

Fine-tuning the Electronic Structure of Organic Dyes for Dye-Sensitized Solar Cells

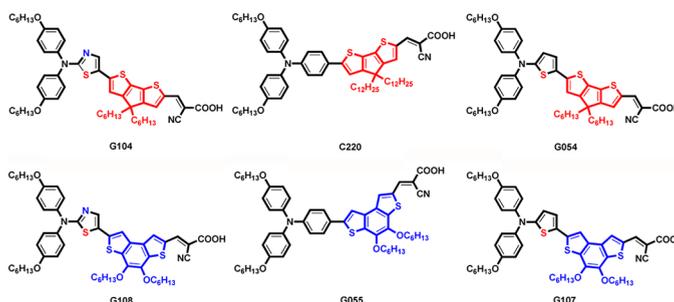
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ABSTRACT



A series of metal-free organic dyes exploiting different combinations of (hetero)cyclic linkers (benzene, thiophene, and thiazole) and bridges (4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CPDT) and benzodithiophene (BDT)) as the central π -spacers were synthesized and characterized. Among them, the sensitizer containing the thiophene and CPDT showed most the broad incident photon-to-current conversion efficiency spectra, resulting in a solar energy conversion efficiency (η) of 6.6%.

In recent decades, increasing attention has been paid to the development of dye-sensitized solar cells (DSCs) as a source of renewable energy,¹ mainly due to their potentially low-cost fabrication, possibility of transparency, and color selectivity, which can be integrated into building and automobile applications.² In order to increase power conversion efficiency and decrease the fabrication cost, extensive research has been focused on the development of new metal-free organic dye sensitizers.³ In particular, donor- π -acceptor (D- π -A) dyes are seen as one of the most promising organic dyes, owing to their efficient

intramolecular charge transfer (ICT) characteristics. Moreover most organic sensitizers are easy to synthesize and generally possess high molar extinction coefficients.⁴

Heterocyclic compounds such as thiophene and thiazole are widely used as building blocks in organic optoelectronics.⁵ To date, the molecular architecture of most donor fragments of the dyes is triphenylamine (TPA) in which a benzene ring typically serves as the linker. However, thiophene, which is a relatively more electron-rich heterocycle, and thiazole, which in contrast is relatively electron-deficient, are seldom employed to connect the nitrogen of the diarylamine with other π -bridges.⁶

Regarded as a fused-ring analogue of 3-alkylthiophene and a structural analogue of fluorene, CPDT has attracted considerable research interest.⁷ Organic dyes using the

(1) Grätzel, M. *Acc. Chem. Res.* **2009**, *42*, 1788.

(2) (a) O'Regan, B.; Grätzel, M. *Nature* **1991**, *353*, 737. (b) Nazeeruddin, M. K.; Kay, A.; Rodicio, I.; Humphry-Baker, R.; Müller, E.; Liska, P.; Vlachopoulos, N.; Grätzel, M. *J. Am. Chem. Soc.* **1993**, *115*, 6382. (c) Hagfeldt, A.; Grätzel, M. *Chem. Rev.* **1995**, *95*, 49. (d) Neale, N. R.; Kopidakis, N.; van de Lagemaat, J.; Grätzel, M.; Frank, A. J. *J. Phys. Chem. B* **2005**, *109*, 23183. (e) Wang, Z. S.; Cui, Y.; Dan-Oh, Y.; Kasada, C.; Shinpo, A.; Hara, K. *J. Phys. Chem. C* **2007**, *111*, 7224. (f) Qin, H.; Wenger, S.; Xu, M.; Gao, F.; Jing, X.; Wang, P.; Nazeeruddin, M. K.; Grätzel, M. *J. Am. Chem. Soc.* **2008**, *130*, 9202. (g) Tian, H. N.; Yang, X. C.; Chen, R. K.; Zhang, R.; Hagfeldt, A.; Sunt, L. C. *J. Phys. Chem. C* **2008**, *112*, 11023. (h) Bessho, T.; Zakeeruddin, S. M.; Yeh, C. Y.; Diau, E. W. G.; Grätzel, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 6646. (i) Yang, H.; Yen, Y.; Hsu, Y.; Chou, H.; Lin, J. *Org. Lett.* **2010**, *12*, 16.

(3) Mishra, A.; Fischer, M. K. R.; Bäuerle, P. *Angew. Chem., Int. Ed.* **2009**, *48*, 2474.

(4) Li, G.; Jiang, K. J.; Li, Y. F.; Li, S. L.; Yang, L. M. *J. Phys. Chem. C* **2008**, *112*, 11591.

(5) (a) Leriche, P.; Frère, P.; Cravino, A.; Alévêque, O.; Roncali, J. *J. Org. Chem.* **2007**, *72*, 8332. (b) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

(6) (a) Lin, L.-Y.; Tsai, C.-H.; Wong, K.-T.; Huang, T.-W.; Wu, C.-C.; Chou, S.-H.; Lin, F.; Chen, S.-H.; Tsai, A.-I. *J. Mater. Chem.* **2011**, *21*, 5950. (b) Lin, L.-Y.; Chen, Y.-H.; Huang, Z.-Y.; Lin, H.-W.; Chou, S.-H.; Lin, F.; Chen, C.-W.; Liu, Y.-H.; Wong, K.-T. *J. Am. Chem. Soc.* **2011**, *133*, 15822.

(7) Coppo, P.; Cupertino, D. C.; Yeates, S. G.; Turner, M. L. *Macromolecules* **2003**, *36*, 2705.

alkyl-functionalized CPDT as the conjugated bridge showed an extremely high molar absorption coefficient and a high power conversion efficiency of 8.95% in liquid cell and 6% in a solid-state DSC.⁸ BDT, the dithiophene analog of phenanthrene, has several isomers, of which benzo[1,2-*b*:4,5-*b'*]-dithiophene and benzo[2,1-*b*:3,4-*b'*]dithiophene have already been widely utilized in the construction of conjugated copolymers⁹ and D- π -A dyes¹⁰ for photovoltaic applications. Another isomer of BDT, benzo[1,2-*b*:4,3-*b'*]-dithiophene, however, to the best of our knowledge, has hardly been investigated in the DSC field.^{9h}

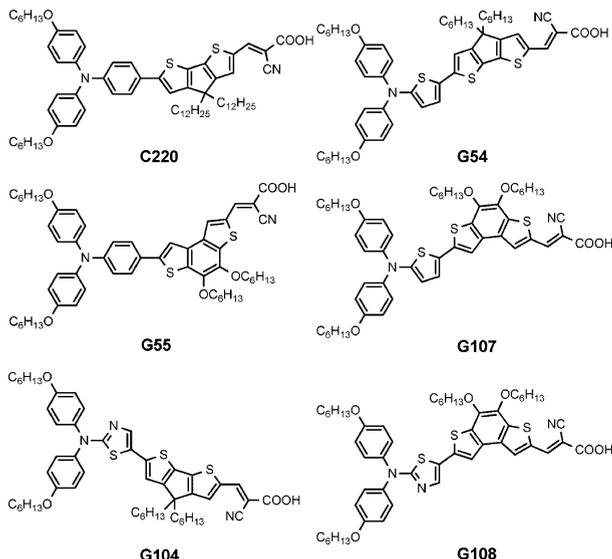


Figure 1. Structure of the synthesized dyes.

Judiciously varying the conjugating π -spacer between the donor and acceptor fragments has been the most popular approach to structural modification for modulating the frontier orbital energy levels and for generating dyes with broad and intense absorption. Therefore, this work elaborates on the use of various (hetero)cyclic linkers (benzene, thiophene, and thiazole) combined with different conjugated π -bridges (CPDT and BDT) to evaluate the impact on the overall efficiency while maintaining

(8) (a) Cai, N.; Moon, S.-J.; Cevey-Ha, L.; Moehl, T.; Humphry-Baker, R.; Wang, P.; Zakeeruddin, S. M.; Grätzel, M. *Nano Lett.* **2011**, *11*, 1452. (b) Li, R.; Liu, J.; Cai, N.; Zhang, M.; Wang, P. *J. Phys. Chem. B* **2010**, *114*, 4461.

(9) (a) Chen, H. Y.; Hou, J. H.; Zhang, S. Q.; Liang, Y. Y.; Yang, G. W.; Yang, Y.; Yu, L. P.; Wu, Y.; Li, G. *Nat. Photonics* **2009**, *3*, 649. (b) Hou, J. H.; Chen, H. Y.; Zhang, S. Q.; Chen, R. I.; Yang, Y.; Wu, Y.; Li, G. *J. Am. Chem. Soc.* **2009**, *131*, 15586. (c) Huo, L. J.; Guo, X.; Zhang, S. Q.; Li, Y. F.; Hou, J. H. *Macromolecules* **2011**, *44*, 4035. (d) Huo, L. J.; Hou, J. H.; Zhang, S. Q.; Chen, H. Y.; Yang, Y. *Angew. Chem., Int. Ed.* **2010**, *49*, 1500. (e) Liang, Y. Y.; Xu, Z.; Xia, J.; Tsai, S. T.; Wu, Y.; Li, G.; Ray, C.; Yu, L. P. *Adv. Mater.* **2010**, *22*, E135. (f) Price, S.; Stuart, A.; Yang, L.; Zhou, H.; You, W. *J. Am. Chem. Soc.* **2011**, *133*, 4625. (g) Wang, M.; Hu, X.; Liu, P.; Li, W.; Gong, X.; Huang, F.; Cao, Y. *J. Am. Chem. Soc.* **2011**, *133*, 9638. (h) Zheng, Q.; Jung, B. J.; Sun, J.; Katz, H. E. *J. Am. Chem. Soc.* **2010**, *132*, 5394. (i) Zhou, H.; Yang, L.; Stuart, A.; Price, S.; Liu, S.; You, W. *Angew. Chem., Int. Ed.* **2011**, *50*, 2995.

(10) Hao, X.; Liang, M.; Cheng, X.; Pian, X.; Sun, Z.; Xue, S. *Org. Lett.* **2011**, *13*, 5424.

cyanoacrylic acid as the electron acceptor. The synthesized organic dyes (C220, G54, G55, G104, G107, and G108) are shown in Figure 1, with the synthetic methodology of the five target molecules being highlighted in Scheme S1. The C220 sensitizer is synthesized according to the reported procedure for comparison.^{8b}

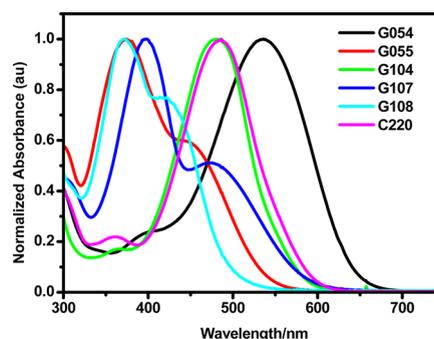


Figure 2. UV-vis absorption spectra of all the dyes in CH₂Cl₂ solution.

The UV-vis absorption spectra of the dyes in CH₂Cl₂ solutions are depicted in Figure 2. Their absorption, electrochemical properties, and frontier orbital energy levels are summarized in Table 1. The electronic absorption spectra reveal two major characteristics depending on the substituted π -bridges. Specifically, the four dyes (G54, G104, and C220) containing CPDT as a bridge exhibit a single prominent band with the absorption maximum around ca. 530–570 nm, while the others (G55, G107, and G108) with BDT as the bridge have two absorption bands at ca. 370–410 nm and at ca. 450–510 nm. Such absorption characteristics indicate that the electron density on CPDT is richer than that of BDT and the absorption bands can be ascribed to the π - π^* transition and intramolecular charge transfer (ICT) transitions of the D- π -A conjugated backbone. Apparently, in either case of the bridges (CPDT or BDT), the absorption maxima of ICT transitions are generally red-shifting in the sequence thiazol < phenyl < thienyl. The phenomenon is in line with the electronic richness of the relative (hetero)cycles, and due to the fortified quinoidal character of thiophene, the adoption of the thiophene linker endows the corresponding dye with the smallest band gap.¹¹ This result clearly indicates that modulation of the electron density of D- π -A dyes can be achieved by altering the electronic nature of the π -bridges.

Cyclic voltammetry (CV) is employed to estimate the first oxidation potential (E_{ox}), which corresponds to the HOMO levels of the dyes (Table 1, SI Figure S1). Normally, two oxidation waves are observed on the voltammograms. The first oxidation waves at lower oxidation potentials are generally from the contribution of triarylamine, whereas the second ones, with higher oxidation

(11) (a) Roncali, J. *Chem. Rev.* **1997**, *97*, 173. (b) Roncali, J. *Acc. Chem. Res.* **2009**, *42*, 1719.

Table 1. Optical and Electrochemical Properties of the Dyes

dye	absorption ^a		oxidation potential data ^c			
	λ_{\max} (nm)	ϵ (M ⁻¹ cm ⁻¹) (λ_{\max})	E_{ox} (V) (vs NHE)	E_{0-0} (V) ^d	$E_{\text{ox}}-E_{0-0}$ (V) (vs NHE)	HOMO/ LUMO (eV) ^f
G54	565	45468	0.635	1.79	-1.15	-5.14/ -3.35
G55	375 459	38688 23212	0.86	2.18	-1.32	-5.36/ -3.18
G104	539	50567	0.96	1.97	-1.01	-5.46/ -3.49
G107	406 502	41683 21258	0.75	1.95	-1.2	-5.25/ -3.3
G108	381 458	42430 25540	1.08	2.15	-1.07	-5.58/ -3.43
C220	552	53605 ^b	0.815	1.87	-1.05	-5.32/ -3.45

^a Measured in 2×10^{-6} M of CH₂Cl₂ solutions at room temperature.

^b Slightly lower than the value measured in chloroform.^{8a} ^c Measured in CH₂Cl₂ containing 0.1 M of tetrabutylammonium tetrafluoroborate (TBABF₄) electrolyte (working electrode: glassy carbon; counter electrode: Pt; reference electrode: Pt; calibrated with ferrocene/ferrocenium (Fc/Fc⁺) as an internal reference and converted to NHE by addition of 630 mV).¹² ^d Estimated from onset wavelength in absorption spectra. ^e NHE vs the vacuum level is set to 4.5 V.¹³

potentials and quasi-reversible behavior, are from the CPDT and BDT π -bridge. It is obvious that the E_{ox} varies in accord with the electron density of the conjugated π -bridges. Generally, the CPDT based dyes have a lower first oxidation potential than that of the BDT based dyes, whereas the thiophene linked molecules exhibit the lowest oxidation potential among the three kinds of (hetero)cyclic linkers. The zero-zero energy (E_{0-0}), estimated from the onset wavelength of the absorption spectra together with the HOMO level energy, is used to calculate the LUMO levels of these dyes (see Table 1). The thus obtained LUMO values are much more negative than the Fermi level of TiO₂ (-0.5 V vs NHE),^{9b} allowing efficient electron injection from the excited dyes into the TiO₂ electrode. All the dyes exhibit more positive HOMO levels than that of the iodide/triiodide redox couple (0.4 V vs NHE) guaranteeing efficient dye regeneration.

To gain further insight into the molecular structure and frontier molecular orbitals of these dyes, the geometries of the dyes are optimized by density functional theory (DFT) calculations at the B3LYP.6-31G(d) level. SI Figure S2 displays the relative energies and electron distributions of the HOMO and LUMO of the dyes. HOMOs are mainly delocalized from the diarylamino donor to the heterocyclic π -spacer, whereas LUMOs show localized electron distributions though the cyanoacrylic acid and its adjacent π -spacer. This separation of electrons will ensure efficient electron injection from the dye to the TiO₂ film.

(12) Mei, J.; Graham, K. R.; Stalder, R.; Reynolds, J. R. *Org. Lett.* **2010**, *12*, 660.

(13) Bürgi, L.; Turbiez, M.; Pfeiffer, R.; Bienewald, F.; Kirner, H.-J.; Winnewisser, C. *Adv. Mater.* **2008**, *20*, 2217.

The DSC performances of all the dyes are evaluated under AM 1.5 G irradiation at 100 mW cm⁻² (details of the devices' fabrication and testing are described in the Supporting Information). Hereby, the focus is on the influence of the two different bridging units CPDT and BDT, together with the three varying linker groups, on the DSC characteristics. First, the effect of the BDT in comparison to CPDT is highlighted in terms of the changes in V_{OC} . When scrutinizing the dyes with the same linkers (C220 vs G55 for the phenyl, G54 vs G107 for the thiophene, and G104 vs G108 for the thiazole linkers), it is apparent that the V_{OC} increases by more than 40 mV in the presence of BDT (Table 2 and Figure 3a). This observation is reflected by the corresponding V_{OC} shifts toward higher values when plotted against capacitance (Figure 4a). For instance, in comparing C220 with G55, the capacitance for the latter is shifted toward higher V_{OC} (Figure 4a), indicating a higher TiO₂ conduction band ultimately resulting in an elevated V_{OC} for the G55 cell. The same trend is observed for G54 vs G107 and G104 vs G108 (Figure 4a), emphasizing the fact that the BDT unit triggers an upward shift of the TiO₂ conduction band, which is beneficial for enhancing the V_{OC} . Since the same TiO₂ layers are employed for all cells and all dyes investigated, it is highly unlikely that changes in TiO₂ trap states are the cause for the observed variations in conduction bands. In terms of V_{OC} , the effect of the linker group is even more dramatic than replacing BDT with the CPDT acceptor. For the same π -bridge, the incorporation of thiophenes or thiazoles instead of the common phenyl as linkers severely reduces the V_{OC} more significantly than 100 mV (Table 2, Figure 3a) even though the difference between thiophene and thiazole is not as major. This behavior is also reflected by the shift in V_{OC} in the dependence of capacitance as illustrated by the photovoltage decay measurements (Figure 4a). Overall, the combination of the BDT bridge and the phenyl linker poses a powerful system in achieving an outstanding V_{OC} , surpassing 800 mV, one of the highest values reported for the I₃⁻/I⁻ redox couple.

Table 2. Photovoltaic Performance Data of the Dyes

dye	combination	J_{sc} (mA/cm ²)	V_{oc} (mV)	FF (%)	η (%)
C220	benzene-CPDT	15.4	756	0.76	8.8
G55	benzene-BDT	9.4	810	0.74	5.6
G54	thiophene-CPDT	14.9	622	0.71	6.6
G107	thiophene-BDT	10.1	671	0.70	4.8
G104	thiazole-CPDT	11.8	603	0.75	5.4
G108	thiazole-BDT	9.6	683	0.78	5.1

Even though the BDT has the advantage of increasing the V_{OC} , the absorption however is blue-shifted compared to the CPDT unit as already shown by the UV-vis absorption spectra. This phenomenon is mirrored in the incident photon-to-current conversion efficiency (IPCE) of the corresponding dyes (Figure 3b). Consequently, all

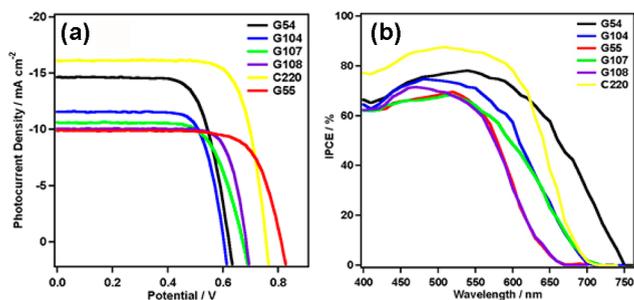


Figure 3. (a) J – V curves for DSSCs based on the dyes under illumination of AM 1.5 G simulated sunlight (100 mW cm^{-2}). (b) IPCE spectra of the same DSSCs.

sensitizers containing BDT exhibit a J_{SC} of only $\sim 10 \text{ mA cm}^{-2}$, whereas all other compounds consisting of CPDT result in better cell performances with a much higher J_{SC} (Table 2), even though all of the BDT based dyes yield more enhanced electron lifetimes than the CPDT counterparts as evidenced by photocurrent decay measurements (Figure 4b).

Having elucidated the effect of the bridging units on the J_{SC} , it is also crucial to understand which role the linkers play in this aspect. Taking into consideration the BDT dyes **G55**, **G107**, and **G108**, it is apparent that the J_{SC} increases with the linkers thiophene > thiazole > phenyl, even though those changes are not significant (Table 2). On the other hand, the sensitizers containing CPDT show a decline in J_{SC} according to the trend phenyl > thiophene > thiazole. Hereby, the linkers impinge a more dramatic impact on the J_{SC} , particularly for the thiazole case where the J_{SC} is reduced by more than 3 mA cm^{-2} (Table 2). This behavior is simply the result of the corresponding blue shifts as indicated by the IPCE (Figure 3b). Based on these findings, the CPDT seems to be more prone to the nature of the linkers than the BDT bridge.

In addition, the linkers also have an effect on the electron lifetimes in the TiO_2 film. As the photocurrent decay measurements indicate (Figure 4b), for both the BDT and CPDT bridges, the phenyl linker leads to the longest lifetimes, whereas the thiophene and thiazole units shorten the lifetimes. There are no notable differences in lifetimes between those two linkers themselves. Furthermore, as compared to the CPDT with the same linkers, the BDT sensitizer based TiO_2 layers exhibit prolonged lifetimes as well. Overall, the BDT bridge is very appealing in terms of both the observed upper shift of the TiO_2 conduction band desired for a high V_{OC} and the longer lifetimes of the electrons.

In summary, we have synthesized a series of metal-free organic sensitizers based on the D- π -A structure and

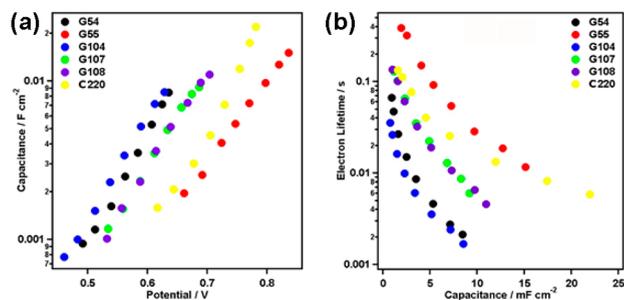


Figure 4. (a) Dependence of capacitance on open circuit potential V_{OC} as measured by voltage decay and (b) dependence of TiO_2 electron lifetimes on capacitance as recorded from photocurrent decay measurements for the investigated dyes.

studied the impact of various conjugated π -spacers on the device performance in DSCs. The power-conversion efficiency of DSCs is higher when CPDT and/or phenyl are used as the π -conjugated spacer. The introduction of CPDT instead of BDT contributed to improving the cell's J_{SC} but deteriorating the V_{OC} , while the use of phenyl rather than thiophene and thiazole mainly resulted in an increased V_{OC} , respectively. Among the synthesized new dyes, **G54** containing CPDT and thiophene yielded the best conversion efficiency of 6.6% due to the relatively highest J_{SC} . On the other hand, although with much poorer absorption ability, BDT and phenyl bridged **G55** showed the highest V_{OC} and longest electron lifetime, which thus dramatically improved the DSC performance (5.6%). These results strongly suggest that metal-free organic dyes could be tuned by appropriate control of the energy levels of π -conjugated spacers through systematic structure modification of the π -system, leading to further development of highly efficient organic dyes.

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Supporting Information Available. Experimental details, DSSCs fabrication, and characterization details for new compounds. The material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.