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Introduction

Research into Dye Sensitized Solar Cells (DSCs) continues to be an extremely active area.¹⁻⁴ After considerable time in which DSCs based on Ru(II)polypyridyl sensitizers were clearly the most efficient, DSCs based on organic sensitizers have recently made huge strides forward in development.^{5,6} In particular, there are many recent examples of DSCs employing iodide/triiodide (I⁻/I₃⁻) with >10% device efficiency based on D– π -A porphyrins designed by Diau and co-workers.⁷⁻⁹ Indeed, with recently developed novel cobalt complex based electrolytes¹⁰⁻¹³ porphyrins have shown their promise with the current highest efficiency recorded for a DSC device of 12.05% being based on a cell containing a porphyrin sensitizer and a tris(bipyridyl) cobalt electrolyte.¹⁴ Regardless of the red/ox couple, porphyrins offer several distinct advantages over Ru(II)polypyridyl sensitizers due to their high molar extinction coefficients, sharp

Effect of porphyrin loading on performance of dye sensitized solar cells based on iodide/tri-iodide and cobalt electrolytes[†]

Ana Aljarilla,^a John N. Clifford,^{*b} Laia Pellejà,^b Antonio Moncho,^b Susana Arrechea,^a Pilar de la Cruz,^a Fernando Langa^{*a} and Emilio Palomares^{bc}

Two zinc-porphyrin sensitizers, **1a** and **1b**, bearing triphenylamine donor groups, were synthesized and their efficiencies measured in nanocrystalline TiO₂ dye sensitized solar cells employing iodide/tri-iodide and tris(1,10-phenanthroline) cobalt electrolytes. Optimized sensitization time for the TiO₂ photoanode was found to depend on the electrolyte employed: devices based on iodide/tri-iodide showed better efficiencies with shorter sensitization times (1.5 hours) whereas those based on tris(1,10-phenanthroline) cobalt showed better efficiencies with longer sensitization times (6 hours). From UV-Vis absorption spectra it is estimated that there is roughly twice as much dye loaded onto the TiO₂ film sensitization time does not affect either dye regeneration or interfacial recombination processes in the presence of either electrolyte. However, sensitization time does have a considerable impact on device photocurrent, and moreover, the effect is different for the two electrolytes studied. This work demonstrates how device preparation must be tailored carefully depending on the electrolyte red/ox couple used.

absorption bands and high photostability.^{15–17} However, their properties in DSCs still need to be fully investigated and molecular structure-device function rules need to be outlined to fully understand performance for devices based on these dyes.

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In this article we investigate the performance of two porphyrin sensitizers, **1a** and **1b** (Scheme 1), in DSC devices employing I^{-}/I_{3}^{-} and tris(1,10-phenanthroline) cobalt electrolytes.

Interfacial processes were investigated using a number of spectroscopic techniques. In particular, these processes were investigated as a function of TiO_2 dye loading. It was found that device efficiency was very sensitive to dye loading. This study underlines how device rules for DSCs based on the I^-/I_3^- electrolyte are not necessary applicable to DSCs based on cobalt



Scheme 1 Structures of dyes 1a and 1b

^aInstitute of Nanoscience, Nanotechnology and Molecular Materials (INAMOL), Campus de la Fábrica de Armas (UCLM), Toledo, Spain. E-mail: Fernando.Langa@ uclm.es; Fax: +34 9252 68840; Tel: +34 9252 68843

^bInstitute of Chemical Research of Catalonia (ICIQ), Avda. Països Catalans 16, Tarragona E-43007, Spain. E-mail: jnclifford@iciq.es; Fax: +34 9779 20224; Tel: +34 9779 20200

^{&#}x27;ICREA, Avda. Lluís Companys 28, Barcelona E-08030, Spain

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electrolytes. This study is pertinent and timely given the increasing interest in DSCs based on cobalt electrolytes.

Results and discussion

Synthesis of 1a and 1b

Scheme 2 illustrates the synthetic route to dyes 1a and 1b. We prepared the free base porphyrins 2a,b in 14% and 11% yield respectively, according to the Lindsey method.¹⁸ This procedure improves significantly the yield with respect to previous procedures described for similar porphyrins (4-6%).¹⁹ 2a,b were reacted with zinc acetate in chloroform giving the metallated porphyrins 3a,b in 91% and 95% yield respectively after purification by column chromatography. Finally, the trimethylsylil group was quantitatively removed by TBAF and in situ reacted with p-iodobenzoic acid under Pd-catalyzed Sonogashira coupling conditions affording the target dyes 1a,b in 70% and 63% yield respectively. The intermediate and final compounds were fully characterized by means of UV-Vis, FT-IR, ¹H and ¹³C NMR spectroscopies; the structures of all compounds were confirmed by MALDI-TOF mass spectrometry (see the Experimental section and ESI⁺). The thermal stabilities of compounds 1a and 1b were evaluated by thermogravimetric analysis (TGA) under nitrogen, with a heating rate of 10 $^{\circ}$ C min⁻¹. The decomposition temperatures (T_d) were estimated from the TGA plot as the temperature of the intercept of the leading edge of the weight loss curve. Under these conditions, compounds 1a and 1b display excellent thermal stability up to 220 °C (Fig. S33 and S34, ESI[†]) which is in principle satisfactory for their application in photovoltaic devices.

Absorption, emission, electrochemistry and computational calculations

The absorption spectra of dyes 1a,b in dichloromethane (CH_2Cl_2) solution are shown in Fig. 1. Both dyes exhibit the typical features of zinc porphyrins, with an intense Soret band between 400 and 500 nm and less intense Q bands in the range 550 to 700 nm (see Table 1). As expected, the absorption bands are not very sensitive to the nature of the substituents, pointing to weak electronic interactions between the porphyrin and the attached moiety in the ground state. Due to the presence of the hexyloxy groups in dye 1b, a bathochromic shift is observed in the Q band, while in the Soret band an enhancement in



Scheme 2 Synthetic route to dyes 1a and 1b.



Fig. 1 Normalized absorption spectra of dyes 1a (---) and 1b (--) in dichloromethane solution (10^{-5} M).

Table 1 Absorption, emission and electrochemical data of dyes 1a and 1b

	$\lambda_{\max}^{a}/nm (\log \varepsilon)$	$\lambda_{ m em}{}^a/$ nm	$E_{\rm red}^{1 \ b}$ (V)		$E_{\rm HOMO}^{c}$ (eV)	E_{LUMO}^{a} (eV)
1a	630 (4.18), 572 (4.02),	652	-0.52	0.33	-5.43	-3.50
1b	450 (5.08), 306 (4.71) 637 (4.39), 579 (4.07), 449 (5.12), 305 (4.77)	669	-0.58	0.28	-5.38	-3.49

^{*a*} 10⁻⁵ M, CH₂Cl₂. ^{*b*} [10⁻³ M] in THF *versus* Fc/Fc⁺, glassy carbon, Pt counter electrode, 20 °C, 0.1 M Bu₄NClO₄, scan rate = 100 mV s⁻¹. ^{*c*} Calculated using equation E_{HOMO} (*vs.* vacuum) = $-5.1 - E_{\text{ox}}^1$ (*vs.* Fc/Fc⁺) in eV.²⁰ ^{*d*} E_{LUMO} was calculated using $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{0-0}$, where E_{0-0} is the intersection of the absorption and emission spectra.

bandwidth is observed. For the fluorescence spectra in CH₂Cl₂ the trend for the variation of the emission wavelength is similar to that of the absorption bands. The emission bands at 652 nm (**1a**, $\lambda_{exc} = 450$ nm) and 669 nm (**1b**, $\lambda_{exc} = 449$ nm) (Fig. S26 and S27 in ESI†) were totally quenched after adsorption onto TiO₂ indicating efficient photoinduced electron transfer from the dyes to the TiO₂ nanoparticles.

The redox properties of 1a,b were investigated by cyclic voltammetry and square wave voltammetry in tetrahydrofuran (THF), (Table 1, Fig. S30-S32, ESI⁺). In the cathodic side, compounds 1a,b show the first reversible oxidation peaks at 0.33 and 0.28 V respectively; the presence of the electrondonating alkoxy groups significantly reduces the oxidation potential of 1b compared to 1a. On the reduction side, both compounds show first reduction potentials at -0.52 V and -0.57 V as irreversible waves, showing that the electrondonating alkoxy groups in 1b increase its reduction potential with respect to 1a, as one would expect. The E_{HOMO} values of 1a to **1b** vary only by 0.05 eV and were determined as -5.43 eV (**1a**) and -5.38 eV (1b), indicating regeneration is energetically feasible by both I^-/I_3^- ($E_{redox} = -4.75$ eV) and Co(II)(phen)₃/ $Co(m)(phen)_3$ ($E_{redox} = -5.06$ eV) red/ox couples. The E_{LUMO} values also indicate that efficient electron injection into the TiO_2 conduction band ($E_{TiO_2} = -4.00$ eV) is energetically possible.

In order to gain insight into the geometries and electronic properties of dyes **1a** and **1b**, computational studies were

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performed using density functional theory (DFT) at the B3LYP/ 6-31G level. Regarding geometry, for both dyes the dihedral angles between the phenyl ring and the porphyrin macrocycle (φ) are similar $(\varphi \sim -65^{\circ})$ and are in agreement with those calculated for similar systems (Fig. 2).²¹ The HOMOs were found to be delocalized through both the porphyrin macrocycle and TPA for both **1a** and **1b**, whereas the LUMOs are extended along the porphyrin system, the linker and the acid group, indicating electronic coupling with the TiO₂ nanocrystals. The HOMO– LUMO gap is similar for both dyes although the LUMO level of dye **1b** is higher (-2.45 eV) than that of **1a** (-2.61 eV) due to the electronic coupling of the alkoxy groups of the TPA moieties. HOMO and LUMO (Fig. 3) are overlapped, favouring the HOMO to LUMO electronic transitions.

Device properties

Fig. 4 and Table 2 show the *IV* curves and device characteristics, namely J_{sc} , V_{oc} , fill factor (FF) and overall efficiency (η), for sensitizers **1a** and **1b** in DSC devices based on I^-/I_3^- and Co(II)(phen)₃/Co(III)(phen)₃ electrolytes.

Employing I^-/I_3^- electrolyte, the best device efficiencies (Fig. 4(a)) were obtained after 1.5 hours sensitization time with maximum efficiencies of 5.14% and 4.15% for **1a** and **1b** respectively (without mask). These values compare well with a recent study by Liu *et al.* involving similar dyes.¹⁹ Upon the longer sensitization time of 6 hours the device efficiency drops to 3.93% and 3.60% for **1a** and **1b** respectively (without mask). The principle reason for this is a loss in J_{sc} . When cobalt electrolyte is used, however, the dependence of device efficiency on sensitization time is reversed (Fig. 4(c)). The best efficiencies are recorded for 6 hours sensitization (3.11% and 2.45% for **1a** and



Fig. 2 Optimized structure for dye 1b (hexyl groups have been changed by methyl for calculations).



Fig. 3 Frontier orbitals of dye 1b: HOMO (left) and LUMO (right).



Fig. 4 I-V curves and IPCE spectra of DSC devices composed of sensitizers **1a** and **1b** based on I^{-}/I_{3}^{-} (a and b) and Co(#)(phen)₃/Co(#)(phen)₃ electrolytes (c and d).

Dye	Time	$J_{\rm sc}~({\rm mA~cm^{-2}})$	$V_{\rm oc}$ (V)	FF (%)	η^{d} (%)
1a	1.5 hours ^a	10.09	0.63	67	4.19(5.14)
1a	$6 h^a$	8.51	0.62	62	3.27 (3.93)
1b	1.5 hours ^{a}	7.83	0.62	70	3.40 (4.15)
1b	$6 h^a$	6.18	0.61	69	2.54 (3.60)
1a	1.5 hours ^b	3.67	0.75	75	2.06 (2.53)
1a	6 h ^b	4.44	0.76	74	2.48 (3.11)
1b	1.5 hours ^b	3.17	0.77	66	1.61 (2.01)
1b	6 h ^b	3.82	0.75	72	2.05 (2.45)
YD2- <i>о</i> - С8 ^с		15.25	0.76	72	8.42 (11.20)

^{*a*} Electrolyte: 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M lithium iodide, 0.05 M iodine and 0.5 M 4-*tert*-butylpyridine in a 1 : 1 mixture of acetonitrile–valeronitrile. ^{*b*} Electrolyte: 0.2 M tris(1,10-phenanthroline)cobalt(n)(TFSI)₂, 0.02 M tris(1,10-phenanthroline) cobalt(m)(TFSI)₃, 0.1 M lithium perchlorate and 0.5 M 4-*tert*-butylpyridine in a 85 : 15 mixture of acetonitrile–valeronitrile. ^{*c*} Electrolyte: 0.5 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M lithium iodide, 0.05 M iodine, and 0.5 M 4-*tert*-butylpyridine in a 85 : 15 mixture of acetonitrile acetonitrile.

1b respectively). Again, the main difference arising from sensitization time is accounted for by a difference in J_{sc} . The increase in device V_{oc} (approx. 140 mV) afforded by employing $Co(II)(phen)_3/Co(III)(phen)_3$ with respect to I^-/I_3^- is in line with increases observed in other studies.²² Finally, under similar conditions the **YD2-***o***-C8** device gave an efficiency of 11.20% (without mask) indicating testing conditions are indeed comparable with studies demonstrating the best literature values for porphyrin based DSCs.²³

Fig. 4(b) and (d) show the IPCE spectra for all of the devices measured in this study. These spectra show the contributions to device current from the Soret and Q bands centred at around 450 and 650 nm respectively. Integration of these spectra agrees with the J_{sc} values for the same devices in Fig. 4(a) and (c).

In order to have an indication of dye loading in these devices, the absorption spectra of thin films of transparent TiO_2 films (6 μ m) were measured after 1.5 hours and 6 hour sensitization in 0.2 mM solutions of **la** and **lb** in chlorobenzene (Fig. 5). These data indicate that there is roughly twice as much dye loading on the film sensitized for 6 hours compared to the equivalent film of 1.5 hours.

Charge extraction, transient photovoltage and transient absorption spectroscopy measurements

Device electron densities and electron lifetimes were probed using charge extraction and transient photovoltage measurements respectively (Fig. 6). To simplify the discussion, and because trends in DSC performance based on **1a** and **1b** are the same, data relating to DSCs fabricated using sensitizer **1a** are presented only.



Fig. 5 Absorption spectra of transparent TiO₂ films (6 μ m) following 1.5 and 6 hour sensitization in 0.2 mM solutions of **Ia** and **Ib** in chlorobenzene.



Fig. 6 Charge density as a function of voltage and electron lifetime as a function of charge density of DSC devices composed of sensitizer **1a** based on I^{-}/I_{3}^{-} (a and b) and Co(II)(phen)₃/Co(III)(phen)₃ electrolytes (c and d).

The data in Fig. 6 demonstrate that sensitization time has little bearing either on the position of the TiO_2 conduction band or on device electron lifetime for **1a** devices based on the two different electrolytes. This is not surprising if we consider that the V_{oc} for devices does not change with sensitization time. Despite the estimated doubling in dye loading for 6 hours sensitization compared to 1.5 hours, V_{oc} , TiO_2 electron density and electron lifetime do not change. This may be because the TiO_2 film is entirely covered by **1a** following 1.5 hours and any subsequent dye loading does not come into direct contact with TiO_2 or improve the dye blocking effect increasing TiO_2 electron lifetime.

Transient absorption spectroscopy was then used to monitor dye regeneration in these devices and these kinetics are shown in Fig. 7.

In the absence of electrolyte (black decays) the kinetics are slow and dispersive, which become faster when electrolyte is added. The $t_{50\%}$ for the device prepared with 1.5 hour sensitization (0.5 ms) is slightly longer than that prepared with 6 hour sensitization (0.1 ms), probably due to the fewer charge separated species generated in this device due to lower dye loading. On the other hand, sensitization time appears to have little effect on $t_{50\%}$ in the presence of electrolyte (approx. 20 µs (I^{-}/I_{3}^{-}) and 90 µs ($Co(\pi)(\text{phen})_{3}/Co(\pi)(\text{phen})_{3}$)). It is noted that kinetics recorded in the presence of the I^{-}/I_{3}^{-} electrolyte are faster due to the potential of this red/ox couple affording more



Fig. 7 Transient absorption kinetics for DSC devices of **1a** prepared following (a) 1.5 hours and (b) 6 hours sensitization. The black, red and blue decays correspond to kinetics recorded in the presence of a blank electrolyte, I^-/I_3^- electrolyte and $Co(II)(phen)_3/Co(III)(phen)_3$ electrolyte respectively. Kinetics were recorded at 620 nm following excitation at 650 nm.



Fig. 8 Emission lifetime decays of **1a** on transparent Al₂O₃ and TiO₂ films following 1.5 and 6 hour sensitization in the presence of I^-/I_3^- and Co(II)(phen)₃/Co(III)(phen)₃ electrolytes. In all cases emission was recorded at 660 nm following excitation at 405 nm.

free energy for regeneration compared to $Co(u)(phen)_3/Co(uu)(phen)_3$.

Fluorescence lifetime measurements

To investigate the difference in the J_{sc} values for **la** devices, fluorescence emission lifetimes were measured using time-correlated single photon counting (Fig. 8).

Dye loading of **1a** onto the above films was controlled so that the absorbance of Al_2O_3 and TiO_2 films in each set of samples was the same. Electron injection yields, Φ , were estimated by integrating the areas under each emission decay, as done previously by Koops *et al.*²⁴ The results show that as the sensitization time increases from 1.5 to 6 hours, Φ drops from 77 to 62%, respectively, in the presence of I^-/I_3^- . On the other hand, in the presence of $Co(\pi)(phen)_3/Co(\pi)(phen)_3$, Φ increases from 27 to 40% on increasing sensitization time from 1.5 to 6 hours. Clearly, Φ values correlate well with J_{sc} for the differently prepared devices.

Dye aggregation has been shown to quench dye excited states in I^-/I_3^- based devices limiting device photocurrent.²⁵ This would explain the drop in J_{sc} in **1a,b** DSC devices at high dye loading in I^-/I_3^- . However, the higher Φ and J_{sc} of $Co(\pi)(phen)_3/$ $Co(\pi)(phen)_3$ devices at high dye loading indicate that this electrolyte has some influence over, and is able to control, aggregation. This can be explained by the bulky nature of the cobalt complexes allowing them to break-up dye aggregates of the planar porphyrin systems, improving J_{sc} and ultimately device performance.

Conclusions

Two zinc-porphyrin sensitizers were synthesized and their efficiencies measured in dye sensitized solar cells employing I^{-}/I_{3}^{-} and $Co(\pi)(phen)_{3}/Co(\pi)(phen)_{3}$ electrolytes. Optimized

sensitization times were found to depend on the electrolyte used with devices based on I^{-}/I_{3}^{-} showing better efficiencies with shorter sensitization times (1.5 hours) while those based on $Co(\pi)(phen)_3/Co(\pi)(phen)_3$ showing better efficiencies with longer sensitization times (6 hours). UV-Vis absorption spectra indicate that there is roughly twice as much dye loaded onto the TiO₂ film sensitized for 6 hours. It was found that dye loading had little influence over device $V_{\rm oc}$, electron density or electron lifetime. However, at shorter sensitization times and lower dye loading, electron injection efficiency and photocurrent were higher in devices based on I^{-}/I_{3}^{-} . The opposite was true for devices based on Co(II)(phen)₃/Co(III)(phen)₃ with higher electron injection efficiencies and photocurrents found for longer sensitization times and higher dye loadings. This work demonstrates how device preparation must be tailored carefully depending on the electrolyte red/ox couple used.

Experimental

Materials

Synthetic procedures were carried out under inert argon atmosphere, in dry solvent unless otherwise noted. All reagents and solvents were reagent grade and were used without further purification. Chromatographic purifications were performed using silica gel 60 SDS (particle size 0.040–0.063 mm).

Instruments

Analytical thin-layer chromatography was performed using Merck TLC silica gel 60 F254. ¹H NMR spectra were obtained on Bruker TopSpin AV-400 (400 MHz) spectrometer. Chemical shifts are reported in parts per million (ppm) relative to the solvent residual peak (CDCl₃, 7.27 ppm). ¹³C NMR chemical shifts are reported relative to the solvent residual peak (CDCl₃, 77.00 ppm). UV-Vis measurements were carried out on a Shimadzu UV 3600 spectrophotometer. For extinction coefficient determination, solutions of different concentration were prepared in CH₂Cl₂, HPLC grade, with absorption between 0.1 and 1 of absorbance using a 1 cm UV cuvette. The emission measurements were carried out on Cary Eclipse fluorescence spectrophotometer. Mass spectra (MALDI-TOF) were recorded on a VOYAGER DE[™] STR mass spectrometer using dithranol as matrix. The thermal stability was evaluated by TGA on Mettler Toledo TGA/DSC Start^e System under nitrogen, with a heating rate of 10 °C min⁻¹. Heating of crystalline samples leads to melting of the solids, but no recrystallization was observed.

Device preparation and characterization

In the present work two different types of TiO₂ films are utilized depending on the measurements being conducted. Highly transparent thin films of 4–8 μ m were utilized for L-TAS measurements and also for UV-Vis absorption studies. On the other hand, for efficient DSCs, devices were made using either 4 μ m or 8 μ m thick films consisting of 20 nm TiO₂ nanoparticles (Dyesol paste) for Co(II)(phen)₃/Co(III)(phen)₃ and I⁻/I₃⁻ electrolytes respectively. A scatter layer of 4 μ m of 400 nm TiO₂ particles (Dyesol paste) was then deposited on these films. Prior

to the deposition of the TiO2 paste the conducting glass substrates were immersed in a solution of TiCl₄ (40 mM) for 30 min and then dried. The TiO2 nanoparticle paste was deposited onto a conducting glass substrate (NSG glass with 8 Ω cm⁻² resistance) using the screen printing technique. The TiO_2 electrodes were gradually heated under airflow at 325 °C for 5 min, 375 °C for 5 min, 450 °C for 15 min and 500 °C for 15 min. The heated TiO₂ electrodes were immersed again in a solution of TiCl₄ (40 mM) at 70 °C for 30 min and then washed with ethanol. The electrodes were heated again at 500 °C for 30 min and cooled before sensitization. In order to reduce scattered light from the edge of the glass electrodes of the dyed TiO₂ layer, a light shading mask was used on the DSCs, so the active area of DSCs was fixed to 0.16 cm². The counter electrode was made by spreading a 5 mM solution of H₂PtCl₆ in isopropyl alcohol onto a conducting glass substrate (TEC15, Pilkington) with a small hole to allow the introduction of the liquid electrolyte using vacuum, followed by heating at 390 °C for 15 min. Dye solutions of 1a and 1b at concentrations of 0.2 mM in chlorobenzene were prepared and films immersed for different periods of time at r.t. The sensitized electrodes were washed with chlorobenzene and dried under air. Finally, the working and counter electrodes were sandwiched together using a thin thermoplastic (Surlyn) frame that melts at 100 °C. The iodide/tri-iodide electrolyte used consisted of 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M lithium iodide, 0.05 M iodine and 0.5 M 4-tert-butylpyridine in a 1:1 mixture of acetonitrile-valeronitrile. The cobalt electrolyte consisted of 0.2 M tris(1,10-phenanthroline)cobalt(II)(TFSI)₂ 0.02 M tris(1,10-phenanthroline)cobalt(III)(TFSI)₃, 0.1 M lithium perchlorate and 0.5 M 4-tert-butylpyridine in a 85:15 mixture of acetonitrile-valeronitrile.

Reference devices containing **YD2-o-C8** dye were made by sensitizing films for approximately 90 minutes consisting of 13 μ m transparent and 4 μ m scatter TiO₂ in 0.1 mM ethanol solutions containing 0.5 mM chenodeoxycholic acid. The electrolyte consisted of 0.5 M 1-butyl-3-methylimidazolium iodide (BMII), 0.1 M lithium iodide, 0.05 M iodine and 0.5 M 4-*tert*-butylpyridine in 85:15 mixture of acetonitrilevaleronitrile.

The IV characteristics of cells were measured using a Sun 2000 Solar Simulator (150 W, ABET Technologies). The illumination intensity was measured to be 100 mW m⁻² with a calibrated silicon photodiode. The appropriate filters were utilized to faithfully simulate the AM 1.5G spectrum. The applied potential and cell current were measured with a Keithley 2400 digital source meter. The IPCE (Incident Photon to Current conversion Efficiency) was measured using a homemade set up consisting of a 150 W Oriel Xenon lamp, a motorized monochromator and a Keithley 2400 digital source meter.

Transient photovoltage, charge extraction measurements and transient absorption spectroscopy measurements were carried out on systems described previously.²⁶ Emission lifetime studies were carried out on transparent 8–10 μ m Al₂O₃ and TiO₂ films with a Lifespec© picosecond fluorescence lifetime spectrometer from Edinburgh Instruments© with an instrument response at half width at half maximum (HWHM) of duration 420 ps.

Synthesis and characterization

General procedure for the synthesis of 2a,b. To a solution of corresponding (diphenylamino)benzaldehyde (3 mmol), pyrrol (4 mmol) and 3-(trimethylsilyl)propiolaldehyde (1 mmol) in CHCl₃ (100 mL mmol⁻¹), under argon and degassed, was added BF₃(OEt)₂ (0.9 mmol). The mixture was allowed to stir under argon for 3 hours. Then, DDQ (2.8 eq.) was added and stirring for one hour; after addition of Et₃N (2 mL) for 30 min, the solvent was removed by rotary evaporation and the product was purified by column chromatography (silica gel, Hex-CHCl₃, 1 : 1).

Synthesis of [10,15,20-tri(N,N-diphenylaniline)-5-ethynyltrimethylsilane]porphyrin (2a). From 3.00 g of (diphenylamino)benzaldehyde (11 mmol), 1.02 mL of pyrrol (14.7 mmol) and 0.547 mL of 3-(trimethylsilyl)propiolaldehyde (3.7 mmol), reacted according to the general procedure, affording 600 mg of 5a as a green solid (14% yield). ¹H NMR (400 MHz, CDCl₃) δ /ppm: 9.69 (d, I = 4.7 Hz, 2H), 9.05 (d, J = 4.7 Hz, 2H), 8.96 (d, J = 4.7 Hz, 2H), 8.93 (d, J = 4.7 Hz, 2H), 8.07 (dd, J = 8.5, 6.4 Hz, 6H), 7.49 (d, J = 8.5 Hz, 6H), 7.45–7.42 (t, J = 7.0 Hz, 24H), 7.20–7.15 (m, 6H), 0.64 (s, 9H), -2.31 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 147.7, 147.6, 135.7, 135.6, 135.5, 135.3, 129.5, 129.2, 124.9, 123.3, 122.1, 121.3, 121.2, 120.9, 107.7, 101.6, 98.6, 0.35. UV-Vis (CH₂Cl₂) λ_{max}/nm (log ε): 670 (3.94), 580 (4.30), 538 (4.02), 435 (5.13), 303 (4.77). FT-IR v/cm⁻¹: 3315, 3058, 3030, 2954, 2137, 1595, 1492, 1328, 1313, 1270, 848, 798, 749, 695. MS (m/z) (MALDI-TOF): calculated for $C_{79}H_{61}N_7Si: 1135.48;$ found: 1135.5 (M⁺).

Synthesis of [10,15,20-tri(N,N-(bis(4-hexyloxy)phenyl)aniline)-5ethynyltrimethylsilane porphyrin (2b). From 3.00 g of 4-(N,N-di-4-(hexyloxy)phenylamino)benzaldehyde27 (6.3 mmol), 0.6 mL of pyrrol (8.5 mmol) and 0.31 mL of (trimethylsilyl)-propiolaldehyde (2.1 mmol) reacted according to the general procedure affording 397 mg of 2b as yellow solid (11% yield). ¹H NMR (400 MHz, CDCl_3) δ /ppm: 9.65 (d, J = 4.7 Hz, 2H), 9.04 (d, J = 4.7 Hz, 2H), 8.94 (d, J = 4.7 Hz, 2H), 8.92 (d, J = 4.7 Hz, 2H), 7.98 (dd, J = 8.6, 6.1 Hz, 6H), 7.39–7.34 (m, 12H), 7.30 (t, J = 8.6 Hz, 6H), 7.00–6.95 (m, 12H), 4.00 (dd, J = 12.6, 6.6 Hz, 12H), 1.87–1.78 (m, 12H), 1.54-1.46 (m, 12H), 1.41-1.35 (m, 24H), 0.96-0.92 (s, 18H), 0.63 (s, 9H), -2.27 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ/ppm: 155.7, 148.5, 140.6, 135.5, 133.55, 133.2, 127.1, 122.6, 117.95, 117.8, 115.4, 107.4, 101.3, 98.1, 68.25, 31.6, 29.3, 25.8, 22.6, 14.1, 0.4. UV-Vis (CH₂Cl₂) $\lambda_{\text{max}}/\text{nm}$ (log ε): 677 (3.72), 591 (4.15), 422 (5.06), 300 (4.68). FT-IR ν/cm^{-1} : 3314, 2951, 2927, 2857, 2137, 1599, 1504, 1469, 1239. MS (m/z) (MALDI-TOF): calculated for C₁₁₅H₁₃₃N₇O₆Si: 1736.01; found: 1736.00 (M⁺).

General procedure for the synthesis of 3a and 3b. To a solution of corresponding porphyrin 2a or 2b (1 mmol) in CHCl₃ (84 mL mmol⁻¹) under argon was added a solution of $Zn(OAc)_2 \cdot 2H_2O$ (5 mmol) in MeOH (2.5 mL mmol⁻¹). The mixture was stirred at room temperature overnight. The reaction was quenched with water and the mixture extracted with CHCl₃ (3 × 50 mL). The combined organic extracts were washed with H₂O and dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the product was purified by column chromatography (silica gel, Hex–CHCl₃, 1 : 1).

Synthesis of [10,15,20-tri-(N,N-diphenylaniline)-5-ethynyltrimethylsilane]porphinato zinc(u) (3a). From 250 mg of porphyrin 2a (0.22 mmol), reacted according to the general procedure, affording 251 mg of 3a as a green solid (95% yield). ¹H NMR (400 MHz, CDCl₃) δ / ppm: 9.79 (d, J = 4.7 Hz, 2H), 9.14 (d, J = 4.7 Hz, 2H), 9.07 (d, J = 4.7 Hz, 2H), 9.05 (d, J = 4.7 Hz, 2H), 8.10–8.05 (m, 6H), 7.49 (t, J = 8.4 Hz, 6H), 7.46–7.43 (t, 24H), 7.19–7.14 (m, 6H), 0.66 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ /ppm: 150.04, 149.94, 147.85, 147.82, 147.36, 136.32, 135.40, 135.32, 132.23, 131.79, 130.93, 129.48, 124.81, 123.21, 122.93, 121.82, 121.36, 121.26, 107.66, 101.12, 99.37, 0.41. UV-Vis (CH₂Cl₂) λ_{max} /nm (log ε): 619 (4.25), 571 (4.19), 444 (5.31), 305 (4.81). FT-IR ν /cm⁻¹: 3060, 3030, 2955, 1924, 2853, 2138, 1589, 1490, 1329, 1315, 1280, 996, 842, 699. MS (*m*/2) (MALDI-TOF): calculated for C₇₉H₅₉N₇SiZn: 1197.39; found (M + H⁺): 1197.6, 1198.6, 1199.6, 1200.5, 1201.5, 1202.5.

Synthesis of [10,15,20-tri-(N,N-(bis(4-hexyloxy)phenyl)aniline)-5-ethynyltrimethylsilane]porphinato zinc(11) (3b). From 230 mg of porphyrin 2b (0.13 mmol), reacted according to the general procedure, affording 217 mg of 3b as green solid (91% yield). ¹H NMR (400 MHz, CDCl₃) δ /ppm: 9.75 (d, J = 4.7 Hz, 2H), 9.13 (d, I = 4.7 Hz, 2H), 9.05 (d, I = 4.7 Hz, 2H), 9.03 (d, I = 4.7 Hz, 2H), 7.98 (dd, J = 8.6, 7.0 Hz, 6H), 7.36 (dd, J = 9.0, 5.8 Hz, 12H), 7.30 (t, J = 8.6 Hz, 6H), 6.95 (dd, J = 9.0, 6.7 Hz, 12H), 3.97 (dd, J = 13.0, 6.5 Hz, 12H), 1.85-1.75 (m, 12H), 1.54-1.45 (m, 12H), 1.41-1.35 (m, 24H), 0.95-0.91 (m, 18H), 0.63 (s, 9H). ¹³C NMR (100 MHz, CDCl₃) δ /ppm: 152.45, 150.9, 150.2, 150.1, 148.3, 140.8, 140.8, 135.3, 135.2, 134.1, 133.0, 132.2, 131.7, 130.7, 127.0, 123.4, 122.15, 118.0, 117.9, 115.4, 107.95, 100.9, 99.0, 68.3, 31.6, 29.3, 25.8, 22.6, 14.1, 0.4. UV-Vis $(CH_2Cl_2) \lambda_{max}/nm (\log \varepsilon)$: 623 (4.22), 570 (4.10), 441 (5.09), 301 (4.79). FT-IR ν/cm^{-1} : 2954, 2951, 2854, 2138, 1604, 1503, 1235. MS (m/z) (MALDI-TOF): calculated for C₁₁₅H₁₃₁N₇O₆SiZn: 1797.92; found: 1798.5 (M⁺).

General procedure for the synthesis of 1a and 1b. To a solution of the corresponding porphyrin 3a or 3b (1 mmol) in CH_2Cl_2 (200 mL mmol⁻¹), TBAF (1.25 mmol, 1 M in THF) was added under argon. The solution was stirred at room temperature for 1 hour. The mixture was quenched with H_2O and extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layer was dried over anhydrous MgSO₄ and the solvent was removed under reducer pressure. The residue and 4-iodobenzoic acid (5 mmol) were dissolved in dry THF (200 mL mmol⁻¹) and Et₃N (120 mL mmol⁻¹). The solution was degassed with argon for 15 min, $Pd_2(dba)_3$ (0.3 mmol) and AsPh₃ (2 mmol) were added to the mixture and the solution was refluxed over night. The solvent was removed under reduced pressure. The product was purified by column chromatography (silica gel, CHCl₃: MeOH 95 : 5).

Synthesis of [10,15,20-tri(N,N-diphenylaniline)-5-carboxyphenylethynyl-porphyrinato] zinc(*u*) (1*a*). From 100 mg of porphyrin 3a (0.22 mmol) reacted according to the general procedure giving 73 mg of 1a as a green solid (70% yield). ¹H NMR (400 MHz, CDCl₃/ d₅-pyridine) δ /ppm: 9.80 (d, *J* = 4.6 Hz, 2H), 9.09 (d, *J* = 4.6 Hz, 2H), 8.97 (d, *J* = 4.6 Hz, 2H), 8.94 (d, *J* = 4.6 Hz, 2H), 8.34 (d, *J* = 8.3 Hz, 2H), 8.11 (d, *J* = 8.3 Hz, 2H), 8.05 (t, *J* = 8.3 Hz, 6H), 7.70– 7.64 (m, 4H), 7.57–7.52 (m, 2H), 7.49–7.38 (m, 24H), 7.16–7.11 (m, 6H). ¹³C NMR (100 MHz, CDCl₃/d₅-pyridine) δ /ppm: 207.05, 152.8, 152.3, 150.7, 149.8, 147.9, 147.1, 137.0, 132.0, 132.7, 132.1, 132.1, 132.0, 131.9, 131.9, 131.4, 131.1, 130.25, 130.1, 128.5, 128.4, 124.6, 121.4, 121.3. UV-Vis $(CH_2Cl_2) \lambda_{max}/nm$ $(\log \varepsilon)$: 630 (4.18), 572 (4.02), 450 (5.08), 306 (4.71). FT-IR ν/cm^{-1} : 3436, 3061, 3031, 2956, 2924, 2186, 1738, 1589, 1405, 1330, 1316, 1278, 1173, 698. MS (m/z) (MALDI-TOF): calculated for $C_{83}H_{55}N_7O_2Zn$: 1245.37; found: 1245.4 (M^+) .

Synthesis of [10,15,20-tri(N,N-(bis(4-hexyloxy)phenyl)aniline)-5-5-carboxy-phenylethynyl-porphyrinato] zinc(11) (1b). From 100 mg of porphyrin 3b (0.13 mmol) reacted according to the general procedure giving 65 mg of 1b as a green solid (63% yield). ¹H NMR (400 MHz, CDCl_3/d_5 -pyridine) δ/ppm : 9.71 (d, J = 4.5 Hz, 2H), 9.03 (d, J = 4.5 Hz, 2H), 8.90 (d, J = 4.5 Hz, 2H), 8.87 (d, J = 4.5 Hz, 2H), 8.27 (d, J = 6.8 Hz, 2H), 8.03 (d, J = 6.8 Hz, 2H), 7.90 (dd, *J* = 8.5, 6.7 Hz, 6H), 7.30–7.19 (m, 24H), 6.91–6.86 (m, 6H), 3.93-3.88 (m, 12H), 1.72 (q, J = 6.7 Hz, 12H), 1.45-1.37 (m, 12H),1.31–1.24 (m, 24H), 0.83 (t, J = 7.0 Hz, 18H). ¹³C NMR (100 MHz, CDCl₃/d₅-pyridine) δ/ppm: 207.0, 155.6, 125.2, 150.9, 149.9, 149.9, 148.0, 140.9, 140.8, 134.9, 134.8, 132.8, 131.9, 131.4, 131.0, 130.1, 126.9, 122.05, 118.0, 117.9, 115.4, 97.4, 95.1, 68.2, 31.6, 30.9, 29.3, 25.75, 22.6, 14.0. UV-Vis $(CH_2Cl_2) \lambda_{max}/nm$ $(\log \varepsilon)$: 637 (4.39), 579 (4.07), 449 (5.12), 305 (4.77). FT-IR v/cm⁻¹: 3424, 3120, 3039, 2852, 2927, 2859, 2185, 1799, 1688, 1603, 1503, 1467, 1314, 1278, 1240, 1167, 998, 828, 794. MS (m/z) (MALDI-TOF): calculated for C₁₁₉H₁₂₇N₇O₈Zn: 1845.90; found: 1846.4 (M⁺).

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