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A structural study of DPP-based sensitizers for DSC applications[†]

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Four D- π -A sensitizers comprising a thienyl-diketopyrrolopyrrole (ThDPP) bridge were synthesized and tested in iodide/triiodide liquid electrolyte DSC devices. The dye series was strategically designed to develop a structure–property relationship. The best performing sensitizer utilized a phenyl-based anchor and triphenyl-amine donor ($\eta = 5.03\%$).

Dye sensitized solar cells (DSCs) have become a powerful alternative to conventional solar energy harvesting devices. The underlying mechanism of device operation, mimicking photosynthesis, is very flexible. Choosing the appropriate nanostructured metal oxide, sensitizer, and redox shuttle offers control over aesthetic properties such as transparency and colour, as well as performance properties such as the attainable output voltage and current density.¹ These advantages, and promising power conversion efficiencies (PCE) of over 10%,² make such devices ideal for integration with consumer electronics such as wireless keyboards, remote controls, and other battery powered devices. Herein, we describe how diketopyrrolopyrrole-based sensitizers can be structurally tuned in an effort to realize this goal of ubiquitous solar energy harvesting.

DPP-based sensitizers have been reported for use in DSCs only a handful of times,^{3–7} a remarkable fact considering the wide-spread use of DPP in many other aspects of materials technology, from car-paint pigments⁸ to small molecule and polymeric organic photovoltaics.⁹ The seminal work on these sensitizers was published in 2010 by Qu *et al.*,⁴ comparing the phenyl-DPP (PhDPP) and ThDPP core. The success of PhDPP in this work led to further optimization of that core with various acceptors/anchors⁶ and donors.⁷ It was unclear, however, why ThDPP did not outperform PhDPP. We recently set out to determine the structural properties that underlie a successful DPP-based sensitizer.

The standard metal-free sensitizer consists of a donor- π -bridge-acceptor motif, where the bridge serves primarily to extend π -conjugation while effectively relaying electron density from the donor to the acceptor. Here, the aryl-DPP core serves as an inherently coloured π -bridge, and ThDPP provides exceptional spectral response compared to PhDPP; this is primarily due to the planarity of the thiophene–DPP bond and reduced aromatic stabilization energy for thiophene compared to benzene (29 *vs.* 36 kcal mol⁻¹¹⁰). Further, planarity of the π -bridge facilitates enhanced spectral response with the D- π -A configuration.

Four sensitizers (Fig. 1) with similar absorption spectra and varying electrochemical and structural features were synthesized (Table 1 and Fig. 2). Two sensitizers with triphenylamine-based donors and two with diphenylamine-based donors were synthesized in combination with either a phenyl- or thienyl-based acceptor/anchor; all sensitizers utilized cyanoacrylic acid to bind the TiO_2 surface. The triphenylamine donor is expected to localize the radical cation away from the DPP bridge at the expense of reduced electron donation from the amine into the bridge and acceptor functionality, compared to the diphenylamine. This is evidenced in the electrochemical data.

It is apparent from the electrochemical and UV-Vis absorbance data that these sensitizers should not be intrinsically handicapped in an iodide/triiodide liquid electrolyte DSC with TiO_2 , *i.e.* the type II energy level alignment is sufficient to generate free charge at the TiO_2 interface and to regenerate the oxidized dye with iodide/triiodide.¹ It is also apparent that the triphenylamine donor broadens the sensitizer absorption breadth, presumably a result of the extended conjugation, and that the thienyl anchor results in a marginal decrease in optical bandgap for DPP04 compared to DPP03. It is not apparent from this data which dye will achieve the best PCE, and this is the reason for developing a structure–property relationship: understanding the role of structural properties, layered over the energy level and absorption properties, is critical for the advancement of sensitizer science.

The photovoltaic characteristics are summarized in Table 2. Overall, structurally, the triphenylamine donor provided increased performance over the diphenylamine with this bridge, *i.e.* DPP03 outperforms DPP01 and DPP04 outperforms DPP02. Additionally, the phenyl anchors outperformed the thienyl: DPP03,

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Fig. 1 Structures of DPP01-04.

Table 1	Electrochemical	and	optical	properties	of all	dyes
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Dye	$Ox^{a}[V]$	Red ^a [V]	$E_{\rm g}^{\ b} [{\rm eV}]$	LUMO ^c [V vs. NHE]
DPP01 DPP02 DPP03 DPP04	+0.77 +0.77 +0.96 +0.97	-0.80 -0.64 -0.74 -0.64	1.66 1.71 1.66 1.60	-0.89 -0.94 -0.70 -0.63

^{*a*} Measured in a 0.1 M Bu₄NPF₆ in DMF solution with glassy carbon working, Pt counter and Pt quasi-reference electrodes; ferrocene was used as an internal standard. Values are reported *versus* NHE according to $E^0(Fc^+/Fc) = 0.69$ V vs. NHE.^{11 b} Taken from the onset of absorbance. ^{*c*} Optical LUMO, *i.e.* the oxidation potential less the bandgap.

comprising a triphenylamine donor and phenyl anchor yielded the highest PCE of 3.51%. DPP04 was the first DPP sensitizer ever reported, in the work by Qu (*vide supra*); this current structure–property relationship study identified two higher performance derivatives of the ThDPP core – deriving their success from the phenyl-based acceptor.

These four sensitizers were further optimized with and without the co-adsorbent chenodioxycholic acid (CDCA). Structural features can promote or inhibit sensitizer-sensitizer interaction, thereby influencing exciton dynamics on the TiO_2 surface and aggregation behaviour. The presence of CDCA is known to suppress sensitizer aggregation, $^{12-14}$ and CDCA was necessary to achieve high performance with these sensitizers. All the DPP-based sensitizers exhibited increased PCE when



Fig. 2 UV-Vis spectra of all dyes in THF solution.

 Table 2
 Output characteristics of DSC devices fabricated with DPP sensitizers

Dye	CDCA [mM]	$J_{\rm sc} [{\rm mA~cm}^{-2}]$	$V_{\rm oc} [V]$	FF	PCE [%]
DPP01	0	5.24	0.54	0.72	2.02
	2.5	8.66	0.55	0.72	3.41
DPP02	0	2.14	0.51	0.74	0.81
	2.5	5.04	0.52	0.73	1.92
DPP03	0	8.89	0.59	0.67	3.51
	2.5	11.9	0.64	0.65	4.93
DPP04	0	3.14	0.56	0.76	1.34
	2.5	5.49	0.58	0.72	2.31

Devices fabricated with TiO_2 thickness of 6 + 4 (20 nm and 400 nm particles) microns, with electrolyte composition 0.6 M DMII, 0.05 M LiI, 0.03 M I₂, 0.25 M TBP, 0.05 M GuSCN in acetonitrile : valeronitrile (85 : 15).

CDCA was utilized as a co-adsorbent. The best dye, DPP03 yielded the highest PCE of 4.93%, which increased further to 5.03% (with an increase in J_{sc}), by employing an anti-reflection film on the cell. Considering the IPCE data (Fig. 3), it is apparent that these performance differences are rooted in the photon-to-electron conversion process, rather than spectral breadth.



Fig. 3 IPCE data for the four sensitizers.

It is noted that all dyes on the TiO_2 surface showed broadened absorption spectra (see ESI†), which is in agreement with IPCEs that also show increased absorbance in the long wavelength region due to the thicker films¹⁵ and 400 nm scattering particles.¹⁶

A limited IPCE can result from several factors, such as inadequate surface coverage on the TiO₂ or an energy level mismatch of the sensitizer excited state with TiO₂; these two simple cases do not appear to be the reason for such failure of the ThDPP core, as these sensitizers performed optimally under similar processing conditions but exhibited pronounced differences in PCE. Structural aspects of a sensitizer are often ignored, if there is not a rational link to parameters such as absorbance, energy levels, or surface coverage. However, recently, the ability of a phenyl ring to insulate the oxidized/ cationic sensitizer from the anionic TiO₂ has recently been suggested as the reason underlying a dramatic performance difference between two otherwise similar sensitizers.¹⁷ Another recent paper demonstrates this effect with a direct comparison between phenyl- and thienyl-based anchors,¹⁸ although this point was not directly addressed. It is possible that the DPP core could require greater molecular-level-insulation from the TiO₂ surface to achieve higher performance: the single phenyl ring here achieves 60% IPCE, while Qu et al.6 have observed >90% IPCE for a biphenyl anchor and \sim 70% for a comparable thiophene-5-phenyl-2-cyanoacrylic acid anchor. Electron lifetime data measured by photovoltage and photocurrent transients confirm that DPP03 should suffer from less backrecombination loss than DPP04 (see ESI[†]). Moreover, a presence of CDCA led to elongated electron lifetimes, which is in agreement with higher V_{oc} s in this IV data and previous studies.13 The utilization of a triphenylamine-based donor and further molecular level insulation of the DPP core from the TiO₂ surface is currently underway.

A structural investigation of ThDPP-based sensitizers for DSC applications revealed that incorporating phenyl units on both the donor and acceptor moieties yields higher PCE for the ThDPP bridge compared to a similar PhDPP-based sensitizer.⁴ This opens the possibility of synthesizing near-IR sensitizers with this promising class of chromophore. Introduction of a phenyl ring between the electron donating nitrogen and the DPP core (1) increased the UV-vis absorbance spectral breadth (2) increased the oxidation potential, and (3) improved the IPCE significantly. Separating the cyanoacrylic acid unit from the DPP core with a phenyl ring compared to a thiophene had minimal impact on the spectral absorbance and

oxidation potential; however, there was a dramatic improvement in IPCE when utilizing the phenyl-based anchor compared to the thienyl, likely due to decreased electron back-recombination as evidence by electron lifetime studies. A maximum efficiency of 4.93% (5.03% with AR film) was achieved for DPP03 compared to 1.92% for DPP02.

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Notes and references

- A. Hagfeldt, G. Boschloo, L. C. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595.
- 2 A. Yella, H. W. Lee, H. N. Tsao, C. Y. Yi, A. K. Chandiran, M. K. Nazeeruddin, E. W. G. Diau, C. Y. Yeh, S. M. Zakeeruddin and M. Gratzel, *Science*, 2011, **334**, 629.
- 3 C. Kanimozhi, P. Balraju, G. D. Sharma and S. Patil, J. Phys. Chem. C, 2010, 114, 3287.
- 4 S. Y. Qu, W. J. Wu, J. L. Hua, C. Kong, Y. T. Long and H. Tian, *J. Phys. Chem. C*, 2010, **114**, 1343.
- 5 J. Warnan, L. Favereau, Y. Pellegrin, E. Blart, D. Jacquemin and F. Odobel, J. Photochem. Photobiol., A, 2011, 226, 9.
- 6 S. Y. Qu, B. Wang, F. L. Guo, J. Li, W. J. Wu, C. Kong, Y. T. Long and J. L. Hua, *Dyes Pigm.*, 2012, **92**, 1384.
- 7 S. Y. Qu, C. Qin, A. Islam, W. J. Wu, W. Zhu, J. L. Hua, L. Han and H. Tian, *Chem. Commun.*, 2012, 48, 6972.
- 8 Z. M. Hao and A. Iqbal, Chem. Soc. Rev., 1997, 26, 203.
- 9 P. M. Beaujuge and J. M. J. Frechet, J. Am. Chem. Soc., 2011, 133, 20009.
- 10 P. A. Peart, L. M. Repka and J. D. Tovar, *Eur. J. Org. Chem.*, 2008, 3875.
- 11 N. G. Connelly and W. E. Geiger, Chem. Rev., 1996, 96, 877.
- 12 A. Kay and M. Grätzel, J. Phys. Chem., 1993, 97, 6272.
- 13 J.-H. Yum, S.-J. Moon, R. Humphry-Baker, P. Walter, T. Geiger, F. Nüesch, M. Grätzel and M. D. K. Nazeeruddin, *Nanotechnology*, 2008, **19**, 424005.
- 14 M. Topic, A. Campa, M. Filipic, M. Berginc, U. O. Krasovec and F. Smole, Curr. Appl. Phys., 2010, 10, S425–S430.
- 15 S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, 516, 4613–4619.
- 16 M. Pastore and F. De Angelis, ACS Nano, 2010, 4, 556.
- 17 S. Haid, M. Marszalek, A. Mishra, M. Wielopolski, J. Teuscher, J. E. Moser, R. Humphry-Baker, S. M. Zakeeruddin, M. Gratzel and P. Bauerle, *Adv. Funct. Mater.*, 2012, **22**, 1291.
- 18 W. H. Zhu, Y. Z. Wu, S. T. Wang, W. Q. Li, X. Li, J. A. Chen, Z. S. Wang and H. Tian, *Adv. Funct. Mater.*, 2011, 21, 756.