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## COMMUNICATION

The  $d^{10}$  route to dye-sensitized solar cells: step-wise assembly of zinc(II) photosensitizers on  $\text{TiO}_2$  surfaces†

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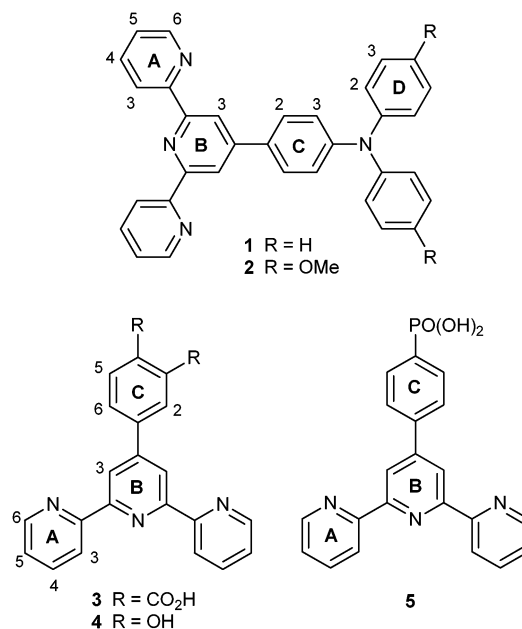
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Dye-sensitized solar cells have been assembled using a sequential approach: a  $\text{TiO}_2$  surface was functionalized with an anchoring ligand, followed by metallation with  $\text{Zn}(\text{OAc})_2$  or  $\text{ZnCl}_2$ , and subsequent capping with a chromophore functionalized 2,2':6',2''-terpyridine; the DSCs exhibit surprisingly good efficiencies confirming the effectiveness of the new strategy for zinc-based DSC fabrication.

Dye-sensitized solar cells (DSCs) are a promising technology for harnessing solar energy<sup>1,2</sup> with the photonic part comprising a semiconducting metal oxide functionalized with a coloured photosensitizer with the HOMO below and the LUMO above the conduction band. Although organic dyes are under active investigation, the commonest photosensitizers are transition metal complexes.<sup>2</sup> However, there are few examples of dye cells using earth abundant metals such as copper,<sup>3–7</sup> and the majority of complexes utilize less readily available transition elements such as ruthenium. Complexes of copper(I) and other  $d^{10}$  metal ions are of increasing interest for photonic applications<sup>8–11</sup> and we are currently investigating the use of zinc(II) complexes in OLEDs and LECs. In the course of these investigations we have isolated a series of intensely coloured zinc(II) complexes and in this communication we report the first use of zinc complexes (other than with porphyrin-type ligands)<sup>12,13</sup> as photosensitizers in DSCs.

Compounds **1**<sup>14–16</sup> and **2**<sup>17–19</sup> (Scheme 1) possess extended  $\pi$ -conjugated systems and the use of the triphenylamino-substituent provides a means of tuning the photophysical properties of the ligand through peripheral functionalization. The ligands were prepared in high yield by reactions of 4'-(4-bromophenyl)-2,2':6',2''-terpyridine with diphenylamine or 4,4'-dimethoxydiphenylamine, and were fully characterized by spectroscopic and mass spectrometric methods (ESI†). Of particular significance is the fact that the ligands are coloured. Their solution electronic absorption spectra extend into the



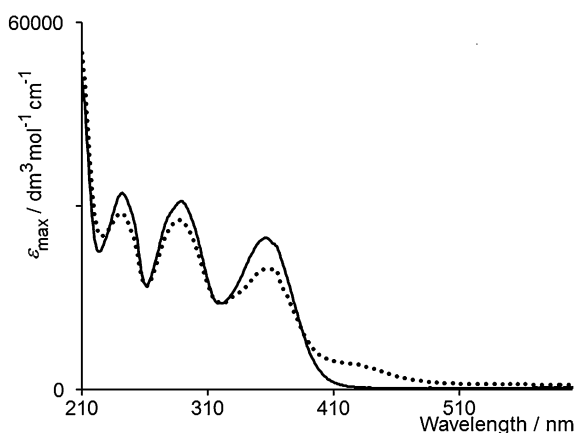
**Scheme 1** Chromophoric ligands **1** and **2**, and anchoring ligands **3–5** with atom numbering for NMR spectroscopic assignments.

visible range (Fig. 1) and show intense absorptions arising from  $\pi^* \leftarrow \pi$  transitions.

The bright orange complexes  $[\text{Zn}(\mathbf{1})_2][\text{PF}_6]_2$  and  $[\text{Zn}(\mathbf{2})_2][\text{PF}_6]_2$  were synthesized by treatment of  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  with the appropriate ligand in EtOH under microwave conditions, followed by addition of aqueous  $\text{NH}_4\text{PF}_6$  to precipitate the hexafluoridophosphate salts (ESI†). The electrospray mass spectra of  $[\text{Zn}(\mathbf{1})_2][\text{PF}_6]_2$  and  $[\text{Zn}(\mathbf{2})_2][\text{PF}_6]_2$  exhibited peak envelopes at  $m/z$  508.2 and 568.2, respectively, corresponding to  $[\text{M} - 2\text{PF}_6]^{2+}$ . Peak separations and isotope distributions were in accordance with those calculated.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were assigned by 2D techniques.‡ In the  $^1\text{H}$  NMR spectra, the significant shift of the proton assigned to  $\text{H}^{\text{A6}}$  to lower frequency ( $\delta$  8.73 to 7.81 ppm on going from **1** to  $[\text{Zn}(\mathbf{1})_2]^{2+}$ , and  $\delta$  8.72 to 7.79 ppm from **2** to  $[\text{Zn}(\mathbf{2})_2]^{2+}$ ) is diagnostic of a change in ligand conformation (*trans,trans* to *cis,cis*) and formation of the  $\{\text{Zn}(\text{tpy})_2\}$  unit. The electronic absorption spectra of MeCN solutions of  $[\text{Zn}(\mathbf{1})_2][\text{PF}_6]_2$  and  $[\text{Zn}(\mathbf{2})_2][\text{PF}_6]_2$  exhibit ligand-based high-energy absorptions

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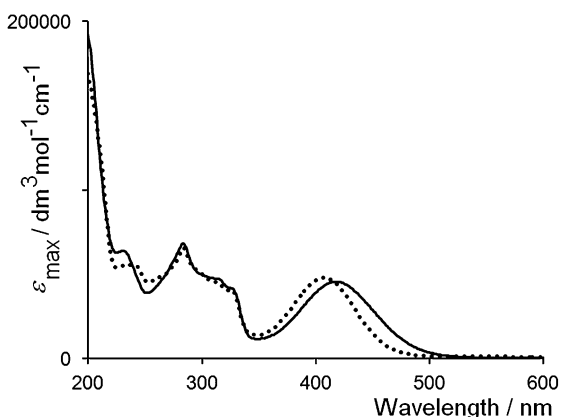
† Electronic supplementary information (ESI) available: Experimental details and Fig. S1 and S2: NMR spectra for ligand exchange experiments. See DOI: 10.1039/c2cc31729j



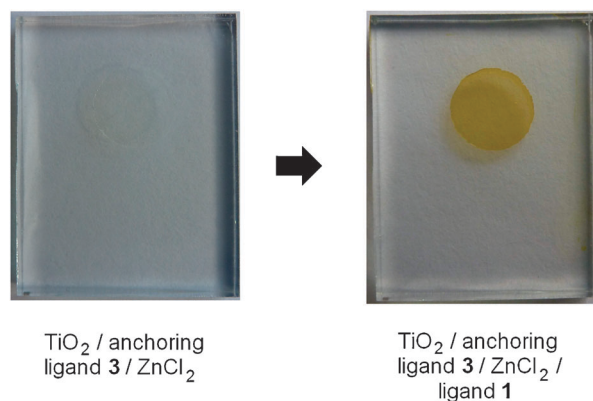
**Fig. 1** Electronic absorption spectra (MeCN,  $1 \times 10^{-5}$  mol dm $^{-3}$ ) of ligands **1** (.....) and **2** (—).

and broad bands with  $\lambda_{\max}$  407 and 420 nm, respectively, which extend well into the visible region (Fig. 2).

We have recently established a sequential method for attaching copper(i)-based dyes to TiO $_2$  nanoparticles. Firstly, an anchoring ligand L<sup>anc</sup> is bound to the surface and then treated with a homoleptic [CuL $_2$ ]<sup>+</sup> complex which exchanges to give the surface-bound (surface-L<sup>anc</sup>)Cu<sup>I</sup>L species.<sup>4</sup> We expected that the ligands in [ZnL $_2$ ]<sup>2+</sup> complexes (L = 2,2':6',2''-terpyridine or 4'-substituted-2,2':6',2''-terpyridine, 4'-Rtpy) would be labile. <sup>1</sup>H NMR spectra of mixtures of [Zn(L<sup>Me</sup>) $_2$ ][PF $_6$ ] $_2$  and [Zn(L<sup>OMe</sup>) $_2$ ][PF $_6$ ] $_2$  (L<sup>Me</sup> = 4'-(4-methylphenyl)-2,2':6',2''-terpyridine, L<sup>OMe</sup> = 4'-(4-methoxyphenyl)-2,2':6',2''-terpyridine) in CD $_3$ CN solution ( $\approx 10^{-3}$  mol dm $^{-3}$ ) provided evidence for exchange of the ligands at room temperature within an hour (Fig. S1, ESI $^\dagger$ ). However, the similarity in the aromatic regions of the spectra of the two complexes (Fig. S1a, ESI $^\dagger$ ) made monitoring the exchange difficult. In contrast, the signals for protons H<sup>B3</sup> (Scheme 1) in [Zn(tpy) $_2$ ][PF $_6$ ] $_2$  and [Zn(L<sup>OMe</sup>) $_2$ ][PF $_6$ ] $_2$  appear at  $\delta$  8.74 and 8.93 ppm, respectively. The <sup>1</sup>H NMR spectra of a CD $_3$ CN solution containing a 1 : 1 mixture of [Zn(tpy) $_2$ ][PF $_6$ ] $_2$  and [Zn(L<sup>OMe</sup>) $_2$ ][PF $_6$ ] $_2$  recorded at room temperature were consistent with the formation of a statistical mixture of [Zn(tpy) $_2$ ]<sup>2+</sup>, [Zn(tpy)(L<sup>OMe</sup>)]<sup>2+</sup> and [Zn(L<sup>OMe</sup>) $_2$ ]<sup>2+</sup>, with equilibrium being reached after  $\approx 2$  hours (Fig. S2, ESI $^\dagger$ ). Compared to exchange



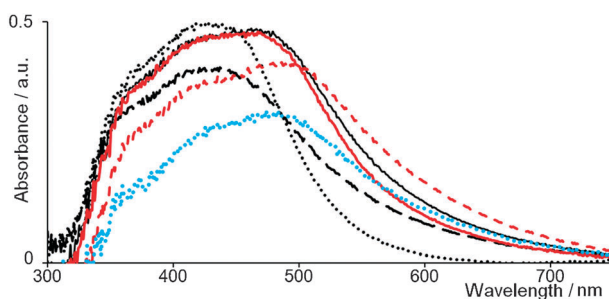
**Fig. 2** Electronic absorption spectra (MeCN,  $1 \times 10^{-5}$  mol dm $^{-3}$ ) of [Zn(**1**) $_2$ ][PF $_6$ ] $_2$  (.....) and [Zn(**2**) $_2$ ][PF $_6$ ] $_2$  (—).



**Fig. 3** Photographs taken during the preparation of the anode for a DSC using anchoring ligand **3**, ZnCl $_2$  and capping ligand **1**.

at copper(i) which is immediate, ligand exchange at zinc(ii) was surprisingly slow. Hence, we adopted an alternative sequential approach to assembling the zinc-containing dye on the semiconductor. The TiO $_2$  surface was first functionalized with anchoring ligand L<sup>anc</sup> (L<sup>anc</sup> = **3** (ESI $^\dagger$ ), **4**<sup>20,21</sup> or **5**,<sup>22</sup> Scheme 1) by immersing the anode in a DMSO solution of L<sup>anc</sup> for 24 hours. This was followed by metallation with Zn(OAc) $_2$  or ZnCl $_2$ , and subsequent capping with the chromophoric ligand **1** or **2** (Scheme 1) by immersing the anode in a CH $_2$ Cl $_2$  solution of the ligand for 64 hours. Full details of the preparation of the solar cells are given in the ESI. $^\dagger$  After capping with ligand **1** or **2**, the electrodes were orange (Fig. 3) and the colour was retained after washing the glass slides with CH $_2$ Cl $_2$ . Fig. 4 illustrates the solid state electronic absorption spectra of TiO $_2$ -anchored ligands **3**, **4** and **5** after successive treatment with either Zn(OAc) $_2$  or ZnCl $_2$  and ligand **2**. Values of  $\lambda_{\max}$  lie in the range 425 to 480 nm, red shifted with respect to 420 nm observed for [Zn(**2**) $_2$ ][PF $_6$ ] $_2$  in MeCN (Fig. 1).

Table 1 gives the DSC efficiency data for sealed solar cells in comparison to those for standard dye N719 measured under the same conditions as the zinc-containing dyes. Measurements were taken 2 days and 7 days after sealing the DSCs. In general, the data in Table 1 reveal little change in the efficiencies over this period, confirming that the heteroleptic Zn(ii) complexes assembled on the TiO $_2$  surface are stable sensitizers for DSCs. The efficiencies are surprisingly good for first trials of {Zn(tpy) $_2$ }-based photosensitizers. To date, we have made no attempt to optimize the performances of the DSCs.



**Fig. 4** Solid state electronic absorption spectra of TiO $_2$ -anchored ligands **3** (—), **4** (···) and **5** (---) after addition of Zn(OAc) $_2$ ; **3** (—), **4** (···) and **5** (---) after addition of ZnCl $_2$  followed by treatment with ligand **2**.

**Table 1** DSC efficiency data<sup>a</sup> compared to standard dye N719 measured under the same conditions

Zinc(II) salt	Outer ligand	Anchor ligand	$I_{SC}/$ A cm <sup>-2</sup>	$V_{OC}/$ V	ff	$\eta/$ %
2 days after sealing of cell						
Zn(OAc) <sub>2</sub>	<b>1</b>	<b>3</b>	0.002	0.545	0.49	0.55
ZnCl <sub>2</sub>	<b>1</b>	<b>3</b>	0.002	0.527	0.55	0.68
Zn(OAc) <sub>2</sub>	<b>2</b>	<b>3</b>	0.002	0.555	0.61	0.54
ZnCl <sub>2</sub>	<b>2</b>	<b>3</b>	0.001	0.498	0.63	0.46
Zn(OAc) <sub>2</sub>	<b>2</b>	<b>4</b>	0.001	0.571	0.66	0.53
ZnCl <sub>2</sub>	<b>2</b>	<b>4</b>	0.001	0.458	0.58	0.33
ZnCl <sub>2</sub>	<b>2</b>	<b>5</b>	0.002	0.530	0.62	0.63
7 days after sealing of cell						
Zn(OAc) <sub>2</sub>	<b>1</b>	<b>3</b>	0.002	0.538	0.52	0.59
ZnCl <sub>2</sub>	<b>1</b>	<b>3</b>	0.003	0.546	0.52	0.71
Zn(OAc) <sub>2</sub>	<b>2</b>	<b>3</b>	0.002	0.544	0.66	0.56
ZnCl <sub>2</sub>	<b>2</b>	<b>3</b>	0.001	0.521	0.64	0.46
Zn(OAc) <sub>2</sub>	<b>2</b>	<b>4</b>	0.001	0.529	0.68	0.41
ZnCl <sub>2</sub>	<b>2</b>	<b>4</b>	0.001	0.521	0.54	0.34
ZnCl <sub>2</sub>	<b>2</b>	<b>5</b>	0.002	0.536	0.61	0.55
Standard dye N719			0.018	0.718	0.58	7.29

<sup>a</sup> Parameter abbreviations:  $I_{SC}$  = short circuit current;  $V_{OC}$  = open circuit voltage; ff = fill factor;  $\eta$  = efficiency.

A comparison of the data in Table 1 suggests that the (surface-**3**)Zn<sup>II</sup>(**1**) system performs most efficiently, but the differences between the efficiencies of the different cells are not significant enough to draw clear conclusions.

We have developed a sequential approach to the assembly of zinc(II)-based DSCs by first functionalizing a TiO<sub>2</sub> semiconductor surface with an anchoring ligand containing a tpy metal-binding domain. Treatment with Zn(OAc)<sub>2</sub> or ZnCl<sub>2</sub> and subsequent reaction with a chromophoric 4'-Rtpy ligand result in the formation of DSCs that exhibit unexpectedly good efficiencies confirming the effectiveness of our new strategy. We are currently evaluating the effects of combining a range of different anchoring and chromophoric ligands on the efficiencies of DSCs based on the {Zn<sup>II</sup>(tpy)<sub>2</sub>} building block.

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## Notes and references

‡ Although [Zn(**1**)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub> has previously been reported,<sup>16</sup> the NMR spectra were not assigned.

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