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solar cells

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An element of surprise—efficient copper-functionalized dye-sensitized solar cells†

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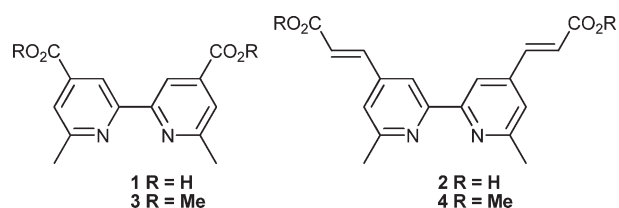
Dye-sensitized solar cells with carboxylate-derivatized {Cu^{I}L$_2$} complexes are surprisingly efficient and offer a long-term alternative approach to ruthenium-functionalized systems.

Dye-sensitized solar cells (DSSCs) are currently under active investigation as alternatives to silicon-based photovoltaic devices for solar energy utilization.[1] Typical DSSCs contain a nanoparticulate semiconductor substrate functionalized with a dye-stuff possessing a narrower band gap than that of the semiconductor.[2] In the commonest type of DSSC, the so-called Graetzel cell, the semiconductor is anatase-like TiO$_2$ and the dye-stuffs are ruthenium-oligopyridine complexes.[3,4] It was early recognized that copper(I) complexes with 2,9-disubstituted 1,10-phenanthroline ligands possessed similar photophysical properties to archetypal [Ru(bpy)$_3$]$^{2+}$ salts (bpy = 2,2′-bipyridine).[5–7] A significant difference between d^{10} copper(I) complexes and low spin d^6 ruthenium(II) complexes lies in the anticipated greater lability of the former. Nevertheless, it is surprising that, to the best of our knowledge, only two reports of DSSCs with copper(I) dyes have been reported.[8,9] In this *communication* we show that copper(I) complexes of 6,6′-disubstituted 2,2′-bipyridines are generally effective sensitizers for TiO$_2$ and demonstrate the tuning of the absorption maximum and report surprisingly high incident-photon to current efficiencies (IPCE) for DSSCs assembled using these dyes.

In order to form stable copper(I) complexes which can be bound to TiO$_2$, the ligands must (i) possess carboxylic or phosphonic acid substituents to link to the surface and (ii) substituents at the 6- and 6′-positions to stabilize the copper(I) state. Accordingly, we considered the two bpy ligands **1** and **2** which differ in the extent of conjugation, which was expected to have an influence on the absorption spectrum. Ligand **1** was obtained by minor variations of the literature procedure[10] whereas **4** was prepared in 74% yield by the Wittig reaction of 6,6′-dimethyl-2,2′-bipyridine-4,4′-dicarbaldehyde[11] with Ph$_3$P=CHCO$_2$Me analogous to the known preparation of the *tert*-butyl ester of **1**.[11] Hydrolysis of **4** with LiOH in 10 : 1 thf–H$_2$O followed by acidification with 2 M HCl gave **2** as a white solid‡ whilst **1** was converted quantitatively to **3** upon boiling with MeOH and H$_2$SO$_4$. The copper(I) complexes [Cu(L)$_2$][PF$_6$] (L = **3** or **4**§) were prepared as red solids by the reaction of the appropriate ligand with [Cu(CH$_3$CN)$_4$][PF$_6$] in CHCl$_3$–MeCN. The complexes of the free acids were prepared by reaction of the sodium salts with copper(II) sulfate followed by reduction with ascorbic acid.[9]

The influence of the extended conjugation is best seen in comparing the complexes [Cu(**3**)$_2$][PF$_6$] and [Cu(**4**)$_2$][PF$_6$]. In MeCN solutions of the former, the MLCT band is observed with λ_{max} 495 nm and ε 450 M^{-1} cm^{-1} whereas in the more conjugated complex [Cu(**4**)$_2$][PF$_6$] the absorption is red-shifted to λ_{max} 506 nm and ε increases dramatically to 3650 M^{-1} cm^{-1}. Both of these observations indicate that the extended conjugation in **4** has the expected effects when the complex is compared to that with **3**. This is confirmed in the complex [Cu(**2**-H)$_2$] which exhibits an MLCT absorption at 515 nm with ε 6740 M^{-1} cm^{-1}.

Complexes of the type [CuL$_2$]$^+$, where L is a diimine ligand, show a wide variety of structural variations,[12] and to confirm the geometry at the metal centre, the solid state structure of the complex [Cu(**3**)$_2$][PF$_6$] has been determined (Fig. 1).¶ The Cu–N distances are in the typical range 2.003(3)–2.039(3) Å and the bite-angles of the bpy-domains are also characteristic (∠N1–Cu1–N2, 80.93(10)°, ∠N3–Cu1–N4, 81.21(11)°). The cation is distorted significantly from the idealized D_{2d} symmetry and the analysis introduced by White *et al.* for 1,10-phenanthroline complexes provides a convenient method of quantifying this (provided that the two rings of each bpy ligand are approximately coplanar as in the case of [Cu(**3**)$_2$][PF$_6$] where the dihedral angles are in the range 2–4°).[13] For [Cu(**3**)$_2$][PF$_6$], values of θ_x, θ_y and θ_z of 97.27, 95.56 and 92.83° (with expectation values of $\theta_x = \theta_y = \theta_z = 90°$ for D_{2d} symmetry); the significant deviation of θ_x and θ_y from 90° indicate rocking and wagging displacements to produce a distorted trigonal pyramidal geometry.

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[b] *Department of Chemistry, University of Basel, Spitalstrasse 51, CH 4056 Basel, Switzerland. E-mail: edwin.constable@unibas.ch; Fax: +41 61 267 1005; Tel: +41 61 267 1001*

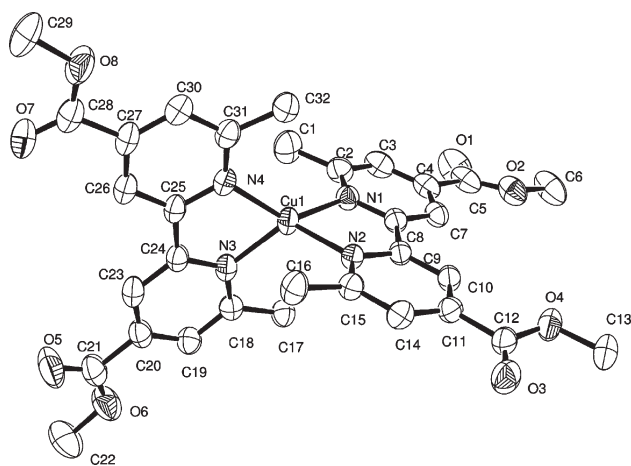**Fig. 1** Solid state structure of the $[Cu(3)_2]^+$ cation present in $[Cu(3)_2][PF_6]$ showing the numbering scheme adopted; hydrogen atoms have been omitted for clarity, thermal ellipsoids depicted at 50% probability. Selected bond lengths (Å) and angles (°): Cu1–N1, 2.009(2); Cu1–N2, 2.016(2); Cu1–N3, 2.039(3); Cu1–N4, 2.003(3); N1–Cu1–N2, 80.93(10); N1–Cu1–N3, 122.14(10); N2–Cu1–N3, 119.26(10); N1–Cu1–N4, 134.76(11); N2–Cu1–N4, 123.77(11); N3–Cu1–N4, 81.21(11).

Preliminary experiments indicated that {CuL$_2$} complexes with **1** and **2** bound strongly to TiO$_2$ nanoparticles whereas complexes with the ester **4** did not bind (Fig. 2). Surprisingly, $[Cu(3)_2][PF_6]$ also gave good dye-modified surfaces and we attribute this to *in situ* hydrolysis of the ester.

Solar cells were constructed using a standard protocol optimized for the production of ruthenium-sensitized dye-cells[14] and evaluated using a standard procedure.[15] In Fig. 3 we present the photovoltaic action spectra and current–voltage characteristics for devices fabricated with complexes of **1** and **2**. We do indeed observe significantly enhanced incident-photon to collected-electron quantum efficiency (IPCE) with complex **2** when compared to the complex **1**. By considering the molar extinction
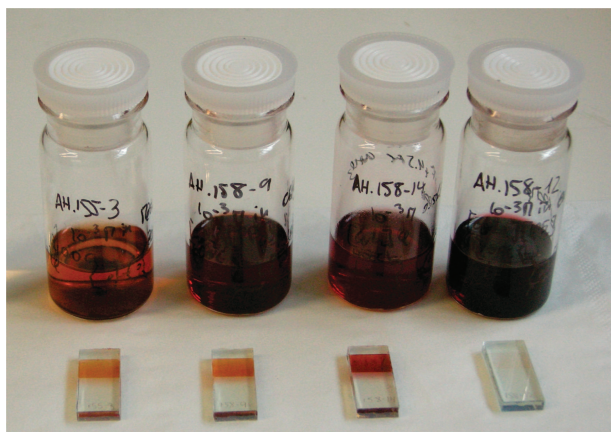

Fig. 2 Binding to TiO$_2$ of 10^{-3} M {CuL$_2$} complexes with (from left to right) **1**, **3**, **2** and **4**. The FTO (fluorine doped tin oxide) conducting glass slides were coated with 6–7 μm TiO$_2$ nanoparticles and then immersed in solutions (MeOH for **1**, CHCl$_3$ for **3** and **4**, and 1 : 9 DMF–CHCl$_3$ for **2**) for a period of 12 h.
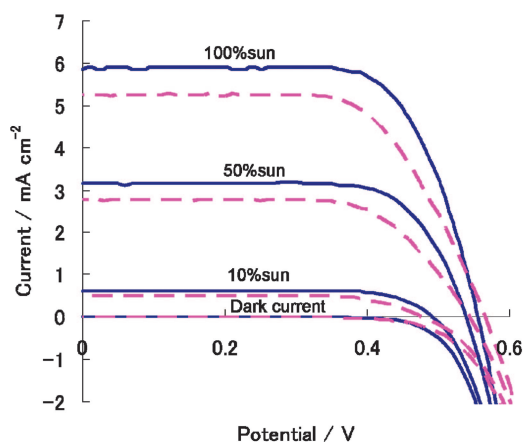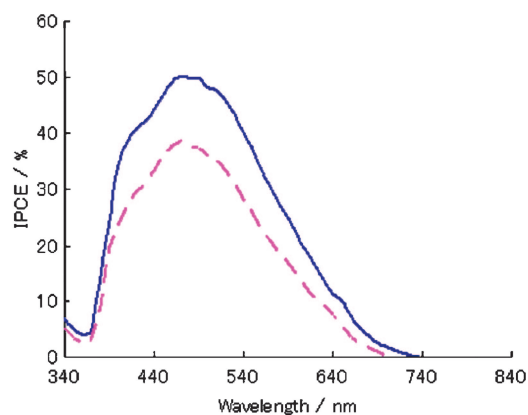

Fig. 3 IPCE (top) and *I*–*V* (bottom) curves for DSSCs prepared with copper(I) complexes of **1** (--) and **2** (—) at light intensity of 100%, 50% and 10% sun, respectively.

coefficients of the two complexes, in the device containing complex **1** we would expect a lower IPCE, and in our measurements we do observe this, with the IPCEs of the device containing the complex **2** being 50% compared to the complex **1**, which yielded only 38%.

Fig. 3 (bottom) shows the current–voltage curves measured under simulated air mass (AM) 1.5 solar illumination at an intensity of 100, 50 and 10 mW cm^{-2} and in the dark. We observe a slightly enhanced short-circuit current density and a reasonable decrease in the open-circuit voltage for the complex **2** compared to the complex **1**, resulting in power conversion efficiencies of 2.3 and 1.9%, respectively. We also tested the effects of solvent on dye deposition and the addition of chenodeoxycholic acid,[4] which is known to reduce dye loading while having a relatively small effect on the short-circuit photocurrent and improving the photovoltage. The data obtained after deposition from ethanol solution are superior to those from acetonitrile or *tert*-butanol solutions. Adding chenodeoxycholic acid did not improve the efficiency compared to comparable cells without chenodeoxycholic acid.

Table 1 shows current–voltage characteristics data for solar cells derivatized with copper(I) complexes of **1** and **2**, which were obtained with a nanocrystalline TiO$_2$ film supported on FTO conducting glass using an electrolyte solution containing 0.6 M *N*-methyl-*N*-butylimidazolium iodide, 0.03 M iodine, 0.1 M LiI, 0.1 M guanidinium

Table 1 Current–voltage characteristics data derivatized with copper(I) complexes of **1** and **2** and a comparison with the ruthenium dye N719[16,a]

L	V_{OC}/mV	Jsc/mA cm^{-2}	FF (%)	Ef (%)	IPCE(max) (%)	nm
1	566	5.25	0.64	1.9	38.6	470
2	556	5.9	0.7	2.3	50.1	470
N719	767	17.7	0.71	9.7	87	550

^{a} 7.4 + 4.4 μm double layer sensitized nanocrystalline TiO$_2$ film on FTO conducting glass; electrolyte: 0.6 M N-methyl-N-butylimidazolium iodide, 0.03 M I$_2$, 0.1 M LiI, 0.1 M guanidinium thiocyanate and 0.5 M tert-butylpyridine in 15 : 85 (v/v) valeronitrile–acetonitrile. V_{OC} = open circuit potential, Jsc = short circuit current, FF = fill factor, Ef = power conversion efficiency, IPCE = incident photon to current efficiency.

thiocyanate and 0.5 M *tert*-butylpyridine in a 15 : 85 (v/v) mixture of valeronitrile and acetonitrile. The data represent the optimized results for cells, measured using 7.4 + 4.4 μm double layer sensitized TiO$_2$ films. In order to reduce scattered light from the edge of the glass electrodes of the dyed TiO$_2$ layer, a light shading mask was used on the DSSCs, so that the active area of the DSSC was fixed at 0.2 cm^2.

The copper complexes {Cu^{I}L$_2$} are surprisingly effective as sensitizers for DSSCs. Although these initial results are not comparable with state of the art ruthenium dyes such as N719, they indicate that with iterative chemical optimization, sensitizers comparable to ruthenium complexes might be prepared. However, the "Techno-Economic" analyses of the two sensitizers clearly show that even though the efficiency of the copper complex is 4 times lower than that of the ruthenium sensitizer N719,[16] the cost is an order of magnitude lower. We are currently developing new copper-based dyes that are (i) red-shifted and (ii) more efficient and evaluating copper-based *versus* organic[17] or state of the art ruthenium[18] dyes for next generation devices.

In conclusion, we have shown that copper(I)-based complexes may effectively replace ruthenium(II) complexes in DSSCs and that the tuning methods applied to the latter are also effective in optimizing the behaviour of copper-sensitized systems.

Notes and references

‡ **2**: ^{1}H NMR (500 MHz, TFA): δ/ppm 8.60 (s, 2H, H3), 8.24 (s, 2H, H5), 8.00 (d, 2H, J 16.0 Hz, H8), 7.15 (d, 2H, J 16.0 Hz, H9), 3.06 (s, 6H, H7). ^{13}C NMR (125 MHz, TFA): δ/ppm 171.93 (C10), 161.26 (C6), 155.42 (C4), 144.11 (C2), 141.54 (C8), 131.78 (C9), 130.89 (C5), 126.26 (C3). Found: C, 60.65; H, 5.60; N, 7.20. Calc. for C$_{18}$H$_{16}$N$_2$O$_4$·2H$_2$O: C, 59.99; H, 5.59; N, 7.77%.
§ **[Cu(4)$_2$][PF$_6$]**: **4** (35.2 mg, 0.1 mmol) in CHCl$_3$ (3 mL) was treated with [Cu(CH$_3$CN)$_4$][PF$_6$] (18.6 mg, 0.05 mmol) in CH$_3$CN (2 mL) to give a red solution that was refluxed for 1 h. After cooling, the complex was precipitated with Et$_2$O. Red powder (41 mg, 45%). ^{1}H NMR (500 MHz, CDCl$_3$): δ/ppm 8.26 (s, 2H), 7.74 (d, 2H, J 15.8 Hz), 7.56 (s, 2H), 6.83 (d, 2H, J 16.1 Hz), 3.87 (s, 6H), 2.26 (s, 6H). UV-Vis, $λ_{max}$/nm ($ε_{max}$/M^{-1} cm^{-1}): 255 (94 200), 324 (24 200), 508 (3650). ESMS m/z: 767.5 ([Cu(**4**)$_2$]$^+$). Found: C, 49.29; H, 4.15; N, 5.71. Calc. for C$_{40}$H$_{40}$CuF$_6$N$_4$O$_8$P·3H$_2$O: C, 49.67; H, 4.79; N, 5.79%.
¶ C$_{32}$H$_{32}$CuF$_6$N$_4$O$_8$P, M = 809.14, monoclinic, space group $P2_1/c$, purple plates, Z = 4, a = 10.8110(2), b = 20.0824(4), c = 16.3507(3) Å, β = 98.681(1)°, V = 3509.3(1) Å^3, D_c = 1.531 Mg m^{-3}, μ(Mo-Kα) = 0.755 mm^{-1}, T = 173 K, 7729 reflections collected. Refinement of 469 parameters using 4831 reflections with $I > 1.5σ(I)$ converged at final R1 = 0.0505 (R1 all data = 0.0890), wR2 = 0.0564 (wR2 all data = 0.0779), gof = 1.241.†

1 M. K. Nazeeruddin and M. Graetzel, *Struct. Bonding*, 2007, **123** 113.
2 F. O. Lenzmann and J. M. Kroon, *Advances in OptoElectronics*, 2007, DOI: 10.1155/2007/65073.
3 B. O'Regan and M. Grätzel, *Nature*, 1991, **353**, 737.
4 N. R. Neale, N. Kopidakis, J. van de Lagemaat, M. Grätzel and A. J. Frank, *J. Phys. Chem. B*, 2005, **109**, 23183.
5 D. R. McMillin, M. T. Buckner and B. T. Ahn, *Inorg. Chem.*, 1977, **16**, 943.
6 N. Armaroli, *Chem. Soc. Rev.*, 2001, **30**, 113.
7 D. R. McMillin and K. M. McNett, *Chem. Rev.*, 1998, **98** 1201.
8 N. Alonse-Vante, J.-F. Nierengarten and J.-P. Sauvage, *J. Chem. Soc., Dalton Trans.*, 1996, 1649.
9 S. Sakaki, T. Kuroki and T. Hamada, *J. Chem. Soc., Dalton Trans.*, 2002, 840.
10 V.-M. Mukkala and J. J. Kankare, *Helv. Chim. Acta*, 1992, **75**, 1578.
11 M. M. Harding, U. Koert, J.-M. Lehn, A. Marquis-Rigault, C. Piguet and J. Siegel, *Helv. Chim. Acta*, 1991, **74**, 594.
12 E. C. Constable, V. Chaurin, C. E. Housecroft, M. Neuburger and S. Schaffner, *CrystEngComm*, DOI: 10.1039/b801019f.
13 J. F. Dobson, B. E. Green, P. C. Healy, C. H. L. Kennard, C. Pakawatchai and A. H. White, *Aust. J. Chem.*, 1984, **37**, 649.
14 S. Ito, P. Chen, P. Comte, M. K. Nazeeruddin, P. Liska, P. Pechy and M. Graetzel, *Prog. Photovoltaics*, 2007, **15**, 603.
15 S. Ito, T. N. Murakami, P. Comte, P. Liska, C. Grätzel, M. K. Nazeeruddin and M. Grätzel, *Thin Solid Films*, 2008, **516** 4613.
16 M. K. Nazeeruddin, R. Splivallo, P. Liska, P. Comte and M. Grätzel, *Chem. Commun.*, 2003, 1456.
17 J.-H. Yum, S.-R. Jang, P. Walter, T. Geiger, F. Nüesch, S. Kim, J. Ko, M. Grätzel and M. D. Nazeeruddin, *Chem. Commun.*, 2007, 4680.
18 F. Gao, Y. Wang, J. Zhang, D. Shi, M. Wang, R. Humphry-Baker, P. Wang, S. M. Zakeeruddin and M. Grätzel, *Chem. Commun.*, 2008, 2635.