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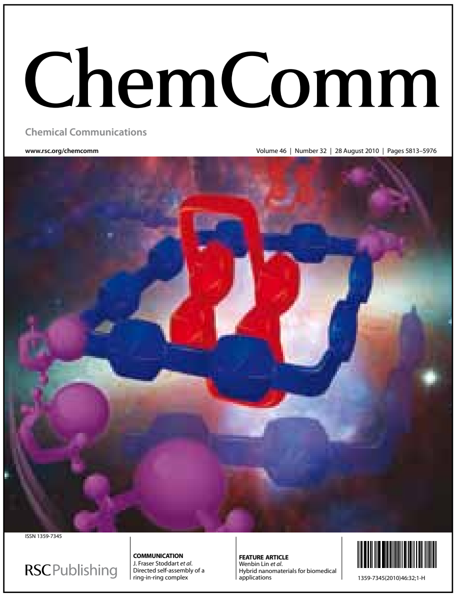

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ARTICLE TYPE

Dye-sensitized solar cells based on multichromophoric supramolecular light-harvesting materials

Dillip K. Panda, Flynt S. Goodson, Shuvasree Ray and Sourav Saha*

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Multichromophoric dye-sensitized solar cells (DSSCs) comprised of a supramolecular zinc-phthalocyanine···peryleneimide (ZnPc···PMI) dyad convert light to electrical energy with much higher power conversion efficiency (PCE = 2.3 %) and incident-photon-to-current-efficiency (IPCE = ca. 40 %) than the devices made of individual dyes.

Owing to their straightforward fabrication techniques, low manufacturing costs, and scopes of introducing various light-harvesting materials, dye-sensitized solar cells (DSSCs)[1] have emerged as an attractive solar energy conversion device. Despite these advantages, most DSSCs developed thus far are comprised of a single chromophore unit—typically Ru(II) complexes, porphyrin, phthalocyanine, or perylenediimide (PDI) derivatives—that can absorb light only at particular wavelengths, leaving the rest of the visible light (400–700 nm) essentially unused for energy conversion.[2] To improve the efficiency of DSSCs and generate photocurrents throughout the Vis-NIR range, various electron donor/acceptor dyads,[3] panchromatic dyes,[4] as well as conjugated polymers[5] with broad absorption cross-sections have been developed. However, the synthesis of extended chromophores and covalently linked electron donor–acceptor systems are often challenging and therefore these materials are far from ideal for practical applications. To circumvent this problem, bulk-heterojunction solar cells[6] have been developed in which composites of electron donors, acceptors, and chromophores are employed as light-harvesting materials. However, irregular morphologies and random orientations of electron donors, acceptors, and chromophores in these devices are not conducive for the all-important vectorial electron transfer process needed for optimal charge-separation and efficient photocurrent generation.[6,7]

Directional and hierarchical noncovalent interactions, such as metal coordination and hydrogen-bonding interactions present a unique opportunity to organize multiple chromophores and electron donors and acceptors in an orderly fashion such that they can undergo vectorial photoinduced electron transfer (PET)[8] to produce long-lived charge-separated states. Although basic photophysical properties and PET phenomena of handful of supramolecular donor/acceptor dyads and triads have been investigated in solutions,[9] photovoltaic devices based on supramolecular light-harvesting complexes are extremely rare.[10] Recently, D'Souza et al.[10] fabricated DSSCs using supramolecular electron donor–acceptor dyads, while we[11] have constructed a multichromophoric supramolecular solar cell using a self-assembled Zn-porphyrin···*N*-pyridyl-peryleneimide (ZnP···PyPMI) dyad as the light-harvesting material. The power conversion efficiencies of these devices, however, are rather low compared to other DSSCs.[12]

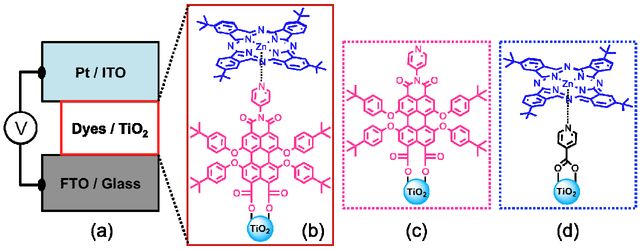

Fig. 1. (a) DSSCs comprised of (b) a supramolecular ZnPc···PyPMI dyad, (c) PyPMI, and (d) ZnPc dyes.

Herein, we demonstrate that by incorporating a stronger electron-donating chromophore, Zn-phthalocyanine (ZnPc), into a supramolecular ZnPc···PyPMI dyad (Fig. 1), the PCE of the DSSCs can be scaled up to 2.3%, which is much greater than the efficiencies of the devices composed of individual ZnPc and PyPMI dyes. The IPCE spectrum shows that the ZnPc··· PyPMI dyad-based DSSC converts light to electricity throughout the 300–650 nm region and the maximum current (IPCE = ca. 40 %) is produced where ZnPc and PyPMI dyes have strong absorption.

First, we verified the formation of a 1:1 ZnPc···PyPMI complex through axial coordination of ZnPc with PyPMI ligand via its pyridyl group (Fig. S1, ESI†). In order to avoid a potential competition between the pyridyl-group and the anhydride terminal of PyPMI, PyPDICy ligand carrying a pyridyl ring on one imide ring and a cyclohexyl group on the other was used for solution NMR studies. In the solid-state devices, PyPMI anchors onto TiO_2 particles through its anhydride end, leaving only the pyridyl-group available for coordinating with a ZnPc molecule. The ^1H NMR titration revealed the formation of a 1:1 ZnPc···PyPDICy complex ($K_a = 5.8 \times 10^4$ M^{-1}, CD_2Cl_2, 298 K) in which the H_a, H_b, and H_c signals of PyPDICy ligand shifted significantly upfield due the shielding effect of ZnPc (Fig. S1, ESI†).[9,13] ESIMS further confirmed (Fig. S2, ESI†) the formation of ZnPc···PyPDICy dyad (m/z = 1946.6).

The UV/Vis spectrum (Fig. S3, ESI†) of the self-assembled ZnPc···PyPDICy dyad in CH_2Cl_2 (350, 440, 545, 585, 610 and

680 nm) is essentially a linear combination of the ZnPc and PyPDICy spectra, indicating that the HOMO–LUMO gaps of the individual dyes remain virtually unchanged in the dyad.

Electrochemical measurements (Fig. S4, Table S1, ESI†) reveal that in ZnPc···PyPDICy dyad, ZnPc becomes a slightly better electron donor, as its E^1_{Ox} decreases from +485 mV (vs. Ag/AgCl in CH_2Cl_2) to +445 mV in the dyad, whereas the reduction of the PyPDICy ligand in the complex (E^1_{Red} = –790 mV vs. Ag/AgCl in CH_2Cl_2) shifts to more negative potential than for the free ligand (–780 mV). These results indicate that the coordination of ZnPc with PyPDICy enhances the electron density of the former, making it a stronger electron donor.

To construct DSSCs, TiO_2-coated (5 µm thick layer of 20 nm particles, Solaronix) FTO substrates were first immersed into a PyPMI solution (0.15 mM in CH_2Cl_2), which allowed the dye to anchor on the surface through its anhydride end.[11,14] After washing away the unbound dyes, the PyPMI-functionalized surface was immersed into a ZnPc solution (2 mM in CH_2Cl_2) to form ZnPc···PyPMI dyads on the surface (Fig. 1). To make a control device comprised of only ZnPc dye, the TiO_2/FTO surface was first functionalized with pyridine-4-carboxylic acid, which was then immersed into a ZnPc solution to capture the dye on the surface. Platinized ITO surface was used as the counter electrode and I^-/I_3^- couple (1.0 M LiI + 0.06 M I_2) in propylene carbonate as a redox mediator to complete the DSSCs.

The surface UV/Vis absorption spectra (Fig. 2a) confirmed anchoring of the dyes onto TiO_2/FTO surfaces and revealed that the surface coverage ($\Gamma_{Dye} = A(\lambda)/10^3\varepsilon(\lambda)$, A = absorbance, ε = molar absorptivity at wavelength λ)[15] of PyPMI and ZnPc dyes in the dyad-coated surface are 2.96 x 10^{-8} and 1.2 x 10^{-8} mol/cm^2, respectively. The uptake of each dye in the dyad-coated surface is essentially the same as that of individual dyes. The greater loading of PyPMI than ZnPc is consistent with the fact that the former is attached to the TiO_2 surface perpendicularly, covering less area per molecule than the latter, which covers more area per molecule by aligning parallel to the surface (Fig. 1). In a typical dyad-coated surface, the PyPMI/ZnPc ratio is 2.5, meaning that only one out of every 2.5 TiO_2-bound PyPMI molecules coordinates with a ZnPc molecule to form a ZnPc···PyPMI dyad.

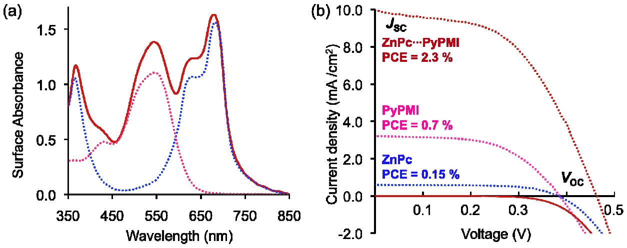

Fig. 2 (a) UV/Vis spectra of TiO_2/FTO surfaces functionalized with ZnPc···PyPMI dyad (red), PyPMI (pink), and ZnPc (blue). (b) *I-V* characteristics of DSSCs composed of ZnPc···PyPMI dyad (red), PyPMI (pink), and ZnPc (blue) under global 1.5 AM illumination conditions (dotted lines) and in the dark (solid lines).

The photocurrents produced by the DSSCs was quantified from current/voltage (*I*/*V*) measurements (Fig. 2b), which revealed open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), fill-factor (FF), and PCE (Table 1). In the absence of light, all three DSSCs made of ZnPc, PyPMI, and ZnPc···PyPMI dyad show similar *I*–*V* curves with J_{SC} = 0 mA/cm^2. However, upon irradiating these devices with a standard AM1.5 light (100 mW/cm^2), the dyad-based device displays much higher J_{SC} (10 mA/cm^2) and V_{OC} (460 mV) than those comprised of ZnPc and PyPMI dyes (Fig. 2b, Table 1). Given that the population of ZnPc···PyPMI dyads on TiO_2/FTO surface (per cm^2) is the same as that of ZnPc in the control device and ca. 2.5 times less than that of PyPMI, the ratio of J_{SC} generated by the same number of ZnPc, PyPMI, and dyad is 1.0 : 2.4 : 18.2. This comparison clearly shows that the ZnPc···PyPMI dyad converts light to electricity much more efficiently than individual dyes. Furthermore, the J_{SC} and PCE of the ZnPc···PyPMI-based DSSC are nearly doubled from those of a Zn-porphyrin···PyPMI-based DSSC (J_{SC} = 5.5 mA/cm^2, PCE = 1.1 %)[11] developed in our laboratory previously. Such a remarkable improvement in efficiency of ZnPc···PyPMI-based device can be attributed to a better electron-donating ability of ZnPc than Zn-porphyrin, which can, in turn, lead to faster electron transfer and better charge-separation in the device.

Table 1 Performance of DSSCs composed of ZnPc···PyPDICy dyad ZnPc, and PyPMI dyes under standard illumination (100 mW/cm^2).

Dye Composition	J_{SC} (mA/cm^2)	V_{OC} (mV)	*FF* (%)	*PCE* (%)
ZnPc···PyPMI	10.0	460	50	2.20 ± 0.12
PyPMI	3.21	390	57	0.72 ± 0.04
ZnPc	0.55	350	63	0.15 ± 0.01

The higher efficiency of DSSCs comprised of the ZnPc···PyPMI dyad than individual dyes can be attributed to two factors: (i) Upon photosensitization the dyad can undergo a two-step vectorial electron transfer to produce long-lived charge-separated states in which electrons (in TiO_2) and holes (in ZnPc) are farther separated (Fig. 3a), whereas the charge recombination could be much faster in the devices made of individual dyes due to the closer proximity of electrons and holes in the charge-separated states and (ii) both ZnPc and PyPMI in the dyad can be sensitized at discrete wavelengths to produce photocurrents throughout the visible range, whereas the single component devices can produce photocurrents at much narrower regions.

To verify that the sensitization of ZnPc and PyPMI dyes is indeed responsible for photocurrent generation and to quantify the internal light-harvesting efficiency of these materials, we measured the IPCE of the devices (Fig 3b). The photocurrents generated in the 300–400 nm region is caused by the excitation of ZnPc (Soret band) as well as TiO_2 particles, whereas the excitation of PyPMI triggers the current production in the 450–625 nm region (Fig. 3b). The IPCE of the dyad-based DSSC (Fig. 3b) reaches ca. 40% at 350 nm, i.e., the Soret-band of ZnPc and at 500–550 nm, where PyPMI has the strongest absorption (Fig. 2a). In contrast, the DSSCs made of either ZnPc or PyPMI produce photocurrents only where the respective dyes absorb light and their IPCEs are much lower compared to that of the ZnPc···PyPMI device. Although the IPCE spectra (Fig. 3b) of all devices match nicely with the surface absorption spectra of the corresponding dyes (Fig. 2a), the excitation of DSSCs at low energy Q-bands of ZnPc (600–750 nm) does not produce any significant current, indicating that it does not initiate PET.

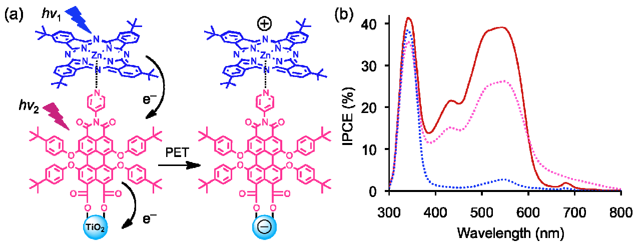

Fig. 3 (a) A plausible PET mechanism in ZnPc···PyPMI dyad leading to electron–hole separation, which is the driving force for photocurrent generation. (b) The IPCE spectra of DSSCs composed of ZnPc···PyPMI dyad (red), PyPMI (pink), and ZnPc (blue).

In conclusion, we have demonstrated that DSSCs can be constructed by incorporating self-assembled multichromophoric donor/acceptor dyads as the light-harvesting materials. On account of broad absorption cross-sections and greater charge separation, ZnPc···PyPMI dyad-based DSSCs display higher V_{OC}, J_{SC}, and PCE and IPCE under standard conditions than those made of individual dyes. To our knowledge, the 2.3% PCE of the supramolecular dyad-based solar cell is the highest among the DSSCs made of self-assembled light-harvesting materials. Furthermore, the self-assembly strategy paves the way for the construction of more efficient supramolecular DSSCs in which multiple electron donors, acceptors, and chromophores can be organized in an orderly fashion to facilitate vectorial PET and maximize the performance of DSSCs.

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Notes and references

Department of Chemistry and Biochemistry and Integrative NanoScience Institute, Florida State University, 95 Chieftan Way, Tallahassee, FL 30306-4390, USA. Tel: +1 850 645 8616; E-mail: saha@chem.fsu.edu

† Electronic Supplementary Information (ESI) available: Synthesis, characterization, K_a calculations from NMR data, ESIMS, UV/Vis spectra, DSSC construction, and photocurrent measurements IV Curve, and IPCE spectra. See DOI: 10.1039/b000000x/

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Table of Contents Graphic:

Dye-sensitized solar cells comprised of supramolecular light-harvesting zinc-phthalocyanine···peryleneimide dyads on TiO_2 films generate photoelectricity throughout the 300–650 nm region with power conversion efficiency reaching up to 2.3 % and incident-photon-to-current-efficieny up to 40 % under one-sun conditions.