New platinum(II) polypyridyl photosensitizers for TiO_2 solar cells

Letter

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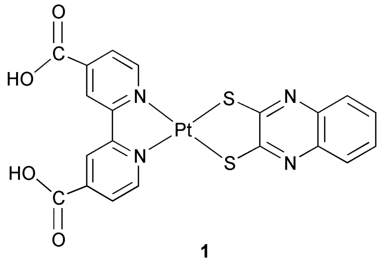
A square-planar platinum(II) based dye containing 4,4′-dicarboxy-2,2′-bipyridine and quinoxaline-2,3-dithiolate ligands achieves efficient sensitization of nanocrystalline TiO_2 solar cells over a wide visible range, generating a short-circuit photocurrent of 6.14 mA cm^{-2} and an open-circuit potential of 600 mV under simulated AM 1.5 solar irradiation, with a solar energy conversion efficiency of 2.6%.

Photoelectrochemical systems with dye-sensitized metal oxide semiconductor electrodes have allowed the construction of low-cost photovoltaic devices over past two decades.[1] Several organic dyes[1–4] and transition metal complexes of Ru(II),[5–8] Os(II)[9] and Fe(II)[10] have been employed in solar cells to sensitize nanocrystalline metal oxide semiconductors. So far, the most successful sensitizers employed in these devices are diimine-type complexes of ruthenium(II) anchored to nanocrystalline TiO_2 films, yielding overall AM 1.5 solar-to-electric power conversion efficiencies of up to 11%.[5,6] Octahedral ruthenium(II) polypyridyl complexes are found to be attractive sensitizers due to their favorable light absorption, redox properties, luminescence emission, excited state lifetime and photostability in the device.[5–8]

Luminescence from square-planar platinum(II) complexes has been known for many years but restricted mainly to the solid state or in frozen glasses.[11–13] In recent years, a number of Pt(II) complexes with chelating diimine and its derivatives have been synthesized that display long-lived solution luminescence under ambient conditions.[14] Eisenberg and co-workers have made elaborate studies on the excited state of mixed-ligand platinum(II) complexes with diimine and dithiolate ligands, over the past decade.[15–17] These complexes have a long-lived charge transfer excited state, which is emissive in fluid solution at room temperature and undergoes electron transfer quenching both oxidatively and reductively.[15,17] The charge transfer excited state energies of Pt(diimine)(dithiolate) complexes can be tuned about 1 eV through changes in the electron donating and accepting abilities of the diimine and dithiolate ligands.[17] Though a large number of square-planar platinum(II) complexes represent a promising class of charge transfer sensitizers, they have not been fabricated into solar cells until now. In order to study the photoelectrochemical performance of Pt(II) based sensitizers, we have synthesized $Pt(H_2dcbpy)(qdt)$, **1**, and $Pt(H_2dcphen)(qdt)$, **2** (H_2dcbpy = 4,4′-dicarboxy-2,2′-bipyridine, $H_2dcphen$ = 4,7-dicarboxy-1,10-phenanthroline, and qdt = quinoxaline-2,3-dithiolate). We have achieved for the first time a solar-to-electric power conversion efficiency of about 2.5%, using these square-planar platinum(II) diimine dithiolate dyes (**1** and **2**) anchored to nanocrystalline TiO_2films.

$Pt(H_2dcbpy)Cl_2$ and $Pt(H_2dcphen)Cl_2$ were prepared by boiling a reaction mixture of potassium tetrachloroplatinate(II) (1.0 mmol), KCl (600 mg) and the corresponding diimine ligand (1.02 mmol) in 50 ml of water for 4 h. A few drops of 0.1 M KOH were added to the mixture to help dissolve the ligand. The light yellow product that precipitated was filtered out, washed with hot water and dried under vacuum. Complexes **1** and **2** were prepared by adding a degassed solution of H_2qdt (0.62 mmol) in MeOH (5 ml) to a degassed solution of $Pt(H_2dcbpy)Cl_2$ or $Pt(H_2dcphen)Cl_2$ (0.6 mmol) in aqueous 0.1 M KOH (30 ml). The solution turned red-orange after 10 min and was allowed to stir at room temperature for 2 h.[16] The product was precipitated out by adding 0.1 M HCl, filtered off and washed several times with water. Both $Pt(H_2dcbpy)(qdt)$ and $Pt(H_2dcphen)(qdt)$ were purified on a Sephadex LH-20 column.

The platinum(II) diimine dithiolate complexes (**1** and **2**) exhibit a broad band in the 350–550 nm range of their respective absorption spectra, with a molar extinction coefficient of 10 000–13 000 M^{-1} cm^{-1} [Fig. 1(*a*)]. This band is assigned as mixed Pt/qdt-to-diimine charge transfer excited state,[16] involving a transition from a HOMO that has a mixture of Pt and qdt orbital character to a LUMO that is a low-energy π^* orbital of the diimine ligands. The visible bands in the absorption spectra of both **1** and **2** broaden and are red-shifted upon adsorption onto TiO_2 (Fig. 2). When excited within the charge transfer absorption band, complex **1** in degassed ethanol–methanol solution at 298 K exhibits a luminescence consisting of a broad band with a maximum at 650 nm, as shown in Fig. 1(*b*). A structured emission with a maximum at 575 nm was observed in an ethanol–methanol glass matrix at 77 K. The excited state lifetime of complex **1** was measured to be 50 μs at 77 K, which decreased with increasing temperature and became 57 ns in fluid solution at 298 K. The very short-lived excited state in fluid solution may be caused by efficient non-radiative decay *via* low-lying ligand field excited states or solvent interactions in the open coordination sites.[13] The



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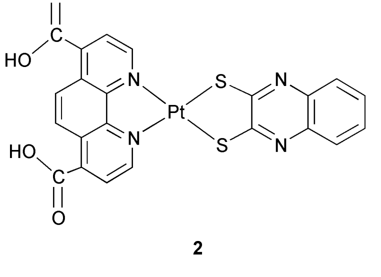

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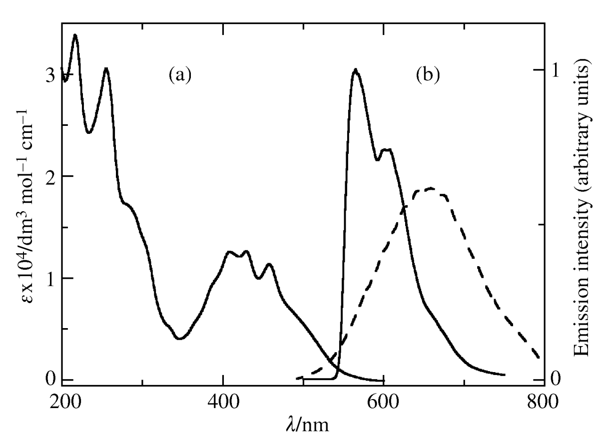

Fig. 1 Absorption and emission spectra of Pt(H$_2$dcbpy)(qdt) in ethanol–methanol (4 : 1, v/v): (*a*) absorption spectrum at 298 K; (*b*) emission spectra at 298 K (– – –) and at 77 K (——).

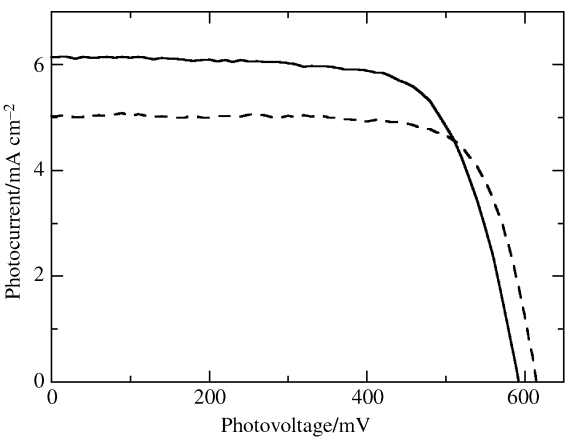

Fig. 3 Photocurrent–photovoltage curve under simulated AM 1.5 solar irradiation of Pt(H$_2$dcbpy)(qdt) (——) and Pt(H$_2$dcphen)(qdt) (– – –) on TiO$_2$. The counter electrode is platinum and the electrolyte solution is 0.6 M dimethylpropylimidazolium iodide, 0.05 M I$_2$, 0.5 M *tert*-butylpyridine and 0.1 M LiI in methoxyacetonitrile. Size of the TiO$_2$ electrode was 0.25 cm^2. Performance parameters are listed in Table 1.

cyclic voltammograms of complexes **1** and **2**, measured in DMF containing 0.1 M tetra-*n*-butylammonium perchlorate, show one irreversible wave for the Pt$^{3+/2+}$ couple at +0.8 and +0.9 V[18] *vs.* SCE, respectively. All the photophysical, electrochemical and photoelectrochemical properties of **1** and **2** are collected in Table 1. The excited state oxidation potentials of these complexes are estimated to be < −1.01 V *vs.* SCE from the electrochemical and spectroscopic data.[19] The excited states have enough thermodynamic driving force to inject an electron into the conduction band[20] of the nanocrystalline TiO$_2$ semiconductor.

Coating of TiO$_2$ nanocrystalline films with complexes **1** and **2** was carried out by dipping 12 nm thick films overnight in a 5 x 10^{-5} M ethanolic solution of **1** or **2**, containing 40 mM deoxycholic acid, 7% *tert*-butylpyridine and 3% DMSO. The surface concentration of both **1** and **2** on TiO$_2$ film is around 9.5 x 10^{-8} mol cm^{-2}. The presence of deoxycholic acid and *tert*-butylpyridine, as a co-adsorbent, are found to be necessary to prevent stacking[13] and/or self-quenching[21] of the dye molecules. Square-planar platinum(II) complexes are known to exhibit intermolecular stacking interactions in solution and in the solid state. Photoelectrochemical experiments of the dye sensitized semiconductor electrode films were performed with a sandwich-type solar cell,[8] in conjunction with a redox electrolyte consisting of a solution of 0.6 M dimethylpropylimidazolium iodide, 0.05 M I$_2$, 0.5 M *tert*-butylpyridine and 0.1 M LiI in methoxyacetonitrile. Fig. 2 shows the photocurrent action spectra of such a cell sensitized by complexes **1** and **2**, where the incident photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. Both **1** and **2** achieved efficient sensitization of nanocrystalline TiO$_2$ solar cells over a wide visible range, displaying a maximum around 500 nm, where IPCE approaches a high value of about 30%. A short-circuit photocurrent of 6.14 mA cm^{-2} and an open-circuit potential of 600 mV with an impressive

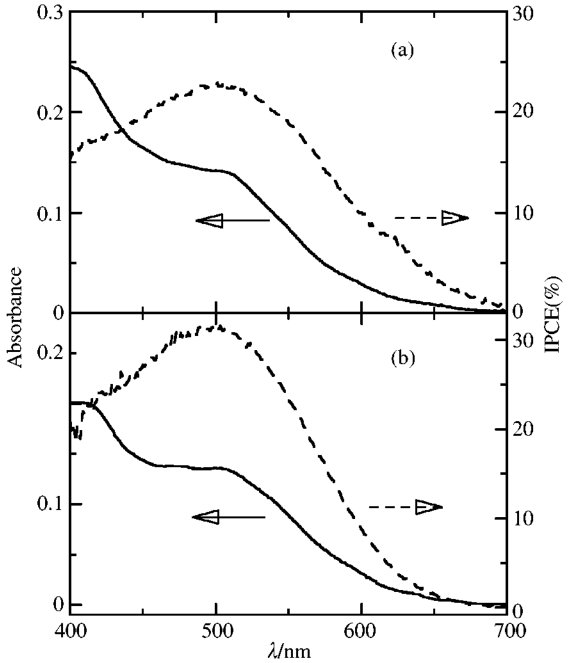

Fig. 2 Absorption spectra (——) of Pt(H$_2$dcbpy)(qdt) (*a*) and Pt(H$_2$dcphen)(qdt) (*b*) anchored to transparent films of TiO$_2$; spectra are corrected for undyed TiO$_2$ film. Photocurrent action spectra (– – –) of Pt(H$_2$dcbpy)(qdt) (*a*) and Pt(H$_2$dcphen)(qdt) (*b*) dyed films of TiO$_2$. The incident photon-to-current conversion efficiency (IPCE) is plotted as a function of wavelength. A sandwich-type cell configuration was used to measure these spectra.

Table 1 Photophysical, electrochemical and photoelectrochemical properties of Pt(diimine)(dithiolate) complexes

Dye	Abs[a] λ_{max}/nm (ε/10^3 M^{-1} cm^{-1})	Emission[a] λ_{max}/nm		τ/μs[a]		$E_{1/2}$/V *vs.* SCE		IPCE /% (max)	I_{SC}/mA cm^{-2}	V_{OC}/mV	ff	η/%
		298 K	77 K	298 K	77 K	$E^{0/-}$	$E^{+/0}$[b]					
1	460, 425 (10.3)	650	557	0.057	50	−1.1	+0.8	23	6.14	593	0.705	2.57
2	480, 420 (15.3)	640	557	0.155	53	−1.0	+0.9	32	5.02	615	0.755	2.33

[a] Measured in ethanol–methanol (4 : 1) solution. [b] E_p anodic peak potential from irreversible couple.

fill factor of 0.71 were obtained for **1** under simulated AM 1.5 solar irradiation, corresponding to an overall efficiency of 2.6% (Fig. 3). These results show that high injection efficiencies can be achieved for this class of square-planar platinum(II) diimine dithiolate sensitizers, leading to efficient photovoltaic devices. A further improvement in the conversion efficiency is possible by increasing the spectral response in the low-energy part of the solar spectrum. Work on the optimization of the cell efficiency and its stability under long-term irradiation is in progress.

Acknowledgements

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Notes and references

† MS (ESI) *m*/*z*: 314.1 $(M-2\,H)^{2-}$, 629.7 $(M-H)^{-}$, 651.3 $(M-H+Na)^{-}$. ^{1}H-NMR (300 MHz, D_2O–NaOD): δ 8.76 (d), 8.38 (s), 8.00 (d), 7.84 (d), 7.54 (q), 7.41 (q), 7.39 (s), 7.17 (d), 7.10 (q), 6.91 (q).

‡ MS (ESI) *m*/*z*: 326.7 $(M-2\,H)^{2-}$, 691.6 $(M-H+K)^{-}$. ^{1}H-NMR (300 MHz, D_2O–NaOD): δ 8.68 (2 H, d), 7.84 (2 H, d), 7.68 (2 H, s), 6.69 (2 H, q), 6.56 (2 H, q).

1 H. Tsubomura, M. Matsumura, Y. Nomura and T. Amamiya, *Nature* (*London*), 1976, **261**, 402.

2 C. Nasr, D. Liu, S. Hotchandani and P. V. Kamat, *J. Phys. Chem.*, 1996, **100**, 11054.

3 J. Moser and M. Grätzel, *J. Am. Chem. Soc.*, 1984, **106**, 10769.

4 K. Sayama, M. Sugino, H. Sugihara, Y. Abe and H. Arakawa, *Chem. Lett.*, 1998, 753.

5 B. O'Regan and M. Grätzel, *Nature* (*London*), 1991, **353**, 737.

6 M. K. Nazeeruddin, A. Kay, I. Rodicio, R. Humphry-Baker, E. Müller, P. Liska, N. Vlachopoulos and M. Grätzel, *J. Am. Chem. Soc.*, 1993, **115**, 6382.

7 R. Argazzi, C. A. Bignozzi, G. M. Hasselmann and G. J. Meyer, *Inorg. Chem.*, 1998, **37**, 4533.

8 (*a*) H. Sugihara, L. P. Singh, K. Sayama, H. Arakawa, M. K. Nazeeruddin and M. Grätzel, *Chem. Lett.*, 1998, 1005; (*b*) K. Sayama, H. Sugihara and H. Arakawa, *Chem. Mater.*, 1998, **10**, 3825.

9 (*a*) T. A. Heimer, C. A. Bignozzi and G. J. Meyer, *J. Phys. Chem.*, 1993, **97**, 11987; (*b*) M. Alebbi, C. A. Bignozzi, T. A. Heimer, G. M. Hasselmann and G. J. Meyer, *J. Phys. Chem. B*, 1998, **102**, 7577.

10 S. Ferrere and B. A. Gregg, *J. Am. Chem. Soc.*, 1998, **120**, 843.

11 (*a*) D. L. Webb and L. A. Rossiello, *Inorg. Chem.*, 1971, **10**, 2213; (*b*) C. E. Johnson, R. Eisenberg, T. R. Evans, T. R. Evans and M. S. Burberry, *J. Am. Chem. Soc.*, 1983, **105**, 1795.

12 A. Islam, Y. Okamoto, N. Ikeda, K. Nozaki, A. Yoshimura, G. Bovak and T. Ohno, *Coord. Chem. Rev.*, 1998, **171**, 355.

13 J. A. Bailey, M. G. Hill, R. E. Marsh, V. M. Miskowski, W. P. Schaefer and H. B. Gray, *Inorg. Chem.*, 1995, **34**, 4591.

14 (*a*) R. Ballardini, G. Varani, M. T. Indelli and F. Scandola, *Inorg. Chem.*, 1986, **25**, 3858; (*b*) D. Sandrini, M. Maestri, V. Balzani, L. Chassot and A. von Zelewsky, *J. Am. Chem. Soc.*, 1987, **109**, 7720.

15 (*a*) J. A. Zuleta, M. S. Burberry and R. Eisenberg, *Coord. Chem. Rev.*, 1990, **97**, 47; (*b*) W. Paw, S. D. Cummings, M. A. Mansour, W. B. Connick, D. K. Geiger and R. Eisenberg, *Coord. Chem. Rev.*, 1998, **171**, 125.

16 (*a*) S. D. Cummings and R. Eisenberg, *Inorg. Chem.*, 1995, **34**, 2007; (*b*) S. D. Cummings and R. Eisenberg, *Inorg. Chem.*, 1995, **34**, 3396.

17 S. D. Cummings and R. Eisenberg, *J. Am. Chem. Soc.*, 1996, **118**, 1949.

18 The irreversible wave observed for the $Pt^{3+/2+}$ couple of complex **2** at +0.9 V *vs.* SCE is 0.15 V more positive than the corresponding process in Pt(phen)(qdt).[15] This is attributed to the electron withdrawing nature of the carboxylic acid functionality, which reduces the electron density around the metal center.[6]

19 The 0–0 transition energies of about 1.9 eV for **1** and **2** are estimated from the rise of their absorption spectra (adsorbed on TiO_2, Fig. 2).

20 G. Redmond and D. Fitzmaurice, *J. Phys. Chem.*, 1993, **97**, 1426.

21 (*a*) W. B. Connick, D. Geiger and R. Eisenberg, *Inorg. Chem.*, 1999, **38**, 3264; (*b*) W. B. Connick and H. B. Gray, *J. Am. Chem. Soc.*, 1997, **119**, 11620.