ChemComm

Cite this: *Chem. Commun.*, 2011, **47**, 4010–4012

www.rsc.org/chemcomm

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N-fused carbazole–zinc porphyrin–free-base porphyrin triad for efficient near-IR dye-sensitized solar cells†

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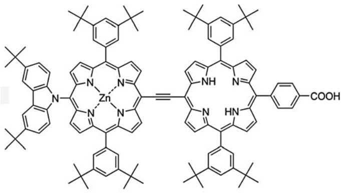
Received 17th August 2010, Accepted 17th January 2011
DOI: 10.1039/c0cc03306e

***N*-fused carbazole–zinc porphyrin–free-base porphyrin triad featuring an ethynyl-linkage was synthesized; efficient sensitization as long as 900 nm was demonstrated and an overall light-to-electricity conversion effciency of 5.21% was achieved under AM 1.5 G one sun illumination.**

Dye-sensitized solar cells (DSCs)[1] have been widely regarded as next-generation photovoltaics for providing electricity at lower expense and with more versatility. Although an overall light-to-electricity energy conversion efficiency above 11% has been entrusted with heteroleptic ruthenium sensitizers,[1b,c] the limited resource and the environmental issue concerning Ru usage make it necessary to seek alternative dyes. Recently, a series of donor-substituted porphyrins featuring direct fusion of diphenylamino groups to the *meso*-position of the porphyrin macro-ring has been developed.[2] They have shown intriguing potential to fabricate highly efficient DSCs and, by device optimization, comparable energy conversion efficiency above 11% has been demonstrated for the first time using such Ru-free dyes.[2a] However, although donor substitution significantly enhanced the light-harvesting abilities of such porphyrin monomer dyes, the light absorption range is still limited, which leaves space for further performance promotion by extending the absorption onset into the near-IR region.[3–5] On the other hand, *meso*,*meso*-ethynyl-linked porphyrin dimers[6] show moderate electronic conjugation and strong excitonic coupling, and sensitizers based on such building blocks have been reported by both Prof. Diau *et al.* and our group for efficient near-IR DSCs.[7] Considering the energy level difference between zinc porphyrin and free-base porphyrin,[8] in the present study, we combined the two strategies above by inserting the free-base porphyrin component as an extended acceptor into the commonly used ethynylbenzoic acid anchor.[2,7b] Meanwhile, as the donor-substitution of the porphyrin macro-ring is only limited to diphenylamino groups, while modification with *N*-fused heterocycles, like carbazole, which has demonstrated novel antenna function in heteroleptic Ru dyes[9] and also serves independently as an efficient sensitizer,[10] is still absent, in the present study, a novel *N*-fused carbazole–zinc porphyrin–free-base porphyrin donor–donor–acceptor triad featuring an ethynyl-linkage was designed and synthesized. The new compound was coded as **DTBC** (3,6-di-*tert*-butyl-carbazol-9-yl) and the molecular structure is illustrated in Fig. 1.

The detailed synthetic procedure is shown in the ESI†. Briefly, an unprecedented substitution of porphyrin macro-ring with heterocycles directly at the N atom and, amination of *meso*-Br-substituted zinc porphyrin (**5**, as coded in ESI†) with carbazole was much more challenging than it seemed with diphenylamines, due to the reduced donating ability of the N lone electron pair participating in conjugation and increased steric hindrance from the completely planar configuration of the carbazole moiety.[11] Fortunately, *N*-fused carbazole-substitution was accomplished in a moderate yield by increasing the base equivalence and extending the reaction time. The carbazole-fused zinc porphyrin was coupled with free-base porphyrin by Sonogashira reaction,[12] and the resulted target compound was identified by ^{1}H NMR, high-resolution ESI-mass, MALDI-TOF-mass and FT-IR spectroscopy.

UV-vis absorption spectra of **DTBC** in chloroform–methanol solution and adsorbed on TiO_2 film are shown in Fig. 2 and corresponding properties are listed in Table S1 (ESI†). As expected, the triad **DTBC** shows dramatically red-shifted Q-bands, the maximum of which is located at 722 nm, compared to those reported for porphyrin monomers[2] due to ethynyl-bridged inter-porphyrin electronic coupling.[6]



DTBC

Fig. 1 Molecular structure of **DTBC**.

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† Electronic supplementary information (ESI) available: Synthesis, cell fabrication, characterizations, supplementary Table S1 and Fig. S1–S3. See DOI: 10.1039/c0cc03306e

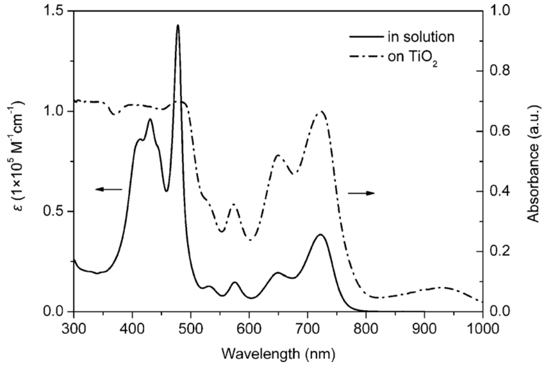

Fig. 2 UV-vis absorption spectra of **DTBC** in chloroform–methanol (2/1) solution (solid line) and adsorbed on TiO_2 film (dash dot line).

This value is also significantly bathochromic even with reference to our previously reported ethynyl-linked zinc porphyrin dimer in the same solvent composition,[7a] which can be attributed to the synergetic influence of carbazole-substitution and extended acceptor component by the free-base porphyrin.[13] In the short-wavelength region, characteristic Soret-band splitting was observed, ascribed to strong axial B_x excitonic coupling and rotation-determined B_y coupling, respectively.[14] Spectrum on TiO_2 resembles that in solution in the Q-band region, indicating negligible dye aggregation due to high coadsorbent (chenodeoxycholic acid, CDCA) equivalence during the dye loading process (ESI†). A new band related to the long-lived dye cation at around 940 nm evolved, demonstrating its slow recombination with injected TiO_2 electrons.[2e]

The oxidation and reduction potentials of **DTBC** were measured by differential pulse voltammetry (DPV, Fig. S1, ESI†) and are also summarized in Table S1 (ESI†). Injection potential (E_{S+/S^*}) was calculated by subtracting the excitation energy (E_{0-0}) from the first oxidation potential ($E_{S+/S}$) of the sensitizer. **DTBC** shows $E_{S+/S}$ of +1.04 V *vs.* NHE, which is low enough below the redox potential of I^-/I_3^- to assure efficient regeneration. However, due to the small optical bandgap, the injection potential (−0.67 V *vs.* NHE) is only slightly above the conduction band edge of TiO_2 (commonly recognized as −0.5 V *vs.* NHE[15]). Such a position, although thermodynamically feasible as well for electron injection, is 0.05 V even more negative than that ever reported for an ethynyl-linked zinc porphyrin dimer,[7b] resulting from the low-lying energy level of free-base porphyrin and the weak electron-donating property of carbazole moiety, which will be discussed below.

Photovoltaic performances and photocurrent action spectra of DSCs incorporated with **DTBC** are shown in Fig. 3. Relevant parameters are listed in Table S1. A detailed cell fabrication procedure is presented in the ESI.† The electrolyte was composed of 0.1 M LiI, 25 mM I_2, 0.6 M 1,2-dimethyl-3-propylimidazolium iodide (DMPII) and 0.2 M 4-*tert*-butylpyridine (TBP) in acetonitrile. As illustrated in Fig. 3b, the IPCE spectrum shows an onset as long as 900 nm and steeply reaches almost a plateau value close to 60% from around 800 nm until 400 nm, demonstrating efficient panchromatic sensitization. This is not only an effective bathochromic extension of the sensitization spectrum compared to monomers where IPCE values at 800 nm were almost zero,[2] but also a significant promotion compared to zinc porphyrin dimers ever reported with an even larger injection driving force.[7b] Such an enhanced spectral responsivity induced by the extended triad structure results in an overall photovoltaic performance of J_{sc} 14.26 mA cm^{-2}, V_{oc} 547 mV, *FF* 0.67 and η 5.21%, which is, to the best of our knowledge, the highest value ever reported for an ethynyl-linked porphyrin array used for DSCs. However, considering the small injection driving force due to the narrow optical bandgap, a TBP-free electrolyte was adopted to lower the TiO_2 conduction bandedge.[16] Consequent promotion in electron injection renders not only a better utilization of longer-wavelength light as indicated by the red-shift of the action spectrum threshold,[16b] but also a drastic elevation of IPCE values up to 80%, yielding a corresponding J_{sc} of 18.16 mA cm^{-2}. Such an excellent panchromatic responsivity constrasts most of the long-wavelength sensitizers even using TBP-free electrolytes despite their superior light absorptivity[5] and is also significantly improved compared to our previously reported zinc porphyrin dimer under the same electrolyte conditions,[7a] mainly attributed to the extended donor–donor–acceptor triad structure. Unfortunately, an enlarged aromatic conjugation system causes severe charge recombination with electrolyte redox species,[17] and combined with positive conduction bandedge shift, the V_{oc} as obtained is around only 400 mV. However, by interfacial engineering like Al_2O_3-coating[18] or electrolyte optimization, it is possible to result in considerable suppression of charge recombination and thus remarkable photovoltaic performance based on the efficient panchromatic photon-to-electron conversion demonstrated above. Such a detailed study will be reported in the next publication.

In order to further understand the structural characteristics of this novel triad molecule, density-functional theory (DFT) calculation was performed at the B3LYP/6-31G level of theory, and orbital distribution of different energy levels were illustrated in Fig. S2 (ESI†). Unsymmetrical spatial distribution was observed for HOMOs and LUMOs as expected. However, it is noteworthy that the location of HOMO orbital is absent on the carbazole moiety. A similar situation was reported for carbazole-fused heteroleptic Ru dyes[9c] which can be ascribed to the lower HOMO energy level than that of metal complex due to its attenuated electron density mentioned above. In our case, despite such an absence, substantial electronic orbital distribution on carbazole is still manifested for HOMO-1 and HOMO-2, which, especially the former, may also be involved and hybridized in the actual optical transition.[19] This contrasts some *N*-fused carbazole-derivative ruthenium dyes[9] and gives rise to a larger transition dipole moment and thus higher oscillator strength, accounting for excellent light-harvesting abilities.[20] Besides, as a well-known hole carrier,[21] there is also an opportunity for the *N*-fused carbazole to accept the positive charge generated after electron injection from the porphyrin framework so as to facilitate dye regeneration. However, due to its lower energy level compared to zinc porphyrin, this may happen only after additional light absorption.[9c]

In conclusion, a *N*-fused carbazole–zinc porphyrin–free-base porphyrin triad featuring an ethynyl-linkage has been designed and synthesized. Based on already reported highly efficient porphyrin monomers, by inserting a free-base

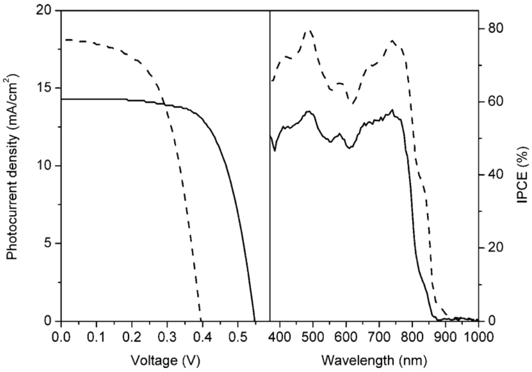

Fig. 3 Photovoltaic properties of **DTBC** in DSCs using electrolyte containing 0.2 M TBP (solid line) and without TBP (dashed line). (a) *I–V* curves of DSCs under AM 1.5 G one sun illumination (100 mW cm^{-2}) with an active area of 0.16 cm^2; (b) corresponding incident photon-to-current conversion efficiency (IPCE) spectra.

porphyrin as an extended acceptor and novel *N*-fused carbazole-substitution, efficient sensitization in the near-IR region was demonstrated and an overall energy conversion efficiency of 5.21% was remarked. The spectral responsivity can be further enhanced by interfacial engineering to 80% with a broad sensitization range above 900 nm, making it a promising candidate for high-efficiency DSCs. Investigation for fundamental understanding of the photophysical and photo-electrochemical properties and efforts for further performance promotion are now in progress.

This work was supported by the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST Program) on the development of organic photo-voltaics toward a low-carbon society, from the Japanese Government.

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