to -20 °C before being diluted to 0.05 m. The electrodes were heated at 500 °C for 30 min and were then allowed to cool to 50 °C before dipping then into the dye solution. Dye solutions were prepared in the concentration range $2-3 \times 10^{-5}$ M either in ethanol or CH₃CN/ tBuOH mixture containing 0.4 mM of 3α , 7α -dihydroxy-5 β -cholic acid (CDCA). The electrodes were dipped into the dye solution for 16 h at 22 °C and the dye-coated electrodes were then rinsed quickly with ethanol to remove any unadsorbed dye and used as such for photovoltaic measurements.

Photovoltaic measurements: Photoelectrochemical data were obtained using a 450 W xenon light source focused to give 1000 W m⁻², the equivalent of one sun at AM 1.5, at the surface of the test cell. A sandwich cell was assembled by using the dye anchored TiO₂ films as the working electrode and conducting glass (TEC-15; the glass had been coated with a fluorine-doped stannic oxide layer; sheet resistance, 12–15 Ω/square) coated with chemically deposited platinum from 0.05 M hexachloroplatinic acid as the counter electrode. A thin layer of electrolyte E01 was introduced into the inter electrode space, and the electrole were tightly held in a cell holder. The composition E01 electrolyte is I₂: 0.05 M, Lil: 0.1 M, 1, 2-dimethyl-3-propylimidazolium iodide (DMPII):0.6 M, *tert*-butylpyridine (TBP):0.5 M in acetonitrile.

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