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## [2.2]Paracyclophane as a bridging unit in the design of organic dyes for sensitized solar cells<sup>†</sup>

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Organic dyes consisting of a [2.2]paracyclophane unit along the main chromophore are examined for their application in sensitized solar cells. These materials exhibit considerably high values of open-circuit voltage ( $V_{\rm oc}$ ) ranging 0.69–0.72 V, and an overall efficiency up to 3.8%.

Conjugated  $\pi$ -chromophores in organic structures are regarded as an indispensable part in performing many functional properties, especially in the applications of opto-electronic devices. The electrons can be delocalized over a long distance through the overlapping of  $\pi$ -orbitals. With proper doping, organic materials can become significantly conductive. However, it is also well-known that the migration of electrons in an organic medium may proceed effectively through a not fully conjugated system.<sup>1</sup> For example, the electrons may tunnel through  $\sigma$ -bonds or migrate across non-bonded connections at high rate. A typical case can be observed in the development of organic field-effect transistors, where an intermolecular  $\pi$ - $\pi$  interaction across stacked aromatic rings has played the key factor. Cyclophanes are a special group of aromatic compounds which consist of two or more phenyl units locked face-to-face by aliphatic chains.<sup>2</sup> Electrons and holes can move across the gap of parallel-aligned aromatic rings to display a detectable flow of current.<sup>3</sup> In our design of dye-sensitized solar cells (DSSCs), the higher energy barrier for charge recombination across a cyclophane bridge may be beneficial to the promotion of quantum efficiency. The concept of inserting a non-conjugated bridge in organic dyes has never been investigated before. In this report the effect of using a [2.2]paracyclophane (PCP) in the structure of DSSC materials is examined for the first time.<sup>4</sup>

In the choice of dye structures, our previous experience indicated that compounds consisting of an arylamine electron donor (D) and a cyanoacrylate electron acceptor (A), both linked by a triarylene bridge (B), performed the best in DSSCs with a remarkable quantum efficiency around 7%.<sup>5</sup> In the bridging units of these compounds the adjacent phenylene rings are not fully co-planar, but twisted ca. 35° with respect to each other. Such a slight distortion does not interrupt much the  $\pi$ -conjugation between the D and A, as evidenced by their absorption spectra. The  $\pi$ -conjugation along the bridge does contribute significantly to the values of short-circuit current  $(J_{\rm sc})$  in DSSC. In order to increase the value of open-current voltage  $(V_{oc})$ , which is another key factor determining the efficiency, it is necessary to reduce the rate of charge recombination after absorption of light. In the case of triphenylene, the dihedral angles between adjacent phenyl rings twist to a larger angle in the charge-separated state. The highly twisted geometry along B therefore reduces the rate of charge recombination between D and A, and extends the lifetime of the charge-separated state. The flexible rotation of the phenyl ring along the bridge is believed to have played a critical role in promoting the quantum efficiency of DSSC.

In this report four compounds containing a PCP unit at the centre of their structures are prepared, *i.e.*, **CP1–CP4** (Fig. 1).<sup>6</sup> A triarylamine donor group and a cyanoacrylate acceptor group are separated by the PCP and located on different sides. The synthetic procedures of **CP1–CP4** are depicted in Scheme 1 (ESI† S1). The *pseudo-para* dibromide 1 was prepared first from PCP through a bromination reaction.<sup>7</sup> The triarylamine moieties were added onto 1 by a Stille coupling reaction catalyzed by PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>.<sup>8</sup> The experimental details for the preparation of all the derivatives of **2** are given in the ESI.† Compound **2** was formylated with DMF to yield **3**, in which the carbaldehyde group was condensed with a cyanoacetic acid by a Knoevenagel reaction in the presence of ammonium acetate leading to **CP2** in 72% yield.<sup>9</sup> The conversion of **2** to **4** 



Fig. 1 Structures of compounds CP1-CP4.

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Experimental data (**CP1–CP4**), the <sup>1</sup>H and <sup>13</sup>C NMR spectra, theoretical calculation, CV spectra, EIS spectra, and electron diffuse lifetime spectra. See DOI: 10.1039/c1cc16248a



Scheme 1 Reagents and conditions of the synthesis: (i) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, N-(4-(tributylstannyl)phenyl)-N-phenylaniline, N-(4-(5-tributylstannylthiophen-2-yl)phenyl)-N-phenylaniline, or N-(4-(5-tributylstannylthiophen-2-yl)phenyl)-N-(4-hexyloxyphenyl)-4-hexyloxyaniline, DMF, 90 °C. (ii) *n*-BuLi, DMF, THF, -78 °C. (iii) (a) PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannane, DMF, 90 °C; (b) AcOH : THF : H<sub>2</sub>O (4 : 2 : 1), 60 °C. (iv) Cyanoacetic acid, NH<sub>4</sub>OAc, AcOH, 90-100 °C.

was accomplished by another Stille coupling reaction with (5-(1,3-dioxolan-2-yl)thiophen-2-yl)tributylstannane, followed by hydrolysis. The final step for the production of **CP1**, **CP3** and **CP4** was another Knoevenagel condensation to fuse a cyanoacrylic acid moiety as the electron acceptor. All structures were confirmed by their spectroscopic data.

The UV-Vis absorption spectra of organic dyes in THF solution are depicted in Fig. 2 and the parameters are listed in Table 1. The compounds with a thiophenyl group next to the cyanoacrylate acceptor (A), *i.e.*, **CP1**, **CP3** and **CP4**, display longer absorption wavelengths than that without, *i.e.*, **CP2**. The spectra of **CP2**, **CP3** and **CP4**, in which a thiophenyl group is linked directly to the triarylamine donor (D), exhibit two major absorption bands at 295–305 nm and 364–383 nm. The two shorter wavelength bands were assigned to localized  $\pi$ – $\pi$ \* transitions, and the long wavelength one to a charge-transfer (CT) transition. The intensity of CT transitions is higher than that of the



Fig. 2 Absorption spectra of organic dyes in THF.

Table 1 Photochemical and electrochemical parameters of the dyes

 $\pi$ - $\pi^*$  transitions. The presence of alkoxy substituents in **CP4** induces a slight red-shift with respect to **CP3**. The presence of the PCP in the main chromophore does impose a significant effect on the CT transition.

The oxidation potentials  $(E_{ox})$ , corresponding to the highest occupied molecular orbital (HOMO) level of the dyes, were measured by cyclic voltammetry. The ionization energy obtained in THF solutions decreased gradually in the order of CP1 (0.88 V) > CP2 (0.82 V) > CP3 (0.81 V) > CP4 (0.57 V) (Table 1). A comparison between CP1 and CP2 is particularly noteworthy, as it reveals an effect by shifting the position of PCP. The low ionization energy of CP4 is caused mainly by the resonance effect of alkoxy substituents. Suitable HOMO and LUMO (lowest unoccupied molecular orbital) levels are required to match the conduction band (-0.5 V vs. NHE) of the TiO<sub>2</sub> electrode and the redox potential (0.4 V vs. NHE) of the iodine/iodide electrolyte. The LUMO levels of the dyes were estimated by the values of  $E_{ox}$  and the 0–0 band gaps at the onset of absorption spectra. The energy levels of all dyes match well with the requirement for the injection of electrons to the conductive band of TiO<sub>2</sub>.

The electronic nature of the dyes was examined by theoretical models. Full geometrical optimizations were performed by using the M062X/6-31G(d) hybrid functional implanted in Gaussian09.10 The triarylamine donor and the cyanoacrylate acceptor are attached to PCP in a pseudo-para orientation. The dihedral angles between the aryl groups and PCP are quite large, *i.e.*,  $65^{\circ}$ -75°. The charge distribution in the frontier molecular orbitals shows that the electron distributions in the HOMOs and LUMOs do not mix with each other across the PCP moiety (ESI<sup> $\dagger$ </sup> Fig. S14), indicating that the  $\pi$ -conjugation is heavily interrupted. Upon exposure to light, electrons migrate from D to A forming a charge separated state, as evidenced by the high intensity of the CT absorption band. However, the lower degree of  $\pi$ -conjugation may slow down the rate of charge recombination, and maintains a longer lifetime for the charge separated state.11

The parameters of DSSCs fabricated with these dyes, *i.e.*, short circuit current  $(J_{sc})$ , open-circuit photovoltage  $(V_{oc})$ , fill factor (ff), and solar-to-electrical photocurrent density  $(\eta)$  measured under AM 1.5 solar light (100 mW cm<sup>-2</sup>), are summarized in Table 1, and the photocurrent–voltage (J-V) and incident photon to current conversion efficiency (IPCE) plots are shown in Fig. 3 and 4. Among all dyes, the devices made with **CP3** performed the best. The order of  $J_{sc}$  values **CP3** > **CP4** > **CP1** is roughly proportional to

Dye	$\lambda_{abs}{}^a \text{ (nm)}/(\epsilon \text{ (M}^{-1} \text{ cm}^{-1}))$	$E_{\text{ox}}^{b}$ (V) (vs. NHE)	$E_{0-0}$ (eV)	$E_{red}^{c}$ (V) (vs. NHE)	$J_{\rm sc}~({\rm mA~cm^{-2}})$	$V_{\rm oc}\left({ m V} ight)$	ff	$\eta^d(\%)$	$\tau^e$ (ms)
CP1	373(26 600)	0.88	2.85	-1.97	6.68	0.71	0.71	3.11	20.4
CP2	364(38700)	0.82	2.97	-2.15	4.37	0.70	0.70	2.13	19.1
CP3	377(41700)	0.81	2.83	-2.02	7.88	0.69	0.70	3.83	17.9
CP4	383(39000)	0.57	2.81	-2.24	7.12	0.715	0.65	3.32	21.5
N719		_		_	15.0	0.755	0.59	6.68	22.6

 $\varepsilon$ : absorption coefficient;  $E_{ox}$ : oxidation potential;  $E_{0-0}$ : 0–0 transition energy measured at the onset of absorption spectra;  $J_{sc}$ : shortcircuit photocurrent density;  $V_{oc}$ : open-circuit photovoltage; ff: fill factor;  $\eta$ : total power conversion efficiency.  $\tau$ : electron diffuse lifetime of DSSCs. <sup>*a*</sup> Absorption in THF. <sup>*b*</sup> Oxidation potential in THF (10<sup>-3</sup> M) containing 0.1 M (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NPF<sub>6</sub> with a scan rate of 50 mV s<sup>-1</sup> (*vs.* NHE). <sup>*c*</sup>  $E_{red}$  calculated by  $E_{ox} - E_{0-0}$ . <sup>*d*</sup> Performance of DSSC measured in a 0.25 cm<sup>2</sup> working area on a FTO (8  $\Omega$ /square) substrate. <sup>*e*</sup> Lifetime ( $\tau$ ) of injected electrons measured by transient photovoltage at open circuit in acetonitrile using LiI (0.5 M) as electrolyte.



**Fig. 3** J-V curves of the DSSC devices made with the dyes. The plots were measured under the light intensity of 1.0 sun.



Fig. 4 IPCE curves of organic dyes.

their relative magnitude of molar absorptivity. The low  $J_{sc}$  value (4.37 mA cm<sup>-2</sup>) of **CP2** was mainly ascribed to its narrow absorption band width (Fig. 2). The trend of relative quantum efficiency follows the same order of  $J_{sc}$  value. However, the values of open-circuit photovoltage ( $V_{oc}$ ) are kept nearly the same for all four dyes.

The purpose of introducing the PCP unit, as mentioned earlier, is to reduce the rate of charge recombination. The effect is supported by the high values of  $V_{oc}$ , *i.e.*, 0.69–0.715 V. The addition of long alkyl chains to the compounds has also been shown to be capable of reducing the dark current by decreasing the rate of charge recombination, thus increasing the  $V_{\rm oc}$  of the solar cells. This effect is revealed by the slightly higher  $V_{\rm oc}$  of **CP4** than that of **CP3**. The dark current of devices was measured in acetonitrile with a LiI electrolyte at open circuit by using a pulsed Nd:YAG laser (ESI<sup>†</sup> Fig. S19). The order of relative values of dark current, as shown in Fig. 3, was found to be consistent with the magnitude of  $V_{oc}$ , *i.e.*, CP4 > CP1 > CP2 > CP3. The data collected from impedance spectra (S18<sup>†</sup>) and the measurements on the lifetime of transient photovoltage decay (S19<sup>†</sup>) also comply well with this trend.<sup>12</sup> The best performance of DSSC device was found in the one made with **CP3**, which exhibited a  $J_{sc}$  value of 7.88 mA cm<sup>-2</sup>,  $V_{oc}$  value of 0.69 V, and ff value of 0.70. The overall conversion efficiency  $(\eta)$  was estimated to be 3.83%. Although the performance is not exceptionally high compared to the known ruthenium complex N719 (Table 1), it is the first organic material which contains a non-conjugated spacer in the central bridge of the molecules. The relatively low quantum efficiency may be improved substantially by extending the absorption wavelength deeper into the visible region.

In summary, we have successfully demonstrated that inserting a [2.2]paracyclophane moiety in the main chain of organic dyes will not jeopardize the light harvesting property of the materials. The non-conjugated chromophore may have an advantage of reducing the rate of charge recombination, and lead to a high value of  $V_{\rm oc}$ . In the present study the drawback of our materials is mainly due to their narrow bandwidth in the absorption spectra, which yielded low values of  $J_{\rm sc}$  with respect to N719. The concept of using a non-conjugated spacer group may broaden our vision in the future design of organic dyes.

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