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Trans-disubstituted benzodiazaporphyrin: a promising hybrid dye between porphyrin and phthalocyanine for application in Dye-Sensitized Solar Cells

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Highlights

A simple trans-disubstituted zinc benzodiazaporphyrin is a promising sensitizer for dye-sensitized solar cells, which opens new opportunities for tetrapyrrole dyes, especially to harvest the low energy part of visible spectrum.

Abstract:

We have synthesized a zinc benzodiazaporphyrin *trans*-substituted by a di-(3,5-*tert*-butyl)phenyl and 4phenyl carboxylic acid groups (coded **CROSSDAP**). This new dye has been characterized by UV-vis absorption and emission spectroscopy, electrochemical measurements and modeled with TD-DFT calculations. **CROSSDAP** exhibits interesting absorption properties which resemble those of a zinc phthalocyanine; that is an intense Q-band localized at 685 nm. **CROSSDAP** was used as sensitizer on nanocrystalline TiO₂ based Dye-Sensitized Solar Cells with iodide/triiodide electrolyte. The solar cell reaches a 3.37% power conversion efficiency under AM1.5 with an IPCE value over 40% at 680 nm. **CROSSDAP** can axially bind an imidazole ligand substituted with a Bodipy dye. When used as additive in the electrolyte, the latter antenna amplifies the light harvesting efficiency of **CROSSDAP** in the 450-550 nm range, a feature which increases the photocurrent up to 8.40 mA/cm² resulting in a PCE of 3.82%. Overall, these results demonstrate that *trans*-substituted benzodiazaporphyrins are attractive new dyes for DSSC, particularly towards the development of efficient sensitizers to harvest the low energy part of the visible spectrum.

Keywords:

Solar cell; Electrochemistry; Density functional theory; Energy Transfer; Antenna, TiO2

Introduction

Dye-sensitized solar cells (DSSCs) represent a clean and sustainable technology for the third generation of photovoltaics.[1] In this area, ruthenium polypyridine complexes have been the most efficient sensitizers for several decades, with photoconversion efficiencies in the range of 10-11%.[2-5] In early 2000, it was discovered that push-pull organic dyes, comprising a π -conjugated spacer functionalized by an electron donating group and an electron withdrawing group, can be particularly efficient sensitizers in DSSCs. [1, 6-9] More recently, push-pull porphyrin derivatives such as **SM315** have attracted a strong interest in DSSCs because cells with such sensitizers have attained a record efficiency of 13% (Figure 1).[10-12]



Figure 1. Structures of efficient porphyrin and phthalocyanine sensitizers used in DSSC.

However, a strong drawback of porphyrin dyes is their weak absorbance both at ca. 450 nm, and above 750 nm where the incoming solar flux is significant. The weak light harvesting efficiency in this region certainly limits the overall photovoltaic performance of this class of dyes. Phthalocyanines are π conjugated macrocycles related to porphyrins which have also been thoroughly investigated as sensitizers in DSSCs, among them PcS20 is a very active one (Figure 1).[12-20] However, the preparation of trans-disubtituted phthalocyanines is an extremely tedious and challenging synthetic task,[21, 22] limiting the possibility of developing push-pull phthalocyanines that are appealing dyes for solar cell applications. Tetrabenzodiazaporphyrins (TBDAPs) can be considered as hybrid dyes between porphyrins and phthalocyanines since two of the bridging meso-positions are occupied by nitrogen, like in phthalocyanines, while the two other meso-positions are regular methene moieties, which can carry substituents.[23] The two interesting and valuable features of benzodiazaporphyrins are, first, the presence of an intense and long wavelength absorption band similar to phthalocyanines, and second, the possibility to envision the preparation of push-pull or dipolar systems by functionalization of the two adjacent carbon meso-positions thanks to the straightforward and efficient synthesis recently reported by Andrianov, and co-workers.[24] Recently, Imahori and co-workers have reported the photovoltaic performances of a diazaporphyrin, however the power conversion turned out to be low, which is attributed to the insufficient electron injection driving force and the formation of aggregates on TiO_2 .[25] We found that the simple trans-disubstituted tetrabenzodiazaporphyrin CROSSDAP (Figure 2) performs quite well in DSSC as compared to similarly substituted porphyrin[26] or phthalocyanine[27] sensitizers.

Owing to the recent synthetic methodology to prepare *trans*-disubstituted benzodiazaporphyrins, the encouraging photovoltaic performances of **CROSSDAP** demonstrate the potential of benzodiazaporphyrins for photovoltaic applications and particularly for DSSCs.



Figure 2. Structures of the dyes studied in this work.

Results and discussion

The synthesis of **CROSSDAP** is illustrated on Scheme 1. The key transformation leading to the formation of a diazabenzoporphyrin core with unsymmetrical aryl substituents (8) was achieved by the cross-dimerization of the corresponding dibenzodipyrrin diacylazides 4 and 7.[24] The parent dipyrrins 4 and 7 were synthesized according to the so-called 4,7-dihydroisoindole method [28, 29] which is a common and convenient strategy for the synthesis of porphyrins and dipyrrins with a π -extended aromatic system.[30-37] In the first step, the dihydroisoindole carboxylate tert-butyl ester 1[28] was reacted with a corresponding aldehyde 2 or 5, followed by oxidation with 2,3-dichloro-5,6-dicyano-1,4benzoquinone (DDQ), yielding aryl dibenzodipyrrins 3 and 6 with a circa 75% yield. tert-butyl ester was selectively cleaved under mild conditions simply by solvolysis in neat TFA, whereas the methyl ester group in 6 is stable under these conditions. The resulting dipyrrin dicarboxylates are pure enough to be used in to the following transformations without additional purification. The intermediate dicarboxylate derivatives were then transformed into the corresponding acylchloride by reaction with SOCI₂ and the latter were subsequently reacted with Bu₄NN₃ to afford the diacylazides 4 and 7 in 65-70% yields. Accordingly, acylazides 4 and 7 were synthesized in a multistep one-pot procedure from 3 and 6, respectively. The large amounts (more than 300 mg) of 4 and 7 can be easily purified by re-precipitation from acetonitrile, whereas silica gel chromatography is better suited for the small quantities. It is worth

noting that the purity of the diacylazides **4** and **7** is critical for the success of the next steps. The formation of diazabenzoporphyrin **8** was achieved by non-selective cross-dimerization between **4** and **7** in refluxing DMF. This stochastic cross-condensation naturally lead to three different dizabenzoporphyrins, which were formed with almost the same yield (around 15%). Unsymmetrical dizabenzoporphyrin **8** has an intermediate polarity among these products and therefore can be easily isolated by column chromatography. The metallation of **8** by zinc acetate was carried out in DMF under reflux and lead to **9** almost quantitatively. The metallation progress can be easily monitored by means of UV-vis spectroscopy by notable changes in the Q-bands region. In the final step, the methyl ester of **9** was hydrolyzed in MeOH/KOH and sufficiently pure **CROSSDAP** acid was precipitated with HCI. Compounds **8** and **9** are both well-soluble in dichloromethane and DMF and show no sign of aggregation in these solvents. The absorption spectra of **9** and **CROSSDAP** are almost identical indicating no significant electronic coupling between the aryl groups and the diazabenzoporphyrin core.



Scheme 1.Synthetic route for the preparation of **CROSSDAP**. Reagents and conditions: a) TsOH, Bu₄NBr, CH₂Cl₂; b) DDQ, toluene, 2 h, rt., (73% for **3** and 87% for **6**); c)neat TFA, 30 min, rt; d) 1.

neat SOCI₂, 15 min, 50° C. 2. Bu₄NN₃, Et₃N, MeCN, 1 h, rt., (70% for **4** and 65% for **7**); e) DMF, reflux, 15 min, (15%); f) Zn(OAc)₂, DMF, reflux, 30 min, (95%); g) KOH, MeOH, 30 min, rt., (95%).

In agreement with published zinc benzodiazaporphyrins, the absorption spectrum of **CROSSDAP** features an intense absorption Q-band at 685 with a high extinction coefficient (ε =9.3x10⁴ M⁻¹cm⁻¹) along with another much less intense vibronically resolved Q-band at higher energy (Figure 3).[38], [23] .The Soret band shows up at 431 nm with a moderate extinction coefficient (ε =5.8x10⁴ M⁻¹cm⁻¹). Overall, the spectrum of **CROSSDAP** resembles more that of a phthalocyanine than that of a porphyrin enabling thus to harvest low energy photons of visible spectrum. **CROSSDAP** is also a fluorescent dye exhibiting a tiny Stoke shift (22 cm⁻¹) suggesting very limited distortion of the first singlet excited state (Figure 3).The 0-0 energy of the first singlet state (E₀₀) is 1.84 eV as measured from the wavelength at the intersection of the absorption and emission spectra.



Figure 3. Electronic absorption (red line) and emission spectra (blue line) of CROSSDAP recorded in dimethylformamide.

Cyclic voltammetry measurements were performed to determine the oxidation potential of **CROSSDAP** in order to calculate the electron injection and dye regeneration driving forces.**CROSSDAP** exhibits two reversible oxidation processes occurring respectively at 0.84 and 1.05 V *versus* saturated calomel

electrode (SCE). The Gibbs free energy enthalpy of the injection (ΔG_{inj}) and the regeneration (ΔG_{reg}) reaction can be calculated according to the following equations:

 $\Delta G_{inj} = E_{Ox1}(CROSSDAP^+/CROSSDAP) - E_{00}- E_{CB}(TiO_2)$

 $\Delta G_{reg} = E_{Ox}(I_2^{-}/I^{-}) - E_{Ox1}(D^{+}/D)$

where $E_{Ox1}(CROSSDAP^+/CROSSDAP)$ corresponds to the first oxidation potential of **CROSSDAP**, $E_{Ox}(I_2^-/I^-)$ to the oxidation potential of $I_2^-/I^-[39]$ and $E_{CB}(TiO_2)$ corresponds to the conduction band potential of TiO₂.[1] These calculations support that electron injection ($\Delta G_{inj} = -0.30 \text{ eV}$) and dye regeneration ($\Delta G_{reg} = -0.29 \text{ eV}$) processes are both sufficiently exergonic to occur spontaneously.





Figure 4. Representation of the frontier molecular orbitals of **CROSSDAP** (right) and the corresponding, zinc porphyrin (center) and zinc phthalocyanine (left) substituted with same anchoring group. Isodensity contour: 0.002 au.

To elucidate the electronic properties of **CROSSDAP** with respect to those of analogously substituted zinc porphyrin and zinc phthalocyanine, we have performed DFT and TD-DFT calculations of their ground and excited state properties, respectively (Figure 4). The optimized structure of **CROSSDAP** reveals that the aryl groups are rotated 90.0 degrees to the plane of the diazabenzoporphyrin. The ground state orbitals of **CROSSDAP** in Figure 4 allows to confirm that these aryl groups do not participate significantly in the frontier orbitals, which are in all cases mainly localized within the macrocycle. This is in contrast with the porphyrin analogue, for which the aryl groups are rotated ca. 65 degrees relative to the macrocycle plane. Consequently, the HOMO and LUMO of the porphyrin exhibit significantly larger density contributions from the benzoic acid anchoring group, implying a larger electronic coupling with the semiconductor upon binding, whereas such a contribution is absent in the frontier molecular orbitals of **CROSSDAP** (Figure 4).

In terms of their energies levels, shown in Figure 5, the computed gap energy for **CROSSDAP** (3.66 eV) falls closely in line with that of the corresponding phthalocyanine (3.63 eV), both of which have more stabilized gap energies than the porphyrin analogue (4.37 eV). The implications of this are evident in the

computed electronic absorption spectra, shown in Figure S1 for all three compounds. In agreement with the experimental spectra of Figure 3, the visible part of the spectra is dominated by intense absorption from the Q-band of **CROSSDAP** (λ =656 nm, *f*=0.668), comparable to that of phthalocyanine (653 nm, *f*=0.713). In the UV range, the first computed Soret band of **CROSSDAP** shows up at 374 nm (*f*=1.477), slightly higher in energy that of porphyrin (λ =388nm, *f*=1.913) but lower than phthalocyanine (λ =320 nm, *f*=0.123). Inspecting the rearrangement of the charge density for the first Soret excited state in Figure 6 across all three compounds, we observe that the electron density difference for both porphyrin and **CROSSDAP** are similarly distributed throughout the macrocycle, again with the notable difference between the two being the participation of the anchoring group. These computational results underpin the consensus that the optical features of **CROSSDAP** lie in between those of porphyrin and phthalocyanine, possessing both the visible absorption of phthalocyanine and the functionalization potential of porphyrin.



Figure 5. CAM-B3LYP ground state energy levels of the frontier molecular orbitals of **CROSSDAP** compared to zinc porphyrin and phthalocyanine. Red: HOMO and LUMO. Black: HOMO-1, LUMO+1.



Figure 6. Density differences between the ground state and the first Soret excited state of phthalocyanine (left), porphyrin (center), and **CROSSDAP** (right). Isodensity contour: 0.0004 au.

Nanocrystalline films of TiO₂ prepared by screen printing were then coated with **CROSSDAP** and used in solar cells with a platinized counter-electrode, sandwiched with an electrolyte based on iodide/triiodide redox couple solubilized in acetonitrile (see experimental part for details). The metrics of the solar cells are gathered in Table 1 and the photoaction spectra are shown in Figure 7. The dye was first loaded on TiO₂ in absence of chenodeoxycholic acid (CDCA) in the dying bath, but unexpectedly the performances were poor owing to the formation of aggregates upon immobilization. The absorption spectra recorded for thin TiO₂ film without scattering layer clearly show the decrease of the aggregates when CDCA was added in the dye bath. Indeed, in the presence of CDCA the envelope of the large Q-band at 650 nm narrows and the intensity of the bands at 608 and 636 nm decreases (Figure S2). The optimal concentration of CDCA was found to be 5 mM, as higher concentrations lead to a lower dye loading and consequently a lower short-circuit current density (Jsc). It is likely that the introduction of bulky substituents or alkyl chains on the diazabenzoporphyrin can decrease the propensity of this aromatic π conjugated macrocycle to aggregate upon immobilization on surface suggesting thus some room to improvement for next generation of benzodiazaporphyrin sensitizers, if one introduces bulky susbtituents on the dye.[18] Nevertheless, the obtained performances of CROSSDAP (3.37%) compare very well with those of simple zinc porphyrin (2.2%)[26] or zinc phthalocyanine (3.52%)[27] as they are in the same range as those published with similar sensitizer bearing the same benzoic acid anchoring group (see Table S1). The photoaction spectrum of the cell sensitized with CROSSDAP is shown in Figure 7 and displays a quite significant photoactivity on the Q-band in the 650-700 nm, but with lower Incident photon-to-current efficiency (IPCE) in the 450-600 nm region owing to intrinsic lower absorbance of the dye in this spectral window. The highest IPCE value reaches about 40% and we be related to limited injection quantum yield of **CROSSDAP**. This is most probably due by the low electronic coupling with TiO₂, as a consequence of the poor extension of the LUMO orbital on the anchoring group (see Figure 4). The introduction of an ethynyl moiety between the meso-position, where the benzoic acid is attached, could most certainly enhance the injection quantum yield and thereby the IPCE for the future TBDAP dves.



Figure 7. Photoaction spectra (IPCE as a function of the incident wavelength) of DSSCs sensitized with **CROSSDAP** (black) and **CROSSDAP+Bodipy** (red).

 Table 1. Photovoltaic characteristics of the DSSCs recorded under simulated solar spectrum AM 1.5 (100 mW/cm²).

Dye	conditions	$J_{ m SC}$	V _{oc}	FF	PCE
		(mA/cm²)	(mV)	(%)	(%)
CROSSDAP	0 mM of	4.05	518	74,4	1,56
	CDCA				
CROSSDAP	5 mM of	7.19	620	75,5	3.37
	CDCA				
CROSSDAP +	5 mM of	8.40	603	75.5	3.82
Bodipy	CDCA				

It is well-known that zinc porphyrins or zinc phthalocyanines can axially bind heteroaromatic amines such as pyridine and imidazole derivatives, suggesting that benzodiazaporphyrines could also display a

similar property.[40-45] We have tested this hypothesis by recording the absorption spectrum of the simple zinc benzodiazaporphyrine **10** upon titration with N-methylimidazole (Figure 8). The Q-band region is almost not affected by the ligation of N-methylimidazole onto zinc benzodiazaporphyrine **10**, while the Soret band exhibits an absorbance decrease along with a red-shift with the appearance of a clear isobestic point at 429 nm (also at 413 and 407 nm) (Figure 8). The Benesi-Hildebrand plot[46] of the absorbance variation at 433 nm as a function of the concentration of the added N-methylimidazole (Figure S4) permits the calculation of an association constant of 7.14x10⁴ M⁻¹, which is a same range as those determined between an imidazole derivative and a zinc tetraarylporphyrin (K ≈5 x10⁴ M⁻¹)[42] or a zinc phthalocyanine (K ≈ 5 x10⁴M⁻¹).[47]



Figure 8. Spectral change of zinc benzodiazaporphyrine10 upon titration with N-methylimidazole. Inset: the expanded Soret band region.

In order to enhance the light harvesting efficiency of **CROSSDAP**, we contemplate the introduction of a supplementary chromophore acting as an antenna to capture photons in the 450-550 nm window and transfer the incident photonic energy to **CROSSDAP** *via* Forster energy transfer mechanism. A previous

study proved that this strategy is quite effective to enhance photocurrent density in DSSC with a zinc porphyrin sensitizer[48]. To this end, we have investigated the photovoltaic performances of a solar cell coated with **CROSSDAP** and in which a **Bodipy** ligand was added in the iodide/triiodide electrolyte. The **Bodipy** molecule used in this study is connected to an imidazole unit and can thus axially bind to **CROSSDAP** *via* a coordination bond with zinc (Figure 2). First, the effective association of the **Bodipy** antenna on the immobilized **CROSSDAP** was confirmed by the observation of the absorption red-shift of its Soret band as shown on the absorption spectrum of the TiO₂ film soaked in a solution of **Bodipy** (Figure S5). Interestingly, the photocurrent density of the supramolecular association **CROSSDAP**. **Bodipy** was indeed raised by about 1.2 mA/cm², enlarging the overall power conversion efficiency of the cell to 3.82% (Table 1 and Figure S6). The photoaction spectra of the resulting cell clearly shows that the IPCE in the region 450-550 nm has indeed increased compared to the cell without the **Bodipy** (Figure 7). This supports the effective participation of this moiety to electricity generation *via* energy transfer since **Bodipy** itself is a poor sensitizer on TiO₂ (PCE≈ 0.22%).[48]

In conclusion, this study demonstrates that *trans*-substituted TBDAP derivatives represent an attractive new class of sensitizers for solar cells. Even a simple dye as **CROSSDAP** is already capable of yielding a PCE in the same range as those measured with simple zinc porphyrin or zinc phthalocyanine dyes. Moreover, this class of dye is certainly valuable for harvesting low energy photons of the visible spectrum due to its intense absorption Q-band in this region. It can be envisioned that introduction of an ethynyl spacer between the benzodiazaporphyrine and the anchoring group will most probably promote charge injection. In addition, the presence of a bulky electron donating group such a *tris*-aryl amine substituent at the opposite meso-position would enhance the charge transfer character of the electronic transitions and decrease aggregation, both improving the electron transfer in TiO₂ and enhancing the light harvesting efficiency of the dye. In light of the recent advances in the synthesis of *trans*-disubstituted benzodiazaporphyrin, such dyes are now within reach. We are actively exploring these possibilities in our laboratories.

Experimental part

15

The starting dihydroisoindole *tert*-butyl ester **1**[<u>30</u>] and **Bodipy** ligand[48] were prepared according to the procedure described in the literature. FTO conductive glass substrates (F-doped SnO₂) were purchased from Pilkington (TEC8).

The redox potential was measured by cyclic voltammetry using a platinum disc as working electrode, a platinum rod as auxiliary or counter electrode and a saturated calomel electrode (SCE) as reference electrode. The scan rate of the potential was fixed to 100 mV/s. The analysed solution comprises 0.001 M of **CROSSDAP** in acetonitrile as solvent and with 0.1 M of Bu₄NPF₆ as supporting electrolyte.

All density functional theory (DFT) and time-dependent DFT calculations (TD-DFT) were performed with the Gaussian09 suite.[49] Full optimizations and frequency calculations for all systems were carried out with the PBE0 functional using tightened thresholds of 10^{-9} a.u. for the SCF convergence.[50] The 6-31G(d) atomic basis set was used in conjuction with the LanL2DZ pseudopotential for the zinc.Solvation effects of acetonitrile were taken into account using the polarizable continuum model (PCM).[51] In a subsequent step, the optical spectra of the three structures were obtained through TD-DFT using the *nonequilibrium* PCM limit , imposing a tightened SCF convergence of at least 10^{-7} a.u. The thirty lowest-lying singlet states within the vertical excitation approximation were calculated using the range-separated CAM-B3LYP hybrid functional and the 6-31+G(d) atomic basis set.[52] For all calculations, *tert*-butyl groups have been replaced by methyl groups to reduce the computational overhead without detriment to the optical properties.

General procedure for preparation of meso-aryl substituted dibenzodipyrromethenes 3 and 6:

Two equivalents of 4,7-dihydroisoindole **1** and one equivalent of a corresponding aryl aldehyde **2** or **5** were dissolved in dry dichloromethane. *Para*-toluene sulfonic acid (TsOH) (0.1 equivalent) and an excess of tetrabutylammonium bromide (Bu_4NBr) were then added to the solution and stirred for 24 h at room temperature. Saturated aqueous NaHCO₃ was added to the solution and stirred vigorously for 10 min. The organic layer was separated, washed with water, dried and evaporated to afford an orange solid. The residue was dissolved in toluene, 3 equivalents of 2,3-dichloro-5,6-dicyanoquinone (DDQ) was added and the solution was stirred for 2 hours at ambient temperature. 10% aqueous solution of Na₂SO₃ was added and stirred vigorously for 10 min. Most toluene was removed under reduced pressure, the residue was diluted by dichloromethane, the organic layer was extracted, washed with

water, dried and concentrated *in vacuo*. The residual solution was applied to a column silica gel column, eluted with dichloromethane, a deep-violet fraction was collected and the solvent removed under reduced pressure.

Meso-(3,5-di-tert-butylphenyl)-dibenzodipyrromethene 3:

Were used 0.4 g of 4,7-dihydroisoindole **1**, 0.2 g of 3,5-di-*tert*-butyl benzaldehyde **2** and 0.6 g of DDQ at the oxidation stage. Yield 0.42 g (73%) of a deep-purple coloured crystalline solid. M.p. 200°C with decomposition.¹H NMR (CDCl₃, 400 MHz): 14.74 (br. s., 1H), 8.15 (d., *J* = 8.08 Hz, 2H), 7.24 (t., *J* = 7.43 Hz, 2H), 7.04 (t., *J*=7.43 Hz, 2H), 6.78 (br. s., 1H), 6.69 (br. s., 2H), 6.39 (d., *J*=8.08 Hz, 2H), 1.57 (s. 18H) 1.76 (s., 18H).¹³C NMR (CDCl₃): 161.63, 149.71, 147.87, 142.44, 141.33, 138.97, 135.64, 131.33, 125.67, 123.53, 122.70, 122.42, 107.56, 101.73, 81.10, 55.62, 27.82. MALDI-TOF (1,8-bis-(diphenylamino)-naphthalene, negative ion), *m/z* 631.54 (M-H)⁻.

Meso-(4-methoxycarbonylphenyl)-dibenzodipyrromethene 6:

Were used 0.5 g of a 4,7-dihydroisoindole **1**, 0.19 g of *p*-methoxycarbonyl benzaldehyde **5** and 0.75 g of DDQ at the oxidation stage. Yield 0.58 g (87%) of a deep-purple coloured crystalline solid.

M.p. 147°C with decomposition.¹H NMR (CDCl₃, 400 MHz): 14.79 (br. s., 1H), 8.36 (d., J = 8.08 Hz, 2H), 8.16 (d., J = 8.08 Hz, 2H), 7.66 (d., J = 8.08 Hz, 2H), 7.23 (t., J = 7.33 Hz, 2H), 6.97 (t., J=7.33 Hz, 2H), 6.09 (d., J=8.08 Hz, 2H), 4.08 (s., 3H) 1.78 (s., 18H).¹³C NMR (CDCl₃): 166.71, 161.00, 141.38, 139.56, 137.50, 135.48, 133.98, 131.38, 131.14, 130.68, 129.63, 126.93, 125.92, 123.07, 121.73, 82.55, 52.54, 28.39. MALDI-TOF (1,8-bis-(diphenylamino)-naphthalene, negative ion), m/z 577.86 (M-H)⁻.

General procedure for preparation of diacylazides 4 and 7:

Dipyrromethene **3** or **6** (0.35 g) was dissolved in trifluoroacetic acid (TFA), stirred for 30 min at room temperature and TFA was evaporated. The intermediate diacids can be additionally purified by precipitated from diethyl ether. Excess of thionyl chloride (SOCl₂) was added to the solid residue, stirred for 15 min at 50°C and evaporated under reduced pressure. The solid was then dissolved in dry acetonitrile, a few drops of Et₃N were added and an excess of tetrabutylammonium azide (*highly hygroscopic and toxic!!!*) was added to the solution. The mixture was stirred for 1 hour at rt, washed with water, dried and concentrated *in vacuo*. The residue was passed through a column with silica, collecting a blue fraction and evaporated to dryness.

Diacylazide 4[24]:

Yield 0.25 g (70%) of a deep-purple coloured crystalline solid.

Diacylazide 7[24]:

Yield 0.25 g (65%) of a deep-purple coloured crystalline solid.

5,15-diaryl-10,20-diazaterabenzoporphrin 8:

An equimolar mixture of azide **7** (0.042 g) and **4** (0.053 g) was dissolved in DCM, evaporated to dryness and DMF (10-15 mL) was added. The mixture was stirring vigorously and was then rapidly heated using a heating fan and refluxed in DMF for 15 min. When heated the mixture gains a deep-blue color first which then turns to red, indicating the decomposition of azide group. In a minute the color begins turning to green and the formation of small crystals of the products can be seen on a wall of a reaction vessel. Dichloromethane was then added to the cooled solution and the resulting solution was washed with water (5x50 mL) and evaporated to dryness. Porphyrinoid **8** was isolated as an intermediate green fraction by column chromatography on silica using DCM:Hexane 5:2 as an eluent. Yield 0.012 g (15%) of a deep-green crystalline solid.

M.p >300°C.¹H NMR (CDCl₃, 400 MHz): 9.69 (d., *J*=7.58 Hz, 2H), 9.62 (d., *J*=7.58 Hz, 2H), 8.59 (d., *J*=8.19 Hz, 2H), 8.20 (m., 4H), 8.14 (s., 1H), 8.05 (d., *J*=7.34 Hz, 2H), 7.93 (t., *J*=7.34 Hz, 2H), 7.73 (t., *J*=7.82 Hz, 2H), 7.60 (t., *J*=7.82 Hz, 2H), 7.29 (d., *J*=6.48 Hz, 2H), 7.00 (d., *J*=7.95 Hz, 2H), 7.24 (s., 3H), 1.62 (s., 18H), -1.25 (br. s., 1H), -1.37 (br. s., 1H). ¹³C NMR has not been recorded because of the aggregation of **8**.

MALDI-TOF (1,8-bis-(diphenylamino)-naphthalene), m/z 834.72 (M-H)⁻.

CROSSDAP:

The mixture of diaryldiazatetrabenzoporphyrin **8** (0.02 g) with an excess of Zn(OAc)₂ dihydrate was refluxed in DMF for 30 min. The metallation progress was monitored by means of UV-Vis spectroscopy and the reaction was stopped when the starting material was completely gone. The reaction mixture was then diluted with dichloromethane, washed with water (3x50 mL), dried and evaporated to dryness. The residue was dissolved in concentrated solution of potassium hydroxide in methanol and stirred for 30 min at room temperature. The reaction mixture was diluted with water, 0.5M HCl was added dropwise

and the precipitate was collected by centrifugation, washed with water and the solid was re-precipitated from DCM/Methanol mixture to afford deep-green crystalline solid. Yield 0.02 g (95%).

¹H NMR (CD₃OD/THF-d8, 400 MHz): 9.71 (m., 4H), 8.72 (br. m., 2H), 8.33 (d., *J*=7.97 Hz, 2H), 8.18 (t., J=1.75 Hz, 1H), 8.12 (d., J=1.75 Hz, 2H), 7.97 (t., *J*=7.20 Hz, 4H), 7.63 (m., 4H), 7.21 (d., *J*=8.11 Hz, 4H), 1.55 (s., 18H).

MALDI-TOF (1,8-bis-(diphenylamino)-naphthalene, negative ion), m/z 881.6 (M-H)⁻. HR ESI-MS: calcd for C₅₅H₄₂N₆O₂Zn 882.26552, found 882.26392.

Preparation of DSSC and photovoltaic characterization

The FTO substrates were cleaned by successive sonication in soapy water, then an ethanolic solution of HCI (0.1 M) for 10 minutes, and finally dried in air. TiO₂ films were prepared in three steps. A first treatment is applied by immersion for 30 min in an aqueous TiCl₄ solution at 80°C. Three successive layers of mesoporous TiO₂ were then screen printed using a transparent colloidal paste (Dyesol DSL 18NR-T) and a final light scattering layer (Dyesol DSL 18NR-AO) was affixed, with 20-minute long drying steps at 150°C between each layer. The obtained substrates were then sintered at 450°C, following a progressive heating ramp (325°C for 5 min, 375°C for 5 min, 450°C for 30 min). A second TiCl₄ treatment was immediately conducted afterwards and the electrodes were fired one last time at 450°C for 30 minutes. Thicknesses (16 µm) were measured by a Sloan Dektak 3 profilometer. The prepared TiO₂ electrodes were soaked while still hot (ca. 80°C) in a 0.2 mM solution of CROSSDAP and chenodeoxycholic acid (5 mM) in a 1:1 mixture (v:v) of toluene and ethanol. After one night of dyeing at room temperature, the electrodes were rinsed in ethanol and dried in air, in the dark. Platinum based counter electrodes were prepared by drop casting two drops of hexachloroplatinic acid in distilled isopropanol (2 mg per mL) on FTO plates, and subsequent firing at 380°C for 30 minutes. The photoelectrode and the counter electrode were placed on top of each other and sealed using a thin transparent film of Surlyn polymer (DuPont, 60 µm) as a spacer. The resulting chamber was filled with an iodine-based electrolyte (50 mM I₂, 0.1 M LiI, 0.6 M 1-ethyl-2,3-dimethylimidazolium iodide and 0.25 M 4-tert-butylpyridine when mentioned, in dry distilled acetonitrile) by vacuum back filling through a predrilled hole in the counter electrode, and the photovoltaic device was sealed afterwards with Surlyn and a cover glass. The cell had an active area of 0.25 cm². Photovoltaic measurements were performed

with a calibrated AM 1.5 artificial solar light simulator (Oriel) and a Keithley 2400 digital source-meter; data were collected with a local software designed by Synervia (labview). The photovoltaic characteristics of the DSSCs were recorded under calibrated Air mass 1.5 spectrum (AM1.5) simulator at 1000 W/m².

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