### Accepted Manuscript

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Accepted Date:

PII:	S0040-4039(14)01187-3					
DOI:	http://dx.doi.org/10.1016/j.tetlet.2014.07.034					
Reference:	TETL 44877					
To appear in:	Tetrahedron Letters					
Received Date:	27 May 2014					
Revised Date:	4 July 2014					

9 July 2014



Please cite this article as: Huang, C.H., Chang, Y.J., Dyes for Sensitized Solar Cells by Using [2.2]Paracyclophane as a Bridging Unit, *Tetrahedron Letters* (2014), doi: http://dx.doi.org/10.1016/j.tetlet.2014.07.034

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Tetrahedron Letters

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### Dyes for Sensitized Solar Cells by Using [2.2]Paracyclophane as a Bridging Unit

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### ARTICLE INFO

#### ABSTRACT

Article history: Received Received in revised form Accepted Available online

Keywords: Dye-sensitized solar cells (DSSCs) [2.2]Paracyclophane Deoxycholic acid (DCA) Nonconjugated spacer Organic dyes that consist of a [2.2]paracyclophane moiety between a triphenylamine donor group and a cyanoacrylic acid acceptor group have exhibited considerably high values of opencircuit voltage ( $V_{oc}$ ) in the range of 0.69–0.74 V. In an experiment that involved using an ion liquid electrolyte (E2 electrolyte), the values of  $V_{oc}$  were increased to 0.03–0.04 V because of a decrease in the concentration of LiI. A typical device demonstrated a maximal incident photon-to-current conversion efficiency (IPCE) of 60% in the region of 350–475 nm, a short-circuit photocurrent density ( $J_{sc}$ ) of 8.80 mA·cm<sup>2</sup>, an open-circuit photovoltage ( $V_{oc}$ ) of 0.74 V, and a fill factor (FF) of 0.65, corresponding to an overall conversion efficiency of 4.24% of **CPG2b**. The photophysical properties were analyzed using a time-dependent density functional theory (TDDFT) model with the M062X functional.

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Recently, several renewable energy sources have been developed because of the increased consumption of fossil fuels and consequent environmental pollution. Solar energy is widely recognized as a solution to the global energy crisis. Since their discovery by O'Regan and Grätzel in 1991,<sup>1</sup> dye-sensitized solar cells (DSSCs) are expected to demonstrate promising potential as an alternative renewable energy source. DSSCs offer the benefits of low-cost processes and attractive features such as flexibility and colorful transparency. Although ruthenium-based and zincporphyrin-based sensitizers have achieved high power conversion efficiencies of over 12%, their use has revealed the problems of limited resources and elaborate purification.<sup>2</sup> Metal-free organic dyes have the advantages of environmental friendliness, high structural flexibility, low cost, generally high molar extinction, and easy preparation and purification. Thus far, metal-free organic dyes are abundant and demonstrate an energy-toelectricity conversion efficiency in the range of 7%-10%.

However, conjugated  $\pi$ -chromophores in organic structures are regarded as indispensable in performing many functional properties of optoelectronic devices, especially in DSSC applications. In a previous study, we demonstrated that, as a bridge unit, the nonconjugated chromophore of [2.2]paracyclophane (PCP) reduced the rate of charge recombination and led to a high value of  $V_{oc}$ . This indicated that a high energy barrier for charge recombination across a [2.2]PCP bridge may improve the value of  $V_{oc}$ .

The [2.2]PCP moiety is well known because the migration of electrons in an organic medium may proceed effectively through a nonfully conjugated system.<sup>4</sup> Electrons can travel across the gap of parallel-aligned aromatic rings, thereby exhibiting a detectable flow of current. However, the relatively low value of

photocurrent can became a drawback because of the breakdown of the  $\pi$ -conjugation.

In designing organic dyes for DSSCs, we expanded the  $\pi$ chromophore of a [2.2]PCP bridge and introduced a long alkoxy chain to improve not only the value of short-circuit current  $(J_{sc})$ but also the value of open-current voltage  $(V_{oc})$ . In our previous investigation, we discovered that using nonconjugated  $\pi$ chromophores for DSSCs is possible by incorporating a unit of paracyclophane to interrupt the  $\pi$ -system.<sup>5</sup> The substituents of alkoxy chains could reduce not only intramolecule aggregation but also the dark current by decreasing the rate of charge recombination. The  $V_{oc}$  value of these materials can be expected to achieve a high standard because of a slow rate of charge recombination. To enhance the efficiency of electron injection, we attempted to increase coplanarity of the bridge unit of [2.2]paracyclophane with an adjacent moiety by connecting an ethenyl group with the donor and acceptor.



Figure 1. The structure of CP3, CPG2a and CPG2b.

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Two novel organic dyes of the **CPG2**-series and its synthetic procedure in this study are shown in Scheme 1. A Heck reaction of pseudo-*para*-4,12-Diethenyl[2.2]paracyclophane  $1^5$  with 4-Bromobenzaldehyde or 4-Bromo-2,5-dihexyloxy-benzaldehyde yielded a dialdehyde compound of **2** in the range of 41%-72%.<sup>6</sup> The conjugating length was elongated again by inserting a triphenylamine (TPA) electron-donating unit through a Wittig reaction TPA-phosphonium salt with **2** in DMF. This yielded a mono-aldehyde compound of **3** in the range of 56%-66%.<sup>7</sup> Knoevenagel condensation was used to complete the two final products by building up the cyanoacrylic acid acceptor unit, thereby providing a favorable yield at **CPG2a** and **CPG2b** for 73% and 70%, respectively. Two final products were crystallized into deep red solids and confirmed according to their spectra (electrochemical impedance spectrum; EIS).

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Scheme 1. Synthesis of CPG2a and CPG2b. (i):  $K_2CO_3$ ,  $NBu_4Br$ ,  $Pd(OAc)_2$ , and  $NEt_3$ . (ii):  $K_2CO_3$ , 18-crown-6, and DMF. (iii):  $NH_4OAc$ ,  $CNCH_2COOH$ , and AcOH.

The absorption spectra of dyes in a diluted THF solution (3 ×  $10^{-5}$  M) are shown in Figure 2(a), exhibiting three major absorption regions appearing at 242–245 nm, 306–308 nm, and 400–419 nm. The first two regions were composed of localized aromatic  $\pi$ - $\pi$ \* transitions, and the final one was assigned to a charge-transfer (CT) transition. The CT band of **CPG2b** is 19 nm and showed more of a redshift because of a higher efficiency of the inductive effect with the hexyloxy substituents. The influence of the electron-donating substituent was shown by a comparison between **CPG2a** and **CPG2b** using theoretical models; the latter exhibited stronger oscillator strengths calculated by TDDFT, that is, 1.92 and 2.80 (Table S1). These values are consistent with their CT transition region; both **CPG2a** and **CPG2b** showed high molar extinction coefficient; that is,  $\varepsilon = 6.54 \times 10^4$  M<sup>-1</sup> cm<sup>-1</sup> and 7.02 × 10<sup>4</sup> M<sup>-1</sup> cm<sup>-1</sup>, respectively (Table 1).

The oxidation potentials  $(E_{ox})$  were measured using cyclic voltammetry (CV) in THF, and the results are listed in Table 1. The HOMO levels corresponded to the first oxidation potentials  $(E_{ox})$  of CPG2a and CPG2b. The LUMO levels were estimated according to the values of  $E_{or}$  and the zero-zero absorption wavelength, whereas the latter was obtained at the onset of absorption spectrum. The HOMO-LUMO energy gap of CPG2b (2.53) was narrower than that of CPG2a (2.72). The estimated LUMO levels of both dyes are sufficiently higher than the conduction band level of  $TiO_2$  (ca. -0.5 V vs. NHE), whereas their HOMO levels are sufficiently lower than that of the electrolyte ion pair  $I^-/I_3^-$  (ca. 0.4 V vs. NHE).<sup>8,9</sup> This ensures an exothermic flow of charges through the photoelectronic conversion process. The HOMO-LUMO energy levels of dyes warrant an efficient charge injection into the photoanode and charge regeneration from the Pt cathode.



Figure 2. (a) Absorption spectra of CPG2a and CPG2b in THF. (b) Oxidative voltammograms of CPG2-series dyes. (c) Computed optimum structure and dihedral angles of the CPG2-series dyes. (d) Computed HOMO and LUMO orbitals of CPG2-series dyes.

The electronic nature of the dyes was examined using theoretical models. Full geometrical optimizations were performed using the M062X/6-31G(d) hybrid functional implanted in Gaussian09.10 The amine donor and the cyanoacrylate acceptor are attached to [2.2]PCP with the vinyl group in a pseudopara orientation. The dihedral angles between the linker and PCP are considerably wide at 101°-115°. The charge distribution in the frontier molecular orbitals shows that the electron distributions in the HOMOs and LUMOs are well separated by the PCP moiety (ESI Fig. S8), indicating that the  $\pi$ conjugation is severely interrupted. The electrons migrate from the donor moiety to the anchoring group 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 the rate of charge recombination and maintain a longer lifetime for the charge-separated state.<sup>1</sup>

The parameters of the DSSC devices fabricated using the two dyes were short-circuit current  $(J_{sc})$ , open-circuit photovoltage  $(V_{\alpha c})$ , fill factor (FF), and solar-to-electrical photocurrent density ( $\eta$ ), measured under AM 1.5 solar light (100 mW·cm<sup>-2</sup>). These parameters are summarized in Table 1, and the photocurrentvoltage (J-V) plots are shown in Fig. 3a. Two types of electrolyte were used to achieve the most favorable result: system E1 was composed of LiI (0.5 M), I<sub>2</sub> (0.05 M), and TBP (4-tertbutylpyridine) (0.5 M) in MeCN, and system E2 was composed of 3-dimethylimidazolium iodide (DMII)(1.0 M) and guanidinium thiocyanate (0.1 M), in addition to LiI (0.05 M), I<sub>2</sub> (0.03 M), and TBP (0.5 M) in a mixed solvent of MeCN and valeronitrile (85:15, v/v). The electrolyte system from E1 to E2 was changed to help prevent leakage and increase the  $V_{\rm oc}$  value to ca. 0.03-0.04 V. The lower concentration of LiI in E2 raised the potential Fermi level of the conduction band of TiO<sub>2</sub>, thus enhancing the  $V_{oc}$  value, which increased the gap between the conduction band of TiO<sub>2</sub> and the electrolyte. The relative quantum efficiency of the **CPG2**-series was higher than that of **CP3**, and the result attributed to the higher efficiency of electron injection to the conduction band of TiO<sub>2</sub>. The devices manufactured using **CPG2b** and electrolyte E2 performed higher when exhibiting a  $J_{sc}$  of 8.80 mA·cm<sup>-2</sup>, a  $V_{oc}$  of 0.74 V, and an FF of 0.65, which totaled an overall quantum efficiency of 4.24%. The order of  $J_{sc}$  values **CPG2b** > **CPG2a** are nearly proportional to their relative magnitudes of molar absorptivity. The lower  $J_{sc}$  value (8.65 mA·cm<sup>-2</sup>) of **CPG2a** was mainly ascribed to its narrow absorption bandwidth and location on the ultraviolet region (Fig. 2a).

However, the purpose of introducing the PCP unit, as mentioned, is to reduce the rate of charge recombination. The long chains have also been shown to be capable of reducing the dark current by decreasing the rate of charge recombination, thus elevating the  $V_{\rm oc}$  of the solar cells. It may effectively improve the film morphology that covers the surface of TiO<sub>2</sub>. <sup>12</sup> This effect is represented by EIS Nyquist and Bode plots in Fig. 3c and Fig. 3d. The order of the relative values of dark current was found to be consistent with the magnitude of  $V_{oc}$ ; that is, CPG2b > CPG2a. Further information on the lifetime also corresponds with this trend and is supported by fitting the middle frequency in the Bode phase plots through the expression  $\tau = 1/(2\pi f)$ . A longer electron lifetime indicates a slower charge recombination, thus leading to a higher value of  $V_{oc}$ . The trend of relative quantum efficiency follows the same order of  $J_{sc}$  and  $V_{oc}$  values. The highest performance of a DSSC device was found in the one manufactured using CPG2b and electrolyte E2, which exhibited a  $J_{\rm sc}$  of 8.80 mA·cm<sup>-2</sup>, a  $V_{\rm oc}$  of 0.74 V, and an FF of 0.65. The overall conversion efficiency ( $\eta$ ) was estimated at 4.24%.



Figure 3. (a) *J-V* curves of the CPG2-series dyes. (b) IPCE plots of the dyes compared with CP3. (c) EIS Nyquist plots of the CPG2-series dyes in the dark. (d) Bode plots of the CPG2-series dyes.

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Table 1.	Photochemical,	, electroche	emical p	paramete	rs, and p	hotovoltaic devi	ces manufacti	ared using E1	and E2 electr	rolytes.
dye	$\lambda_{abs}^{a}$ nm	$\lambda_{abs}$ nm	$E_{\rm ox}^{\ b}$	$E_{0-0}^{c}$	$E_{\rm red}^{\rm d}$	$J_{\rm sc} ({\rm mA}\cdot{\rm cm}^{-2})$	$V_{\rm oc}(V)$	FF	$\eta^f(\%)$	$\tau^{g}$ (ms)
-	(ε/ M <sup>-1</sup> cm <sup>-1</sup> )	(film)	(V)	(V)	(V)	E1/E2 <sup>e</sup>	E1/E2	E1/E2	E1/E2	E1/E2
CPG2a	400 (65400)	386	0.60	2.72	-2.12	8.65/ 8.02	0.69/ 0.72	0.66/ 0.69	3.95/ 3.97	17.30/22.28
CPG2b	419 (70900)	414	0.55	2.53	-1.98	9.28/ 8.80	0.70/ 0.74	0.65/ 0.65	4.20/ 4.24	19.94/26.04
CP3 <sup>h</sup>	377 (41700)		0.81	2.83	-2.02	7.88/	0.69/	0.70/	3.83/	17.9/
N719			1 10 <sup>i</sup>	$2.60^{i}$	-1 50 <sup>i</sup>	15 62/17 47	0 74/ 0 75	0.62/0.60	7 26/ 7 90	

 $\varepsilon$ : absorption coefficient;  $E_{ox}$ : oxidation potential;  $E_{0.0}$ : 0-0 transition energy.

<sup>a</sup> Absorptions were measured in THF. <sup>b</sup> Oxidation potentials of dyes ( $10^{-3}$  M) in THF 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.* Fc<sup>+</sup>/Fc). <sup>c</sup>  $E_{0.0}$  was determined from the onset of the absorption in THF. <sup>d</sup>  $E_{red}$  was calculated by  $E_{ox} - E_{0.0}$ . <sup>e</sup> Electrolyte 1 (E1): LiI (0.5 M), I<sub>2</sub> (0.05 M), and TBP (0.5 M) in MeCN. Electrolyte 2 (E2): 3-dimethylimidazolium iodide (1.0 M), LiI (0.05 M), I<sub>2</sub> (0.03 M), guanidinium thiocyanate (0.1 M), and TBP (0.5 M) in MeCN:valeronitrile (85:15, v/v). <sup>f</sup> Performance of DSSCs was measured in a 0.25 cm<sup>2</sup> working area on an FTO (8Ω/square) substrate under AM 1.5 conditions. <sup>b</sup> Values in the blanks were obtained by fitting the middle-frequency in the Bode phase plots through the expression  $\tau = 1/(2\pi f)$ , where *f* is the frequency. <sup>h</sup> see ref. 5. <sup>i</sup> see ref. 13.

In summary, we successfully synthesized two novel DSSCs materials containing a [2.2]paracyclophane as the bridge moiety of **CPG2a** and **CPG2b**. Compared with our previous work, we extended  $\pi$ -chromophore and enhanced light harvesting, thus substantially improving the  $J_{sc}$  by extending the absorption wavelength. The nonconjugated moiety and long alkoxy chains may have an advantage in reducing the rate of charge recombination and may lead to a high  $V_{oc}$  value. Furthermore, replacing the electrolyte system from E1 to E2 can help prevent short circuits and increase the value of  $V_{oc}$ . The effect is supported by the higher resistance in the EIS of **CPG2b**.

#### Acknowledgments

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This work was supported by the National Science Council (NSC 101-2113-M-035-001-MY2) and Academia Sinica in Taiwan. The molecule weight is grateful for a Postdoctoral Fellowship in Academia Sinica, Taiwan. The computations were performed using the computer facilities at the Academia Sinica Computing Center, Academia Sinica.

#### **Supplementary Material**

The <sup>1</sup>H and <sup>13</sup>C NMR spectra of all compounds, absorption spectra in THF solution, absorption spectra on  $TiO_2$  film, TDDFT-calculated molecule orbitals, low-energy transitions, CV spectra, HOMO/LUMO levels, *J-V* curve, and IPCE and EIS spectra were used. Supplementary data associated with this article can be found in the online version, at doi:xxx.

#### **References and notes**

1. O'Regan, B; Grätzel, M. Nature 1991, 353, 737-740.

a) Gao, F.; Wang, Y.; Shi, D.; Zhang, J.; Wang, M.; Jing, X.; Humphry-Baker, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. J. Am. Chem. Soc. 2008, 130, 10720–10728; b) Yella, A.; Lee, H.-W.; Tsao, H. N.; Yi, C.; Chandiran, A. K.; Nazeeruddin, M. K.; Diau, E. W.-G.; Yeh, C.-Y.; Zakeeruddin, S. M.; Grätzel, M. *Science* **2011**, *334*, 629–633.

- a) Ito, S.; Miura, H.; Uchida, S.; Takata, M.; Sumioka, K.; Liska, P.; Comte, P.; Péchy, P.; Grätzel, M. Chem. Commun. 2008, 5194–5196; b) Tian, H.; Yang, X.; Cong, J.; Chen, R.; Liu, J.; Hao, Y.; Hagfeldt, A.; Sun, L. Chem. Commun. 2009, 6288–6290; c) Wu, Y.; Marszalek, M.; Zakeeruddin, S. M.; Zhang, Q.; Tian, H.; Grätzel, M.; Zhu, W. Energy Environ. Sci., 2012, 5, 8261– 8272; d) Lin, R. Y.-Y.; Lin, H.-W.; Yen, Y.-S.; Chang, C.-H.; Chou, H.-H.; Chen, P.-W.; Hsu, C.-Y.; Chen, Y.-C.; Lin, J. T.; Ho, K.-C. Energy Environ. Sci., 2013, 6, 2477–2486; e) Cai, S.; Hu, X.; Zhang, Z.; Su, J.; Li, X.; Islam, A.; Han, L.; Tian, H. J. Mater. Chem. A, 2013, I, 4763–4772; f) Chang, Y. J.; Chou, P.-T.; Lin, Y.-Z.; Watanabe, M.; Yang, C.-J.; Chin, T.-M.; Chow, T. J. J. Mater. Chem., 2012, 22, 21704–21712.
- a) Morisaki, Y.; Chujo, Y. Angew. Chem., Int. Ed., 2006, 45, 6430-6437; b) Morisaki, Y.; Chujo, Y. Bull. Chem. Soc. Jpn., 2009, 82, 1070-1082; c) Salhi, F.; Lee, B.; Metz, C.; Bottomley, L. A.; Collard, D. M. Org. Lett., 2002, 4, 3195-3198.
- 5. Chang, Y. J.; Watanabe, M.; Chou, P.-T.; Chow, T. J. Chem. Commun. 2012, 48, 726–728.
- Escossure, A. d. I.; Martínez-Díaz, V.; Thordarson, P.; Rowan, A. E.; Nolte, R. J. M.; Torres, T. J. Am. Chem. Soc. 2003, 125, 12300-12308.
- Bazan, G. C.; Oldham, Jr., W. J.; Lachicotte, R. J.; Tretiak, S.; Chernyak, V.; Mukamel, S. J. Am. Chem. Soc. 1998, 120, 9188-9204.
- Daeneke, T.; Kwon, T.-H.; Holmes, A. B.; Duffy, N. W.; Bach, U.; Spiccia, L. *Nature Chemistry* 2011, *3*, 211-215.
- a) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49-68; b) Hara,
  K.; Sato, T.; Katoh, R.; Furube, A.; Ohga, Y.; Shinpo, Suga, S.;
  Sayama, K.; Sugihara, H.; Arakawa, H. *J. Phys. Chem. B* **2003**, *107*, 597–606.
- 10. Zhao, Y.; Truhlar, D. G. Acc. Chem. Res., 2008, 41, 157-167.
- a) Hara, K.; Dan-oh, Y.; Kasada, C.; Ohga, Y.; Shinpo, A.; Suga, S.; Sayama, K.; Arakawa, H. *Langmuir* **2004**, *20*, 4205-4210; b) Tian, H.; Yang, X.; Cong, J.; Chen, R.; Teng, C.; Liu, J.; Hao, Y.; Wang, L.; Sun, L. *Dyes and Pigments* **2010**, *84*, 62-68.
- a) Kroeze, J. E.; Hirata, N.; Koops, S.; Nazeeruddin, M. K.; Schmidt-Mende, L.; Grätzel, M.; Durrant, J. R. *J. Am. Chem. Soc.* 2006, *128*, 16376–16383; b) Ning, Z.; Zhang, Q.; Pei, H.; Luan, J.; Cui, Y.; Tian, H. *J. Phys. Chem. C* 2009, *113*, 10307–10313.
- Nazeeruddin, M. K.; Angelis, F. D.; Fantacci, S.; Selloni, A.; Viscardi, G.; Liska, P.; Ito, S.; Takeru, B.; Grätzel, M. J. Am. Chem. Soc. 2005, 127, 16835–16847.