

Dye-sensitized solar cells with 13% efficiency achieved through the molecular engineering of porphyrin sensitizers

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Dye-sensitized solar cells have gained widespread attention in recent years because of their low production costs, ease of fabrication and tunable aesthetic features, such as colour and transparency. Here, we report a molecularly engineered porphyrin dye, coded SM315, which features the prototypical structure of a donor- π -bridge-acceptor and both maximizes electrolyte compatibility and improves light-harvesting properties. Linear-response, time-dependent density functional theory was used to investigate the perturbations in the electronic structure that lead to improved light harvesting. Using SM315 with the cobalt(II/III) redox shuttle resulted in dye-sensitized solar cells that exhibit a high open-circuit voltage V_{OC} of 0.91 V, short-circuit current density J_{SC} of 18.1 mA cm⁻², fill factor of 0.78 and a power conversion efficiency of 13%.

Dye-sensitized solar cells (DSCs) are an attractive solar energy conversion technology because of their low production cost, ease of fabrication and tunable aesthetic features, such as colour and transparency^{1–4}. Initial forms of this technology used ruthenium(II)-based dyes in conjunction with iodide-based electrolytes to achieve a certified solar-to-electric power conversion efficiency (PCE) of 11.9% under full sun illumination (AM 1.5G, 1,000 W m⁻²)⁵. Surpassing the 12% PCE threshold required a paradigm shift in the chemical components utilized within this photo-electrochemical device⁶.

A new generation of DSCs is based on a combination of light-harvesting donor- π -acceptor (D- π -A) dyes in conjunction with cobalt-based redox mediators^{6–9}. The strong molar absorptivity of D- π -A dyes enables the use of thin TiO₂ films, potentially reducing fabrication costs relative to ruthenium(II) sensitizers, with concomitant improvements in the open-circuit voltage V_{OC} when used with cobalt-based redox mediators. The synthetic flexibility of D- π -A dyes has enabled the engineering of enhanced compatibility toward these alternative redox couples by introducing steric bulk into the donor component and π -system, minimizing the unfavourable recombination between the electrolyte and the TiO₂ surface^{6–9}. By using these new light harvesters, DSCs have achieved a maximum PCE of 12.3% under full sun illumination, utilizing the tris(2,2'-bipyridyl)cobalt(II/III) ([Co(bpy)₃]^{2+/3+}) redox shuttle. However, to achieve this PCE, the light harvesting of the porphyrin dye YD2-o-C8 was supplemented by the organic co-sensitizer Y123 (ref. 6). This landmark result began a renaissance for the DSC, validating the combination of D- π -A dyes and cobalt redox mediators as an effective strategy in developing high-efficiency DSCs¹⁰.

The development of single-molecule panchromatic D- π -A sensitizers remains a molecular engineering challenge in efforts to improve the overall PCE of DSC devices. Until now, achieving a panchromatic light-harvesting response in DSCs has relied on

co-sensitization, energy-relay strategies or tandem device configurations^{6,11–21}. Although gains in PCE are often realized through improved light harvesting utilizing these strategies, the fabrication and optimization of these devices can be laborious and technically challenging. The development of a single D- π -A sensitizer with a panchromatic light response in a DSC remains a main objective in the realization of maximum PCEs with standard device fabrication protocols^{6,22}.

Porphyrin-based D- π -A dyes provide a highly flexible platform for the development of panchromatic sensitizers^{6,23,24}. The porphyrin chromophore has intrinsically strong light absorption in the Soret and Q-bands, but there is a lack of significant absorption in the spectral region between these two features. Typical porphyrin D- π -A sensitizers comprising dialkylamine or diarylamine donors, in conjunction with an ethynylbenzoic acid acceptor, yield dyes with a vivid green colour, bereft of absorption between 500–600 nm (refs 6,24–29). Despite the high efficiency of these dyes in DSCs, further improvements to light harvesting through the use of stronger acceptors remains relatively unexplored^{30,31}. Studies unrelated to the DSC have demonstrated that integration of proquinoidal units into the porphyrin structure causes strong perturbations to the electronic structure of the macrocycle^{32–35}. These perturbations in benzothiadiazole-porphyrin analogues result in improved light harvesting by broadening and redshifting absorbance of the Soret and Q-bands.

In this work, we reengineered the prototypical structure of D- π -A porphyrins to simultaneously maximize cobalt-electrolyte compatibility and improve the light-harvesting properties. Functionalization of the porphyrin core with the bulky bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amine³⁶ donor and a 4-ethynylbenzoic acid yielded the green dye SM371, which exhibited a slightly improved PCE of 12% compared to the previously reported YD2-o-C8 (11.9%)⁶. Incorporation of the proquinoidal benzothiadiazole (BTD) unit into this structure afforded the dye SM315, a

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1 panchromatic porphyrin sensitizer (Fig. 1). **SM315** exhibited significant broadening of Soret and Q-band absorbance features compared to **SM371**, yielding improved light harvesting in both the green (500–600 nm) and red (up to 800 nm) region of the spectrum. **SM315** demonstrated an enhancement in green light absorption, resulting in an improved J_{SC} (18.1 versus 15.9 mA cm⁻² for **SM315** and **SM371**, respectively) when utilized in the DSC. Ultimately, the panchromatic sensitizer **SM315** achieved a record 13.0% PCE at full sun illumination without the requirement of a co-sensitizer.

11 Results and discussion

12 **Opto-electronic properties of the porphyrin sensitizers.** The syntheses of the dyes **SM371** and **SM315** are provided in the Supplementary Information. The donor group bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amine was specifically used in the two dyes as it has demonstrated compatibility with cobalt-based electrolytes and yields high open-circuit photovoltages^{7–9,36}. Table 1 summarizes the UV–vis, fluorescence and cyclic voltammetry data for **SM371** and **SM315**.

20 Figure 2 shows the solution (THF) absorption spectra of the **SM371** and **SM315** sensitizers. **SM371** features an absorption spectrum typical of porphyrins functionalized with a diarylamine donor and ethynylbenzoic acid acceptor, with maxima from the Soret band (B-band) at 447 nm and from the Q-bands at 580 nm and 646 nm. The introduction of the BTD acceptor unit had a significant impact

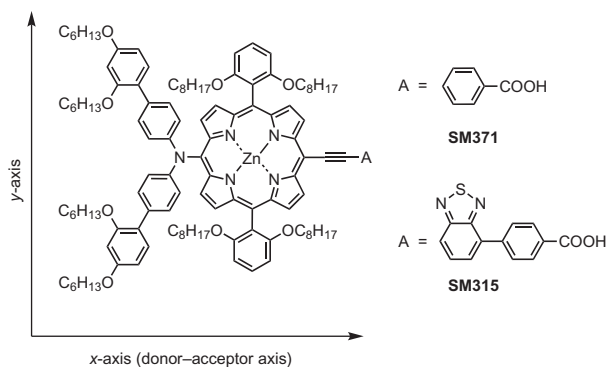


Figure 1 | Structures of the two dyes used in the study. The structures are coded **SM371** and **SM315**. They both feature a porphyrin core and a bulky bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amine donor. Their acceptor groups differs, with **SM315** featuring a benzothiadiazole group.

26 on the absorption spectrum of **SM315**, most evident by the splitting of the Soret band, resulting in a shoulder at 440 nm on the maximum at 454 nm. Furthermore, the absorption of **SM315** between the Soret and Q-bands (450–550 nm) displayed significant enhancement compared to **SM371**, leading to the panchromatic character of the BTD-functionalized dye. The Q-band at 581 nm remained relatively constant compared to that of **SM371**, but the

Table 1 | Optical and electrochemical data for SM371 and SM315.

Dye	λ_{abs} (nm)/ ϵ (10^3 M ⁻¹ cm ⁻¹)	λ_{em} (nm)*	E_{0-0} (eV) [†]	E_{ox1} (V)	E_{red1} (V)
SM371	447/199, 580/12, 646/29	674	1.88	0.89	-1.21
SM315	440/105, 454/117, 581/12, 668/53	732	1.79	0.88	-0.99

*Emission maxima obtained in THF by excitation at 440 nm.

[†]Zero-zero excitation energy, determined by the intersection of normalized absorbance and emission spectra.

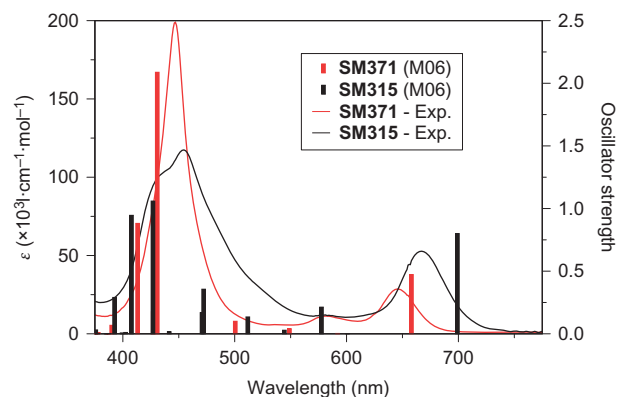


Figure 2 | Absorption spectra of the dyes studied. The experimental spectra (in THF) are shown as continuous lines and the theoretical electronic transitions are shown as bars for both **SM371** (red) and **SM315** (black). Theoretical data were computed using LR-TDDFT/M06/IEF-PCM(THF).

lowest-energy Q-band absorption of **SM315** was significantly redshifted to 668 nm. Both the spectral splitting and the redshifting of absorbance maxima for **SM315** are consistent with previously reported porphyrin–BTD ensembles^{32,37}.

The splitting of the Soret band in **SM315** can be rationalized using point-dipole exciton coupling theory³⁷. The Soret band (B-band) is a composition of two perpendicularly polarized transitions within the molecule, denoted B_x and B_y , where the x -axis has the greatest degree of conjugation (that is, the donor–acceptor axis, Fig. 1)^{38,39}. In a symmetrical zinc tetraphenylporphyrin the B_x and B_y transitions are degenerate. Functionalization of the porphyrin with donor and acceptor moieties to afford **SM371** increased the conjugation and charge transfer (CT) character along the donor–acceptor axis (that is, x -axis) of the dye, causing the Soret absorption originating from the B_x transition to be redshifted with increased molar absorptivity. Overall, the Soret band in **SM371** appears both broad and redshifted, as the B_x and B_y transitions are no longer degenerate. The presence of the BTD-functionalized acceptor in **SM315** further increased the electronic asymmetry and CT character of the dye, causing a redshifted B_x transition, which resulted in the Soret band appearing as two distinguishable maxima in the absorbance spectrum. Furthermore, the presence of the BTD acceptor increased the x -axis polarizability of **SM315**, indicative of increased oscillator strength for the B_x transition, rationalizing the differences in molar absorptivity between the two Soret maxima.

Another noticeable difference in the spectra of the two dyes is the redshift and increase in molar absorptivity of the lowest-energy Q-band for **SM315**. For both dyes, the absorbance originating from the Q_y transition remains relatively unperturbed, appearing at 580 nm and 581 nm in **SM315** and **SM371**, respectively. The increased conjugation along the x -axis of **SM315** strongly shifted absorbance from the Q_x transition to produce a maximum at 668 nm. The significant increase in molar absorption coefficient is consistent with the increased oscillator strength of the Q_x transition from enhanced x -axis polarizability within the **SM315** upon introduction of the BTD unit.

Comparison of the frontier Kohn–Sham (KS) orbitals between the two compounds highlighted the effect of the BTD acceptor on the electronic structure of **SM315** (Fig. 3). The KS highest occupied molecular orbital (HOMO) of both dyes was predominantly localized on the donor and was not affected by the choice of acceptor. The location of the KS lowest unoccupied molecular orbital (LUMO) in **SM315** demonstrated a significant shift towards the BTD component of the acceptor. Hence, the electronic transition

Q9

Q2

Q3

Q4

1 in **SM315** with a dominant HOMO \rightarrow LUMO contribution was
2 expected to exhibit an enhanced CT character compared to **SM371**.

3 The calculated absorption spectra for **SM371** and **SM315** (Fig. 2)
4 were obtained by using linear-response time-dependent density
5 functional theory (LR-TDDFT) and the M06 functional⁴⁰. An integral
6 equation formalism of the polarizable continuum model (IEF-
7 PCM) with a relative permittivity of 7.43 was used to simulate the
8 solvent (THF) used for the experimental absorption data (see
9 Supplementary Information for full computational details and a
10 discussion of the protocol used). The LR-TDDFT/M06/IEF-
11 PCM(THF) methodology predicted a strong alteration of the
12 Soret band for **SM315**, with two distinct transitions appearing at
13 408 nm and 427 nm (3.04 and 2.90 eV, respectively), with similar
14 oscillator strengths, consistent with the splitting observed exper-
15 imentally, which contributes to the panchromatic character of the
16 dye. Analysis of the transition density difference plots
17 (Supplementary Fig. 2) for the two Soret transitions of **SM315**
18 revealed that the lower-energy Soret absorption exhibited a signifi-
19 cant contribution from the BTD acceptor (that is, greater polariz-
20 ability along the donor-acceptor axis due to an enhanced CT
21 character), consistent with the rationalization provided from
22 point-dipole exciton coupling theory (*vide supra*). In contrast, the
23 LR-TDDFT/M06/IEF-PCM(THF) absorption spectra of **SM371**
24 indicated that the Soret band is dominated by a strong transition
25 at 431 nm and a weaker second transition computed at 413 nm,
26 reproducing the trends in Soret band splitting observed experimen-
27 tally between the two dyes.

28 The calculated absorption of **SM315** presented a vertical transi-
29 tion with moderate oscillator strength (0.213) at 578 nm
30 (2.15 eV), with significant donor-to-acceptor character (HOMO-1
31 \rightarrow LUMO, 83%). This small absorption, in line with the experimen-
32 tal observation, also contributes to the enhanced panchromatic
33 light-harvesting ability of **SM315**, together with a series of absorp-
34 tion lines between 601 nm and 430 nm. The calculated absorption
35 spectra afforded a first vertical excitation at 658 nm (1.88 eV) and
36 699 nm (1.77 eV) for **SM371** and **SM315**, respectively, consistent
37 with the experimental values of 646 nm (1.92 eV) and 668 nm
38 (1.86 eV) for the lowest-energy Q-bands. For both dyes, this first

electronic transition is characterized by a dominant HOMO \rightarrow LUMO
contribution of comparable magnitude, 91% for **SM371** and 88% for
contribution of comparable magnitude, 91% for **SM371** and 88% for **SM315**, confirming the CT character of both dyes
(further supported by transition density plots; Supplementary Figs
1,2). The presence of the BTD moiety in **SM315** results in an
extended delocalization of the LUMO onto this acceptor site,
enhancing the CT character of this band, together with a shift
towards lower energy and higher oscillator strength. The second
transition is computed at a similar energy for both dyes, 600 nm
(**SM315**) and 592 nm (**SM371**), and displays in both cases small
oscillator strength and a similar character (Supplementary Figs 1
and 2).

Characterization of the surface-mounted dyes was achieved by
adsorbing the sensitizer onto a 1- μm -thick TiO_2 substrate following
acquisition of a Fourier transform infrared (FTIR) spectrum
(Supplementary Fig. 3). On adsorption to TiO_2 , the FTIR spectra
revealed the disappearance of the carbonyl stretch, $\nu(\text{C}=\text{O})$, at
1,690 cm^{-1} from the neat dye, with a concomitant increase in the
intensity of the band at 1,380 cm^{-1} , which originates from the sym-
metric carboxylate band, $\nu(\text{COO}_{\text{sym}}^-)$. This change is characteristic
of bidentate binding by both oxygen atoms of the carboxylate func-
tional group to the titania of the substrate, consistent with previous
reports^{41–43}.

UV-vis characterization of the surface-mounted dyes was
achieved by adsorbing the sensitizer onto a 1- μm -thick TiO_2 sub-
strate (data presented in the Supplementary Information;
Supplementary Fig. 4). Both dyes experienced a slight blueshift on
adsorption to the titania, which was attributed to the decrease in
dipole following loss of the carbonyl moiety of the anchoring
group, consistent with observations from FTIR analysis of the sub-
strate. The degrees of blueshift for absorptions derived from the B_y
and Q_y transitions were less than for those derived from the B_x and
 Q_x transitions, consistent with the rationale provided by point-
dipole exciton coupling theory (*vide supra*). Measurement of the
light-harvesting efficiency (LHE) of **SM371** and **SM315** on trans-
parent TiO_2 films (3.5 μm) is provided in the Supplementary
Information (Supplementary Fig. 5). The LHEs for **SM371** and
SM315 exhibited maxima that correlated with those observed in

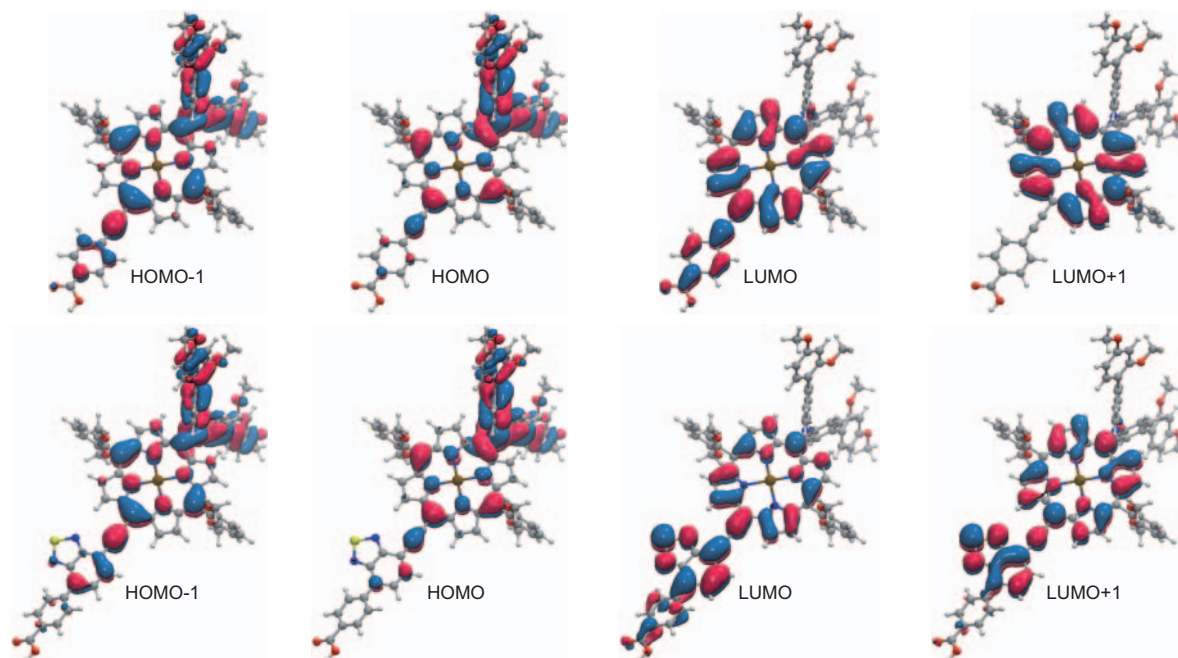


Figure 3 | Contour plots of selected KS orbitals for the dyes studied. The orbitals were calculated for geometry-optimized **SM371** (top) and **SM315** (bottom), using DFT/M06/IEF-PCM(THF). (Isovalue set to 0.02 a.u.).

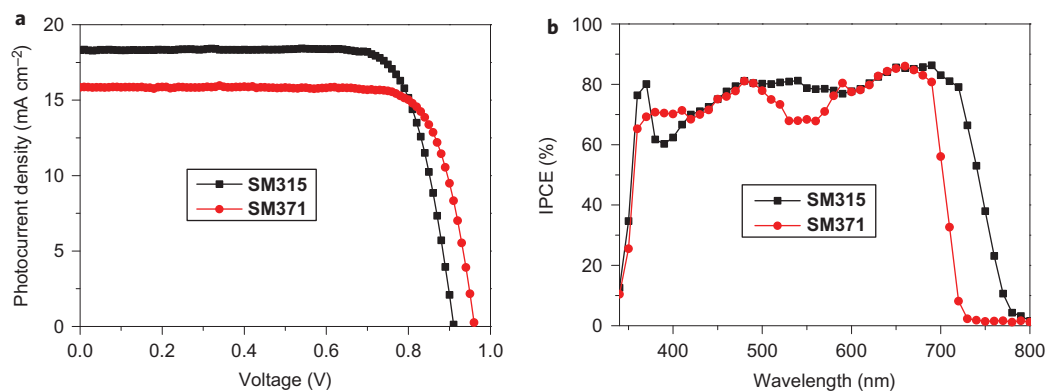


Figure 4 | Photovoltaic performance of devices made with SM371 and SM315. **a, b**, J - V curve under AM 1.5G illumination ($1,000 \text{ W m}^{-2}$) (**a**) and photocurrent action spectrum (**b**) for SM371 (red) and SM315 (black).

1 the experimental absorption spectrum. Measurement of LHE
 2 revealed that SM315 has a near-quantitative LHE throughout the
 3 visible region, which is a dramatic improvement over SM371. The
 4 splitting and redshifting of Soret and Q-band absorptions upon
 5 introduction of the BTD unit into the dye structure is directly
 6 responsible for the significant improvements in LHE demonstrated
 7 by SM315. The dye loading on the TiO_2 films was obtained by des-
 8 orbing the dyes, and the amount of dyes loaded was estimated to be
 9 $8.35 \times 10^{-7} \text{ mol cm}^{-2}$ for the case of the SM315 dye. Assuming a
 10 uniform coverage on the titania without any aggregates, the
 11 SM315 dye occupies a surface area of $\sim 1.98 \text{ nm}^2$ on the TiO_2 .

12 The steady-state fluorescence spectra for SM371 and SM315 are
 13 provided in the Supplementary Information (Supplementary Fig. 6).
 14 SM371 exhibited an emission spectrum that mirrored the absorp-
 15 tion spectrum, but that of SM315 was broad and featureless, indicat-
 16 ing that an enhanced ICT character of the excited state could be
 17 achieved by using the strongly electron-deficient BTD unit,
 18 thereby increasing the acceptor property of the dye⁴⁴. Calculation
 19 of the Stokes shift for the two dyes revealed that SM315
 20 ($1,309 \text{ cm}^{-1}$) experienced a greater shift than SM371 (643 cm^{-1}).
 21 The acquisition of time-resolved luminescence in THF solution
 22 and on TiO_2 substrates provided insight into the electron injection
 23 dynamics of the two dyes (Supplementary Fig. 7). The fluorescence
 24 lifetime in solution (1.2 ns) and on TiO_2 substrates (63 and 60 ps for
 25 SM371 and SM315, respectively) was identical for both dyes. This is
 26 indicative of the injection efficiency (η_{inj}) for both dyes approaching
 27 unity, as a result of efficient photoinduced electron injection from
 28 the dye into the mesoporous anode.

29 **Electrochemical characterization.** The electrochemical
 30 characterization of SM371 and SM315 was performed in DMF.
 31 The oxidation potential of the dyes is critical for the functioning
 32 of the DSC, as it determines the optimal cobalt redox couple to
 33 be utilized within the cell. The first oxidation potentials of SM371
 34 and SM315 were both quasi-reversible, with values of +0.88 V
 35 and +0.89 V (versus NHE), respectively. The computed vertical
 36 ionization energies (of the ground-state geometry) in DMF are
 37 nearly identical for both dyes (4.86 eV and 4.85 eV for SM371
 38 and SM315, respectively), consistent with the trend observed in
 39 oxidation potential and the observation that the HOMO of
 40 SM315 is not strongly affected by the BTD moiety.

41 The reduction potentials of SM371 and SM315 were -1.21 V and
 42 -0.99 V (versus NHE), respectively. The similarity of E_{ox} for the two
 43 dyes demonstrated a considerable advantage of the BTD-functiona-
 44 lized anchor, as it does not noticeably impact the oxidation potential
 45 of the dye. The BTD-functionalized anchor exclusively influenced
 46 the optical bandgap and absorption features of SM315 (*vide*
 47 *supra*), allowing us to engineer the absorption features and

oxidation potential of the porphyrin in a separate, modular
 48 fashion. The difference in reduction potential demonstrated the
 49 ability of the BTD unit to stabilize the LUMO, consistent with the
 50 redshift observed in the absorption spectrum of SM315.
 51

52 Further insight into the interfacial electron transfer (that is, from
 53 the photoexcited dye to the semiconducting photoanode) was
 54 performed by intensity-modulated photoinduced absorption (PIA)
 55 measurements on TiO_2 films sensitized with SM371 and SM315
 56 (Supplementary Fig. 8). Measuring the change in absorbance of
 57 the sensitized films in the absence of electrolyte (that is, acetonitrile
 58 solvent) revealed a decrease in absorbance from the Q-band, with
 59 concomitant evolution of an absorbance at 800 nm, diagnostic of
 60 formation of the porphyrin cation radical for both dyes²⁸.
 61 Interestingly, the amount of dye cation radicals generated by
 62 SM315 in the absence of the electrolyte appears to be less than for
 63 SM371, indicating that the injected electron recombines with the
 64 photo-oxidized sensitizer faster for SM315 than for SM371. This
 65 back reaction is facilitated by the presence of the strongly electron-
 66 deficient BTD moiety in SM315 and is consistent with previous
 67 reports where the undesirable electron-recapture event could be par-
 68 tially ameliorated through the introduction of a phenyl spacer
 69 between the BTD and the anchoring group⁴⁵. In the presence of
 70 the cobalt electrolyte, absorbance features pertaining to the por-
 71 phyrin cation radical disappear entirely, indicating efficient regener-
 72 ation of the porphyrins by the Co(II) species of the redox couple⁶.

73 **Photovoltaic performance.** Dyes SM371 and SM315 were utilized
 74 in DSCs using thin ($7 \mu\text{m}$) mesoporous TiO_2 films to enable
 75 compatibility with the $[\text{Co}(\text{bpy})_3]^{2+/3+}$ redox couple, essential in
 76 obtaining DSCs exhibiting a high V_{OC} . Figure 4 shows the J - V
 77 curve for the two devices measured under AM 1.5G illumination
 78 ($1,000 \text{ W m}^{-2}$ at 298 K) (data summarized in Table 2). DSCs
 79 fabricated using SM371 gave a high V_{OC} (0.96 mV) and J_{SC}
 80 (15.9 mA cm^{-2}), achieving an overall PCE of 12.0%, a slight
 81 improvement compared to the porphyrin sensitizer YD2-o-C8,
 82 which has a similar structure⁶. Despite exhibiting a slightly lower
 83 V_{OC} of 0.91 V, the best cell made with SM315 attained a higher
 84 J_{SC} (18.1 mA cm^{-2}) and an overall PCE of 13.0%, outperforming
 85 SM371 as a result of the improvement in visible and near-infrared
 86 light harvesting. A histogram of 50 different devices made with

Table 2 | Summary of photovoltaic performance data for SM371 and SM315 under AM 1.5G illumination ($1,000 \text{ W m}^{-2}$).

Dye	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF	PCE (%)
SM371	0.96	15.9	0.79	12.0
SM315	0.91	18.1	0.78	13.0

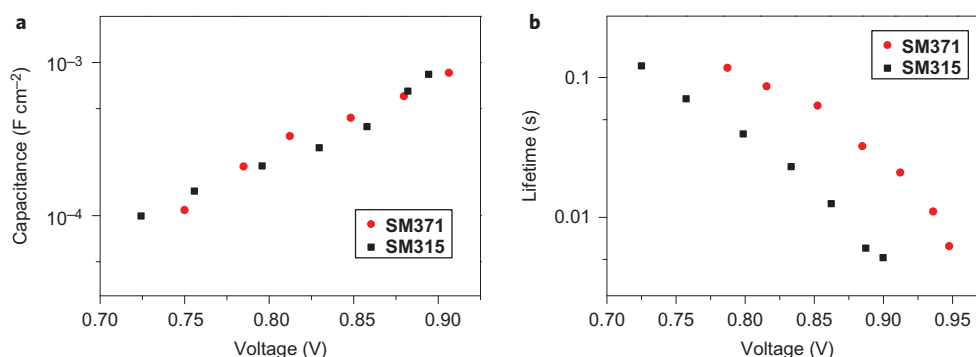


Figure 5 | Transient photocurrent and photovoltage measurements carried out on devices made with SM315 and SM371. a,b, Chemical capacitance (a) and electron lifetime (b) as a function of V_{OC} obtained through transient photocurrent and photovoltage measurements.

1 SM315 dye is shown in Supplementary Fig. 10. A higher average
2 PCE was obtained at 64% sun intensity (13.25%) than at full sun
3 intensity (12.75%). The lower average at full sun intensity is
4 mainly due to mass transport limitations of the cobalt
5 redox mediator.

6 **SM371** possessed a near identical photocurrent action spectrum
7 (Fig. 4b) to that of dyes with comparable donor and acceptor sub-
8 stitution (that is, YD2-o-C8), with maximum IPCE values of 80%
9 obtained at 480, 590 and 640 nm. **SM315** demonstrated impress-
10 ively high IPCE values across the whole visible wavelength range,
11 maintaining a value of 80% from 450 nm to 750 nm, with the
12 DSC harvesting light up to 800 nm, demonstrating the utility of
13 the BTD-functionalized anchor for visible and infrared light-har-
14 vesting properties. The overlap integral of the photocurrent action
15 spectrum with the standard AM 1.5G solar emission spectrum is
16 in excellent agreement (within 2%) with the measured photocur-
17 rent, demonstrating that any spectral mismatch between the simu-
18 lated and true AM 1.5G sunlight is negligibly small.

19 Transient photovoltage and photocurrent measurements were
20 used to investigate the origin of reduced V_{OC} for DSCs sensitized
21 with **SM315**. A reduction in V_{OC} can originate from either (1)
22 downward shift of the conduction band or (2) the enhanced recom-
23 bination of injected charges in the TiO₂ film with the dye or electro-
24 lyte^{6,46–48}. A downward shift of the TiO₂ conduction band (that is,
25 displacement of the trap-state distribution function to lower
26 energy) would cause the density of occupied states (DOS) to be
27 higher for **SM315** than for **SM371**^{6,46–48}. Measurement of the
28 chemical capacitance (C_{μ} , Fig. 5a) as a function of V_{OC} allows
29 insight into the DOS in devices made with either dye, as C_{μ} and
30 DOS are directly proportional to each other. At a given V_{OC} , C_{μ}
31 is nearly identical for both dyes, ruling out a downward shift of
32 the conduction band shift as the origin of the decreased V_{OC} in
33 **SM315**-sensitized DSCs.

34 Measurement of the electron lifetimes as a function of V_{OC}
35 (Fig. 5b) afforded insight into the electron recombination occurring
36 at the TiO₂-electrolyte interface. At a given V_{OC} , the electron
37 lifetime in cells sensitized with **SM371** was two to six times longer
38 than for **SM315**-sensitized DSCs. Evidence from previous work
39 clearly demonstrates that the direct connection of the BTD group
40 to the anchoring group accelerated conduction-band electron recap-
41 ture by the sensitizer and the utilization of a phenyl spacer retards the
42 electron recapture⁴⁵. In this work, the PIA spectrum of **SM315**
43 (Supplementary Fig. 8b) clearly demonstrated that even with a
44 phenyl spacer in place, the electron recapture by **SM315** is faster
45 than by **SM371**. This indicates that the phenyl spacer does not com-
46 pletely attenuate the accelerating effect of the BTD moiety on charge
47 carrier recombination (*vide supra*). The result of the accelerated
48 electron recapture by **SM315** (compared to **SM371**) at the TiO₂-
49 electrolyte interface resulted in a V_{OC} decrease of 50 mV in the

device. However, this loss in V_{OC} is overcompensated by a gain in
50 J_{SC} , resulting in the superior performance of the **SM371** dye. 51

52 Long-term stability measurements were carried out on three
53 individual devices sensitized with **SM315** by subjecting them to
54 continuous light soaking at full solar light intensity for 500 h at
55 298 K (Supplementary Fig. 11). The cells were kept at their
56 maximum power point during the illumination. We obtained
57 excellent stability over this long period, showing that the
58 **SM315** is a very stable dye and not prone to degradation, even
59 if exposed to intense sunlight for long illumination times.
60 During the 500 h of light soaking, devices employing **SM315**
61 underwent over one million turnovers without showing any sig-
62 nificant loss in stability. The initial drop in PCE of ~10–20%
63 for the three devices is attributed to desorption of a small
64 amount of sensitizer from the TiO₂ surface, decreasing the photo-
65 voltaic performance. In the future, the introduction of stronger
66 anchoring groups into the high-performance **SM315**-type design
67 should serve to minimize any dye desorption and further
68 improve the stability of the device.

Conclusion 69

Judicious molecular engineering of push-pull porphyrins has
70 allowed the realization of two high-performance sensitizers,
71 **SM371** and **SM315**, exhibiting unprecedented solar-to-electric
72 PCEs under standard AM 1.5G illumination. The green dye
73 **SM371** exhibited slightly better performance (12.0%) than the
74 previous state-of-the-art YD2-o-C8. Introduction of the BTD-functio-
75 nalized acceptor into the dye structure afforded the broadly
76 absorbing sensitizer **SM315**. The enhanced visible and long wave-
77 length absorbance properties of **SM315** were rationalized by LR-
78 TDFT analysis. The dramatically improved absorption properties
79 of **SM315** resulted in a near-quantitative LHE across the visible
80 spectrum and up to 800 nm, leading to greater photocurrents in
81 the DSC device compared to **SM371**. Fabrication of DSCs utilizing
82 the [Co(bpy)₃]^{2+/3+} redox couple and **SM315** demonstrated pan-
83 chromatic light harvesting without the use of co-sensitization,
84 leading to a record 13% PCE at full sun illumination. 85

Methods 86

87 Details of the synthesis and characterization of the dyes, computational
88 investigations, DSC fabrication and photovoltaic characterization (J - V , IPCE, PIA,
89 transient photovoltage/photocurrent decay, stability measurements) are described in
90 the Supplementary Information.

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Author contributions

A.Y. and S.M. proposed the research. S.M. synthesized and characterized the dyes with
assistance from P.G. A.Y. fabricated and optimized the DSCs and conducted all the
photovoltaic characterization. Electrochemical characterization was performed by P.G.
R.H.B. performed photo-physical characterization and assisted in interpreting the results
with assistance from A.Y. and M.G. R.H.B. designed the instruments and contributed to
interpreting the results. B.F.E.C. and N.A.A. performed the computational characterization,
with I.T. and U.R. contributing to the analysis and interpretation of the results. M.K.N. is
responsible for overseeing the sensitizer project. S.M. and M.G. prepared the manuscript,
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Additional information

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Competing financial interests

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