ChemComm

COMMUNICATION



Cite this: DOI: 10.1039/c6cc09992k

Received 15th December 2016, Accepted 17th January 2017

DOI: 10.1039/c6cc09992k

rsc.li/chemcomm



View Article Online

On how electron density affects the redox stability of phenothiazine sensitizers on semiconducting surfaces[†]

Valerie A. Chiykowski, Brian Lam, Chuan Du and Curtis P. Berlinguette*

The stabilities of three organic dyes that differ only by two substituents (-OMe, -H and -Br) about the phenothiazine donor unit were evaluated when immobilized on a semiconductor surface. All three dyes delivered modest power conversion efficiencies (PCEs) in the dye-sensitized solar cell (DSSC), but maintained 75% of their initial PCE over 300 h of sustained simulated sunlight. Electrondonating substituents increased the stability of the phenothiazine radical unit created after light-induced charge injection into the semiconductor; however, this did not translate to higher DSSC stability, which appears to be more sensitive to the basicity of the anchoring group for this series.

Organic chromophores are capable of producing PCEs greater than 10% in the DSSC.^{1–5} High performance metal-free sensitizers typically contain a "donor– π -bridge–acceptor" electronic structure where an electron-rich donor group is connected to an electrondeficient acceptor group through a conjugated bridge.^{6,7} The acceptor group is most often a carboxylic acid group that functions to covalently link the dye to a semiconductor surface such as TiO₂.^{8–10} This asymmetric electronic structure is imperative for facilitating efficient light-induced charge transfer from the organic donor unit to the semiconductor.^{6,7,11,12} This scenario leaves the lowest unoccupied β -spin orbital (β -LUSO) for the photo-oxidized dye localized on the "donor" unit and poised for regeneration by the redox active mediator species (*e.g.*, 1[–], Co^{II}).^{13–17}

While metal-free dyes that yield high PCEs are now known,^{3,4,18–20} commercial deployment requires robust performance.^{21,22} Organic dyes are notoriously unstable and do not satisfy this criterion.^{23–25} The discovery of commercially viable organic dyes therefore hinges on our ability to identify and resolve relevant degradation processes. In the case of organic dyes, light-induced charge transfer from the dye to the semiconductor yields a reactive

radical cationic species that ostensibly participates in deleterious reactions that may compromise the sustained performance of DSSCs.²⁴

We set out to increase the stability of organic dyes by preparing a series of dyes bearing a phenothiazine (PTZ) donor unit (Fig. 1). The sulfur tether increases the coplanarity of the aromatic rings within the PTZ unit, resulting in a more delocalized hole that is known to accommodate higher stability in the oxidized form.^{24,26} The higher radical cation stability of this unit has been exploited for preventing overcharging in lithium-ion batteries and near-infrared imaging,²⁷⁻³⁰ and was very recently utilized in the DSSC as both a donor and conjugated bridge.³¹⁻³⁵ We hypothesized that substitution at the C-3 and C-7 positions of the PTZ unit with electron-donating groups (EDGs) would engender even higher redox stability (Fig. 1) by stabilizing the radical cation formed upon one-electron oxidation. To test this assertion, methoxy groups were installed at these two positions (Dye-OMe) and the properties were evaluated against the dibromo (Dye-Br) and unsubstituted (Dye-H) benchmark compounds (Fig. 1). It is shown herein that the stability of oxidized dyes in solution and when immobilized on TiO₂ improves with electrondonating substituents; however, this trend did not correlate to device stability as no significant difference in stability for the series was observed during accelerated aging tests.



higher stability in oxidized form

Fig. 1 Molecular representations of **Dye-Br**, **Dye-H** and **Dye-OMe**, which contain different substituents at the C3 and C7 positions.

Departments of Chemistry and Chemical & Biological Engineering, The University of British Columbia, 2036 Main Mall, Vancouver, BC, V6T 1Z1, Canada. E-mail: cberling@chem.ubc.ca

[†] Electronic supplementary information (ESI) available: Experimental procedures, ¹H and ¹³C NMR spectra, mass spectra, spectroscopic, spectroelectrochemical and time-dependent DFT data. See DOI: 10.1039/c6cc09992k

The three novel organic dyes under investigation were accessed through Ullmann condensation of commercially available or synthetically-derived phenothiazine donor units to produce tertiary amines (Scheme S1, ESI[†]).^{36,37} The thiophene bridge was attached through a palladium-catalyzed Suzuki coupling to the tertiary amines **P1-H** and **P3-OMe** intermediates. The cyanoacrylic acid anchoring group was added by a Knoevenagel condensation following previously reported literature procedures to yield final products **Dye-Br**, **Dye-H** and **Dye-OMe**.³⁸ The structure of each dye was determined by ¹H and ¹³C NMR spectroscopy (Fig. S9–S16, ESI[†]) as well as high resolution mass spectrometry (HR-MS).

The sulfur bridge was shown by density functional theory (DFT) to maintain the phenothiazine donor unit perpendicular to the bridge thereby disrupting the conjugation between the HOMO and LUMO orbitals (Fig. 2a). The HOMO resides entirely on the phenothiazine donor unit while the LUMO is located primarily on the cyanoacrylic acid acceptor moiety and partially on the thienyl π -bridge. TD-DFT calculations predict a HOMO \rightarrow LUMO transition at \sim 760 nm, but this was not observed experimentally. The dominant lowest energy absorption band for the PTZ-R series at \sim 400 nm (Fig. 2b and Table 1) is instead assigned as a HOMO-2 or HOMO-3 \rightarrow LUMO transition involving charge transfer from the π -bridge to the acceptor unit. The wavelength maxima for these bands are bathochromically shifted from 370 to 411 nm with increasingly electron-rich substituents. The absorption spectra of the dyes adsorbed to mesoporous TiO₂ (Fig. 2b, inset) followed the same trend, but were collectively blue-shifted by 40 nm.



Fig. 2 (a) Calculated frontier orbitals of optimized structures for the **Dye-**X series plotted at an absolute isovalue of 0.001. (b) UV-vis absorption spectra for the **Dye-X** series recorded in MeCN. Inset: Absorption spectra for the three dyes immobilized on TiO_2 .

Table 1 Summary of spectroscopic and electrochemical properties for Dye-Br, Dye-H and Dye-OMe in MeCN

Dye	λ_{\max}^{a} (nm)	$\lambda_{ m Fluor}{}^{b}$ (nm)	$E_{1/2}^{c}$ (V vs. NHE)	$\frac{E_{0-0}}{(eV)}^d$	$\frac{E(S^{+}/S^{*})^{e}}{(V \ \nu s. \ NHE)}$
Dye-Br	370 (1.4)	531	1.16	2.98	$-1.82 \\ -1.61 \\ -1.78$
Dye-H	384 (1.1)	565	1.02	2.63	
Dye-OMe	411 (1.3)	572	0.78	2.56	

^{*a*} Corresponds to maximum of lowest-energy absorption band; ε in units of 10⁴ M⁻¹ s⁻¹ indicated in parentheses. ^{*b*} Maximum wavelength of emission band after excitation at λ_{max} . ^{*c*} PTZ⁰+/PTZ⁰ redox couple in 0.1 M *n*-NBu₄PF₆ electrolyte solution at 50 mV s⁻¹ and referenced against Ag/AgCl in saturated KCl solution (+197 mV *vs.* NHE). ^{*d*} *E*₀₋₀ determined from intersection of normalized absorption and emission spectra. ^{*e*} Calculated with the relationship: $E(S^+/S^*) = E_{1/2} - E_{0-0}$.

Cyclic voltammograms recorded for each dye in 0.1 M n-NBu₄PF₆ MeCN solutions (Fig. 3) revealed that oxidation of the PTZ unit occurs at +0.78, +1.02 and +1.16 V vs. NHE for Dye-OMe, Dye-H and Dye-Br, respectively. This trend confirms that the electron density at the C-3 and C-7 positions has a marked shift on the HOMO energy. The chemical stability of the oxidized dyes was inferred by evaluating the ratio of anodic to cathodic currents. Dve-Br was determined to be the least chemically stable on the basis that the anodic current was significantly larger than that of the cathodic scan. The anodic: cathodic current ratio converged on 1 for Dye-OMe implicating higher stability of the PTZ^{•+} unit. Moreover, 50 successive scans of dyes in solution produced a nominal decrease in current for Dye-OMe, while similar experiments for Dye-Br showed a significant diminution in current with subsequent scans corresponding to a relatively lower oxidative stability in solution.

The stability of each oxidized dye on TiO₂ was also analyzed spectroelectrochemically. The working electrode (**Dye-R** on TiO₂) was oxidized for 1 min at a potential +0.1 V more positive than the **Dye-R**^{•+}/**Dye-R** redox potential to produce spectroscopic features at 500–700 nm that are diagnostic of a PTZ^{•+} unit (Fig. S2, ESI⁺).³⁷



The applied bias was then removed and the intensities of the absorption bands corresponding to PTZ^{\bullet^+} were monitored as a function of time to quantify the lifetimes of the oxidized forms. The final spectra were not superimposable with the initial spectra indicating that the source of signal diminution is due to dye decomposition rather than electrochemical one-electron reduction back to the neutral dye (Fig. S2, ESI⁺). **Dye-OMe** persisted the longest in the oxidized form with a half-life ($t_{1/2}$) of 13 min; the $t_{1/2}$ values for **Dye-H** and **Dye-Br** were measured to be 6 and 3 min, respectively (Fig. 4). These results are aligned with our expectation that the radical cationic form of the dyes are stabilized with electron-rich substituents.

We then set out to examine the performance of the dyes in the DSSC with an iodide-based electrolyte. The relevant energies of the dyes that govern the interfacial chemistry were deemed appropriate for sensitization: the excited-state reduction potentials, $E(S^+/S^*)$ (Table 1), were more negative than -0.50 V and therefore capable of injecting into the conduction band of TiO₂; and the HOMO levels were sufficiently positive to participate in the one-electron redox chemistry relevant for regeneration by iodide (Table 1).³⁹ Note that the HOMO level of **Dye-OMe** was measured to be +0.78 V νs . NHE and therefore lies at the threshold for regeneration by iodide (I^-/I_2^{-\bullet} ~ +0.8 V vs. NHE),¹³ but effective regeneration at these potentials are known.^{40,41} Data extracted from current-voltage plots (Fig. 5a) collected for devices containing each dye are listed in Table 2. The open-circuit potentials (V_{oc}), short-circuit currents (J_{sc}) and PCEs were progressively higher for **Dye-Br** < **Dye-H** < **Dye-OMe**. The J_{sc} values track the relative HOMO energies and the corresponding incident photon-to-current efficiencies (IPCEs; Fig. S3, ESI[†]). The higher minority carrier concentrations are also likely responsible for the higher $V_{\rm oc}$ values, as the negatively shifted HOMO level of Dye-OMe did not yield a lower photovoltage.

The temporal stabilities of the DSSCs with each of the three sensitizers were tested by subjecting each device to 300 h of



Fig. 4 Temporal change in UV-vis absorption at 580, 520 and 640 nm for the one-electron oxidized forms of immobilized **Dye-Br**, **Dye-H** and **Dye-OMe**, respectively. The dyes were each oxidized by applying a bias 100 mV more positive than the measured $E_{1/2}$ value for each dye for 1 min in 0.1 mM *n*-NBu₄PF₆ in MeCN. The first data points (*i.e.*, t = 0 s) corresponds to data recorded immediately after the system is returned to V_{oc} . Dashed lines indicate $t_{1/2}$.



Fig. 5 (a) Comparison of *I*–*V* curves for **Dye-Br** (blue), **Dye-H** (black) and **Dye-OMe** (red) at 0 h (solid) and 300 h (dashed) of sustained 1 Sun irradiation and constant temperature of 45 °C. (b) Open-circuit potential (V_{oc}) for dyes **Dye-Br**, **Dye-H** and **Dye-OMe** in a DSSC under constant illumination at AM 1.5 (1 Sun) and 45 °C for 300 h.

sustained 1 Sun irradiation at a constant temperature of 45 °C. Current–voltage (*I–V*) curves were recorded periodically to assess device stability (Fig. 5b). All three sensitizers retained > 75% of the original V_{oc} s and PCEs over this period, with very little differences in degradation rates across the series. These accelerated aging tests demonstrate that the PTZ unit is indeed a stable building block for organic sensitizers. The nominal differences in device stabilities revealed that there is little correlation between device stability and stability of the oxidized dyes for this series. In fact, the highest rate of dye deterioration was measured for **Dye-OMe**, the dye that displayed the longest PTZ⁺ lifetime.

These results implicate other factors such as dye desorption playing a more dominant role in affecting DSSC stability. We analyzed the relative rates of dye desorption for the series by immersing sensitized TiO₂ substrates in electrolyte solutions and tracking the changes in dye coverage spectrophotometrically (Fig. S7, ESI[†]). Dye-OMe desorbed fastest, with merely 32% of the dye molecules remaining on the semiconductor after 5 days in the electrolyte. Substrates stained with Dye-H and Dye-Br retained 50% and 80%, respectively, of the dyes on the surface over this same period. This trend tracks the pK_as of the dyes that we measured in DMSO: 2.63, 2.73 and 2.91 for Dye-Br, Dye-H and Dye-OMe, respectively (Fig. S8, ESI⁺). These results point to the PTZ substituents affecting the acidity of the carboxylate unit and the binding to the TiO2. The most acidic Dye-Br likely loses the carboxylic acid proton on the anchoring group and the resulting carboxylate anion can form a more stable covalent bond with the TiO₂ than the protonated Dye-OMe that forms an intermolecular hydrogen bond with the semiconductor surface.

 Table 2
 Characterization parameters of solar cells sensitized by Dye-Br,

 Dye-H and Dye-OMe under 1.5 AM (1 Sun)

Dye	$J_{\rm sc}$ (mA cm ⁻²)	$V_{\rm oc}$ (mV)	Fill factor (FF)	η (%)
Dye-Br Dye-H Dye-OMe	$5.2 \pm 0.1 \\ 7.3 \pm 0.1 \\ 8.7 \pm 0.1$	$720 \pm 11 \\ 740 \pm 11 \\ 745 \pm 3$	$\begin{array}{c} 0.78 \pm 0.01 \\ 0.75 \pm 0.02 \\ 0.72 \pm 0.06 \end{array}$	$2.7 \pm 0.1 \\ 3.8 \pm 0.1 \\ 4.3 \pm 0.3$

The electrolyte solution contained 1.0 M 1,3-dimethylimidazolium iodide (DMII), 60 mM I_2 , 0.5 M *tert*-butylpyridine, 0.05 M NaI and 0.1 M GuNCS in a mixed solvent system of MeCN and valeronitrile (85:15, v/v). Averaged parameters with standard deviations from no fewer than two different devices are listed.

Published on 03 February 2017. Downloaded by Freie Universitaet Berlin on 03/02/2017 13:28:11.

Phenothiazine-based donor units are demonstrated to be stable chromophoric units in the DSSC. The stability of this unit following light-induced charge injection into a semiconductor is increased when electron-rich substituents are installed at the C3 and C7 positions. Notwithstanding, higher stability of the oxidized $PTZ^{\bullet+}$ units does not necessarily translate to higher DSSC stability, which is more sensitive to the pK_a of the linker unit for the series of dyes tested here. Studies are underway to extend the range of light absorption for these redox stable phenothiazine dyes to drive up the DSSC performance,⁴² and to explore alternative modes for securing the dyes to semiconductor surfaces.

Notes and references

- 1 B. O'Regan and M. Grätzel, Nature, 1991, 353, 737.
- 2 A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo and H. Pettersson, *Chem. Rev.*, 2010, **110**, 6595–6663.
- 3 W. Zeng, Y. Cao, Y. Bai, Y. Wang, Y. Shi, M. Zhang, F. Wang, C. Pan and P. Wang, *Chem. Mater.*, 2010, 22, 1915–1925.
- 4 Z. Yao, M. Zhang, H. Wu, L. Yang, R. Li and P. Wang, *J. Am. Chem. Soc.*, 2015, **137**, 3799–3802.
- 5 C.-C. Chou, F.-C. Hu, H.-H. Yeh, H.-P. Wu, Y. Chi, J. N. Clifford, E. Palomares, S.-H. Liu, P.-T. Chou and G.-H. Lee, *Angew. Chem.*, *Int. Ed.*, 2013, 53, 178–183.
- 6 P. G. Bomben, K. C. D. Robson, B. D. Koivisto and C. P. Berlinguette, *Coord. Chem. Rev.*, 2012, 256, 1438–1450.
- 7 K. C. D. Robson, P. G. Bomben and C. P. Berlinguette, *Dalton Trans.*, 2012, **41**, 7814.
- 8 E. Galoppini, Coord. Chem. Rev., 2004, 248, 1283-1297.
- 9 C.-H. Lee, Y. Zhang, A. Romayanantakit and E. Galoppini, *Tetrahedron*, 2010, **66**, 3897–3903.
- 10 T. Hewat, S. McDonald, J. Lee, M. Rahman, P. Cameron, F.-C. Hu, Y. Chi, L. J. Yellowlees and N. Robertson, *RSC Adv.*, 2014, 4, 10165–10175.
- 11 S. Ardo and G. J. Meyer, Chem. Soc. Rev., 2009, 38, 115-164.
- 12 P. G. Johansson, Y. Zhang, G. J. Meyer and E. Galoppini, *Inorg. Chem.*, 2013, 52, 7947–7957.
- 13 G. Boschloo and A. Hagfeldt, Acc. Chem. Res., 2009, 42, 1819-1826.
- 14 K. C. D. Robson, K. Hu, G. J. Meyer and C. P. Berlinguette, J. Am. Chem. Soc., 2013, 135, 1961–1971.
 15 S. L. C. Simon, F. C. L. Barlano, W. D. Swards, C. W. Kallett, C. D.
- 15 S. J. C. Simon, F. G. L. Parlane, W. B. Swords, C. W. Kellett, C. Du, B. Lam, R. K. Dean, K. Hu, G. J. Meyer and C. P. Berlinguette, *J. Am. Chem. Soc.*, 2016, **138**, 10406–10409.
- 16 W. B. Swords, S. J. C. Simon, F. G. L. Parlane, R. K. Dean, C. W. Kellett, K. Hu, G. J. Meyer and C. P. Berlinguette, *Angew. Chem.*, 2016, **128**, 6060–6064.
- 17 K. Hu, A. D. Blair, E. J. Piechota, P. A. Schauer, R. N. Sampaio, F. G. L. Parlane, G. J. Meyer and C. P. Berlinguette, *Nat. Chem.*, 2016, 8, 853–859.

- 18 G. Li, A. Yella, D. G. Brown, S. I. Gorelsky, M. K. Nazeeruddin, M. Grätzel, C. P. Berlinguette and M. Shatruk, *Inorg. Chem.*, 2014, 53, 5417–5419.
- 19 D.-Y. Chen, Y.-Y. Hsu, H.-C. Hsu, B.-S. Chen, Y.-T. Lee, H. Fu, M.-W. Chung, S.-H. Liu, H.-C. Chen, Y. Chi and P.-T. Chou, *Chem. Commun.*, 2010, 46, 5256.
- 20 S. Mathew, A. Yella, P. Gao, R. Humphry-Baker, B. F. E. Curchod, N. Ashari-Astani, I. Tavernelli, U. Rothlisberger, M. K. Nazeeruddin and M. Grätzel, *Nat. Chem.*, 2014, 6, 242–247.
- 21 R. Katoh, A. Furube, S. Mori, M. Miyashita, K. Sunahara, N. Koumura and K. Hara, *Energy Environ. Sci.*, 2009, **2**, 542.
- 22 T. Duan, T.-Y. Hsiao, Y. Chi, X. Chen, Y. He and C. Zhong, *Dyes Pigm.*, 2016, **124**, 45–52.
- 23 W. Zhu, Y. Wu, S. Wang, W. Li, X. Li, J. Chen, Z.-S. Wang and H. Tian, *Adv. Funct. Mater.*, 2010, **21**, 756–763.
- 24 Y. Wu and W. Zhu, Chem. Soc. Rev., 2013, 42, 2039-2058.
- 25 A. Baheti, K. R. Justin Thomas, C.-P. Lee, C.-T. Li and K.-C. Ho, *J. Mater. Chem. A*, 2014, **2**, 5766.
- 26 A. Baheti, K. R. Justin Thomas, C.-T. Li, C.-P. Lee and K.-C. Ho, ACS Appl. Mater. Interfaces, 2015, 7, 2249-2262.
- 27 S. Ergun, C. F. Elliott, A. P. Kaur, S. R. Parkin and S. A. Odom, *Chem. Commun.*, 2014, **50**, 5339–5341.
- 28 T.-S. Hsieh, J.-Y. Wu and C.-C. Chang, Dyes Pigm., 2015, 112, 34-41.
- 29 A. P. Kaur, M. D. Casselman, C. F. Elliott, S. R. Parkin, C. Risko and S. A. Odom, *J. Mater. Chem. A*, 2016, 4, 5410–5414.
- 30 A. P. Kaur, C. F. Elliott, S. Ergun and S. A. Odom, J. Electrochem. Soc., 2015, 163, 1–7.
- 31 H.-H. Gao, X. Qian, W.-Y. Chang, S.-S. Wang, Y.-Z. Zhu and J.-Y. Zheng, J. Power Sources, 2016, 307, 866–874.
- 32 G. B. Bodedla, K. R. J. Thomas, C.-T. Li and K.-C. Ho, RSC Adv., 2014, 4, 53588–53601.
- 33 Z.-S. Huang, H. Meier and D. Cao, J. Mater. Chem. C, 2016, 4, 2404-2426.
- 34 J.-S. Luo, Z.-Q. Wan and C.-Y. Jia, Chin. Chem. Lett., 2016, 27, 1304–1318.
- 35 Z. Iqbal, W.-Q. Wu, Z.-S. Huang, L. Wang, D.-B. Kuang, H. Meier and D. Cao, *Dyes Pigm.*, 2016, **124**, 63–71.
- 36 M. V. Jovanovic and E. R. Biehl, J. Org. Chem., 1984, 49, 1905-1908.
- 37 S.-H. Lee, C. T.-L. Chan, K. M.-C. Wong, W. H. Lam, W.-M. Kwok and V. W.-W. Yam, J. Am. Chem. Soc., 2014, 136, 10041–10052.
- 38 K. C. D. Robson, B. Sporinova, B. D. Koivisto, E. Schott, D. G. Brown and C. P. Berlinguette, *Inorg. Chem.*, 2011, **50**, 6019–6028.
- 39 F. Wu, L. T. L. Lee, J. Liu, S. Zhao, T. Chen, M. Wang, C. Zhong and L. Zhu, Synth. Met., 2015, 205, 70–77.
- 40 F. M. Jradi, X. Kang, D. O'Neil, G. Pajares, Y. A. Getmanenko, P. Szymanski, T. C. Parker, M. A. El-Sayed and S. R. Marder, *Chem. Mater.*, 2015, 27, 2480–2487.
- 41 Y.-T. Li, C.-L. Chen, Y.-Y. Hsu, H.-C. Hsu, Y. Chi, B.-S. Chen, W.-H. Liu, C.-H. Lai, T.-Y. Lin and P.-T. Chou, *Tetrahedron*, 2010, 66, 4223–4229.
- 42 V. A. Chiykowski, B. Lam, C. Du and C. P. Berlinguette, *Chem. Commun.*, 2017, DOI: 10.1039/c6cc09178d.