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Multichromophoric dye-sensitized solar cells based on supramolecular zinc-porphyrin...perylene-imide dyads[†]

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Multichromophoric dye-sensitized solar cells (DSCs) based on self-assembled zinc-porphyrin \cdots peryleneimide dyads on TiO₂ films display more efficient light-to-electrical energy conversion than DSCs based on individual dyes. Higher efficiency of multichromophoric dyes can be attributed to co-sensitization as well as vectorial electron transfer that lead to better electron-hole separation in the device.

Ease of construction, low manufacturing cost, and improved dyes and electrolytes render dye-sensitized solar cells (DSCs)¹ an attractive device for light-to-electrical energy conversion. Most DSCs developed thus far involve a single chromophore unit—usually a Ru(II) complex, zinc-porphyrin (ZnP), zincphthalocyanine (ZnPc), or perylenediimide (PDI) derivativethat displays intense visible absorption, albeit within narrow wavelength regions, leaving the rest of the solar spectra, especially in the longer wavelength regions, unused for energy conversion.² To overcome this limitation and improve the light-harvesting efficiency, co-sensitization of TiO₂ particles with multiple chromophores that can absorb wide regions of light has been introduced.³ Covalent attachment of two or more chromophores⁴ makes the synthesis of multichromophoric dyes a challenging process. Alternatively, different dyes can be immobilized on TiO2 surfaces via chemisorption and physisorption processes.⁵ However, if the electron donor and acceptor chromophores attached to the TiO₂ surface are randomly distributed, it hampers the possibility of vectorial electron transfer⁶ from the donor-chromophore via acceptor-chromophore to n-type TiO_2 particles, a process that is crucial for optimal charge-separation and photocurrent generation. Although metal-ligand coordination has been employed to anchor ZnP onto TiO₂ surfaces⁷ as well as to assemble supramolecular dyads and triads based on ZnPc and dipyridyl-PDI (DPPDI) in solutions,⁸ this strategy has been rarely exploited to construct multichromophoric DSCs.





Scheme 1 Schematic representation of chemisorption of PyPMI-2 on a TiO_2 -coated FTO electrode followed by self-assembly of a ZnP-1…PyPMI-2 dyad *via* metal–ligand coordination. The dyad-functionalized TiO₂-FTO surface is used as a working electrode in the DSC.

In this communication, we demonstrate that coordination of **ZnP-1** with *N*-pyridyl-peryleneimide-2 (**PyPMI-2**) leads to the formation of a supramolecular **ZnP-1**···**PyPMI-2** dyad on the TiO₂ surface (Scheme 1). DSCs composed of this dyad on a TiO₂-coated F:SnO₂ (FTO) photoanode, platinised indiumtin-oxide (Pt/ITO) cathode, and I^-/I_3^- redox mediator generate a much higher open-circuit voltage (V_{OC}), short-circuit current (J_{SC}), and energy conversion efficiency ($\eta = 1.1 \pm 0.06\%$) under 1.5 air-mass (AM) conditions than DSCs made of individual dyes.

Because of complementary electronic and absorption properties ZnP, PMI, and PDI derivatives were chosen as chromophore units for multichromophoric DSCs. To prevent self-aggregation and improve the solubility of these chromophores in nonpolar solvents, 4-*tert*-butylphenyl groups were introduced at all four *meso*-positions of ZnP and 4-*tert*butylphenoxy groups were attached to all four bay-positions of PMI and PDI derivatives (Scheme S1, ESI†). The *N*-pyridyl group of **PyPMI-2** is designed to serve as an axial ligand of **ZnP-1** to form the supramolecular **ZnP-1**...**PyPMI-2** dyad. The remaining anhydride unit of **PyPMI-2** was exploited for its chemisorption on the TiO₂ surface.⁹

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Fig. 1 ¹H NMR titration spectra of PyPDICy-3 with ZnP-1 (CD_2Cl_2) .

To determine the binding affinity (K_a) from ¹H NMR titration experiments (Fig. 1), PyPMI-2 was replaced with PyPDICy-3 to avoid competition between the pyridine ligand and the anhydride terminal. The ¹H NMR spectrum of free ZnP-1 (CD₂Cl₂, 298 K) displays a singlet at 8.98 ppm corresponding to H_z protons on the pyrrole rings and two doublets at 8.14 and 7.79 ppm that represent H_v and H_x on 4-tertbutylphenyl rings, respectively. The ¹H NMR spectrum of free PyPDICy-3 (CD₂Cl₂, 298 K) displays two doublets at 8.73 and 7.25 ppm that represent H_a and H_b of the N-pyridyl ring and two singlets at 8.17 and 8.11 ppm that correspond to H_c and H_d on the PDI core, respectively. Protons of 4-tert-butylphenoxy groups $(H_e, H_f, H_g, and H_h)$ appear as doublets at the 7.25–7.29 and 6.83–6.85 ppm region. ¹H NMR titration (Fig. 1) of PyPDICy-3 with ZnP-1 (CD₂Cl₂, 298 K) caused upfield shifts of the **ZnP-1**'s H_z signal to 8.91 ppm ($\Delta \delta$ = -0.07 ppm) and of the H_x signal to 8.12 ppm ($\Delta \delta$ = -0.02 ppm) at a 1 : 1 ZnP-1/PyPDICy-3 ratio (2 mM each), indicating a complex formation. Dramatic upfield shifts of N-pyridyl and PDI core protons due to the shielding effects of perpendicular ZnP-1 ring-current confirm its axial coordination with ZnP-1. For instance, PyPDICy-3's H_b becomes very broad and shifts to 6.32 ppm ($\Delta \delta = -0.93$ ppm), H_c to 7.95 ppm ($\Delta \delta = -0.22$ ppm), and H_d to 8.06 ppm ($\Delta \delta =$ -0.06 ppm). The H_a signal disappears, which is characteristic of axial coordination of pyridyl ligands with ZnP.^{8,10} Protons on 4-tert-butylphenoxy groups of PyPDICy-3 also shift slightly upfield. Addition of >1 equiv. of ZnP-1 to PyPDICy-3 did not change the NMR spectrum any further, indicating a fast equilibrium of the complexation process at room temperature. The K_a of a 1 : 1 **ZnP-1**···**PyPDICy-3** complex $(4.5 \times 10^5 \text{ M}^{-1})$ CD₂Cl₂, 298 K) was derived from NMR chemical shifts of the diagnostic H_b signal using the nonlinear least-squares fit method (see ESI[†]).¹¹ This K_a value is consistent with that measured for a similar ZnPc...imidazole coordination complex.¹⁰ ESIMS further confirms (Fig. S1, ESI⁺) the ZnP-1... PyPDICy3 dyad

Table 1 E_{Ox} and E_{Red} (mV) of **ZnP-1**, **PyPDICy-3**, and **ZnP-1**...**PyPDICy-2** dyad (vs. Ag/AgCl in CH₂Cl₂)

Entry	E^{1}_{Ox}	E^2_{Ox}	E^{1}_{Red}	$E^2_{\rm Red}$
ZnP-1 PyPDICy-3 ZnP-1···PyPDICy-3	+830 +1340 +780	+1140 +1220	$-1000 \\ -780 \\ -820$	-1670 -950 -970

formation (m/z = 2044.7) from **ZnP-1** (901.3) and **PyPDICy3** (1142.4).

The UV/Vis spectrum of the **ZnP-1**···**PyPDICy-3** dyad in CH₂Cl₂ displays (Fig. S2, ESI†) absorption peaks at 420 (λ_{max}), 450, 545, and 575 nm, which is essentially a linear combination of **ZnP-1** (420 (λ_{max}), 550, and 570 nm) and **PyPDICy-3** (450, 545, and 575 (λ_{max}) nm) spectra, indicating that such a complex formation does not change the HOMO–LUMO gap of individual dyes.

Cyclic voltammetry measurements (Table 1 and Fig. S3, ESI[†]) demonstrate that coordination of **ZnP-1** with **PyPDICy-3** renders the former a better electron donor, as E^{1}_{Ox} decreases from + 830 mV (*vs.* Ag/AgCl in CH₂Cl₂) for free **ZnP-1** to + 780 mV in the dyad, whereas the reduction of **PyPDICy-3** in the complex ($E^{1}_{Red} = -820$ mV *vs.* Ag/AgCl in CH₂Cl₂) requires a slightly more negative potential than for the free ligand (-780 mV). These changes in redox properties indicate that coordination of **ZnP-1** with pyridine lone-pair electrons of **PyPDICy-3** enhances the electron density of the former, while diminishing the electron density of the latter.

For the construction of working electrodes, **PyPMI-2** was anchored through its anhydride end by immersing a TiO₂-coated (a 5 µm thick layer of 20 nm particles, Solaronix) FTO substrate into a **PyPMI-2** solution (0.15 mM in CH₂Cl₂).⁹ After washing off the unbound dyes, the **PyPMI-2**-functionalized TiO₂ surface was immersed into **ZnP-1** solution (2 mM in CH₂Cl₂) to form the **ZnP-1**...**PyPMI** dyad on the surface (Scheme 1). To make a control device, only **ZnP-1** was attached to a pyridine-4carboxylic acid functionalized TiO₂/FTO surface *via* similar metal–ligand coordination. To complete the construction of DSCs, the Pt/ITO surface was used as a counter electrode and the I^-/I_3^- couple (1.0 M LiI + 0.06 M I₂ in propylene carbonate (PC) or MeCN) as a redox mediator (Scheme 1).

Immobilization of ZnP-1, PyPMI-2, and the ZnP-1...PyPMI dyad on TiO₂-coated FTO surfaces was confirmed by UV/Vis spectroscopy (Fig. 2a). The dyad-functionalized TiO₂/FTO surface displays both ZnP-1 and PyPMI-2 peaks at 420 and 550 nm regions, respectively, whereas individual ZnP-1 and PyPMI-2 functionalized surfaces display their characteristic absorption peaks. In the absence of PyPMI-2 or pyridine-4-carboxylic acid on the TiO₂ surface, ZnP-1 does not bind to the surface and can be easily washed away.

Finally, light-to-electrical energy conversion by these DSCs was demonstrated by current–voltage (*I–V*) measurements (Fig. 2b). To understand the effects of multichromophoric dyes on light-harvesting properties of DSCs, *i.e.*, V_{OC} , J_{SC} , fill-factor (FF), and η of the **ZnP-1**...**PyPMI-2** dyad-based device were compared to those of DSCs made of individual **ZnP-1** and **PyPMI-2** dyes (Table 2). All three devices show similar *I–V* curves in the dark and under the same visible light source (100 mW cm⁻²). **ZnP-1**...**PyPMI-2** dyad-based DSC displays



Fig. 2 (a) UV/Vis spectra of TiO₂–FTO surfaces functionalized with the **ZnP-1**...**PyPMI-2** dyad (green), **PyPMI-2** (red), and **ZnP-1** (violet). (b) I-V characteristics of DSCs composed of the **ZnP-1**...**PyPMI-2** dyad (green), **PyPMI-2** (red), and **ZnP-1** (violet) showing photocurrent generation (J_{SC} and V_{OC}) under 1.5 AM conditions (dotted lines) and negligible dark currents (solid lines).

Table 2 Performance of DSCs based on the ZnP-1...PyPDICy-2 dyad ZnP-1, and PyPMI-2 dyes under standard illumination (100 mW cm^{-2})

Dye composition	$J_{\rm SC}/{\rm mA~cm^{-2}}$	$V_{\rm OC}/{\rm mV}$	FF (%)	η (%)
ZnP-1···PyPMI-2 PyPMI-2	5.51 3.21	410 390	49 57	1.10 ± 0.06 0.72 ± 0.04
ZnP-I	0.4/	340	60	0.09 ± 0.02

much higher J_{SC} (5.51 mA cm⁻²) and V_{OC} (410 mV) than those displayed by ZnP-1 and PyPMI-2 based DSCs (Fig. 2b and Table 2). Consequently, the energy conversion efficiency of the dichromophoric ZnP-1... PvPMI-2 dvad-based device $(\eta = 1.10 \pm 0.06\%)$ is 12-times greater than that of the **ZnP-1**based DSC and 1.5-times larger than that of the PyPMI-2based device. The greater efficiency of dichromophoric DSC can be attributed to the better light-harvesting ability of the ZnP-1...PyPMI-2 dyad over broader wavelength regions. Much greater V_{OC} , J_{SC} , and η were observed for all DSCs with a PC-based I^-/I_3^- redox mediator (Fig. 2 and Table 2) than with a MeCN based electrolyte (Fig. S4 and Table S1, ESI[†]). Greater efficiencies of the PC-based DSCs than that of the MeCN-based devices can be attributed to the higher dielectric constant of PC (64) than of MeCN (37.5), which facilitates better charge separation in the former devices.¹²

It is conceivable that in the ZnP-1...PyPMI-2 dyad-based DSC, excitation of either ZnP-1 or PyPMI-2 to the singlet excited states could trigger photoinduced electron transfer (PET), which would lead to electron and hole movement in the opposite directions.^{7b} For instance, PET from either the ¹*ZnP-1 excited state through PyPMI-2 to TiO₂ or from ZnP-1 via the ¹*PyPMI-2 excited state to TiO₂ would generate ZnP-1^{•+} radical cations and inject electrons to n-type semiconducting TiO₂ via PyPMI-2^{•-} radical anions. Characterization of these photophysical processes will be conducted through transient absorption spectroscopy measurements. Nevertheless, the greater efficiency of the dyad-based DSC over the individual dyes suggests that both pathways perhaps contribute to light-toelectrical energy conversion in the dyad system, as these chromophores absorb light in entirely different regions (Fig. 2b). In addition, vectorial electron transfer in the ZnP-1... PyPMI-2-TiO₂ device leads to better charge separation than one-step PET from ¹*ZnP-1 or ¹*PyPMI-2 to the TiO₂ surface in monochromophoric devices. Lower V_{OC} and J_{SC} of the ZnP-1

based DSC than the **PyPMI-2** based device could be attributed to the insulating nature of pyridine-4-carboxylic acid that binds **ZnP-1** on TiO_2 in comparison with direct chemisorption of **PyPMI-2** on the electrode (*via* Ti–O bond formation) that facilitates electron injection.

In conclusion, we have self-assembled ZnP, PMI, and PDI dyes *via* metal–ligand coordination and immobilized them on TiO₂ surfaces to construct multichromophoric DSCs. Broad light-absorbing **ZnP-1**...**PyPMI-2** dyad-based DSCs display higher V_{OC} , J_{SC} , and efficiency ($\eta = 1.1 \pm 0.06\%$) under 1.5 AM conditions than those made of individual dyes. To improve the efficiency of DSCs, we have undertaken a supramolecular assembly of multichromophoric DSCs using red and NIR absorbing dyes.

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