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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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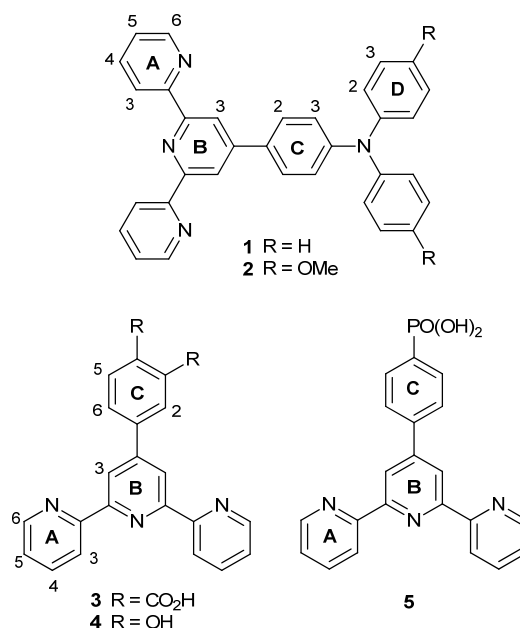
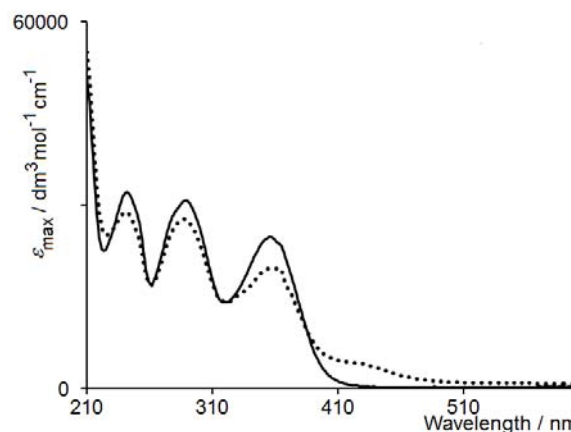
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Dye-sensitized solar cells have been assembled using a sequential approach: a  $\text{TiO}_2$  surface was functionalized with an anchoring ligand, followed by metallation with  $\text{Zn}(\text{OAc})_2$  or  $\text{ZnCl}_2$ , and subsequent capping 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>3,4,5,6,7</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>8,9,10,11</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>14,15,16</sup> and **2**<sup>17,18,19</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.<sup>†</sup> Of particular significance is the fact that the ligands are coloured. Their solution electronic absorption spectra (Fig. 1) show intense absorptions arising from  $\pi^* \leftarrow \pi$  transitions.

Scheme 1. Chromophoric ligands **1** and **2**, and anchoring ligands **3-5** with atom numbering for NMR spectroscopic assignments.Fig. 1 Electronic absorption spectra (MeCN,  $1 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ) of ligands **1** (.....) and **2** (—).

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.<sup>†</sup> 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 accord with those calculated.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were assigned by 2D techniques.<sup>¶</sup> 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  $\mathbf{1}$  to  $[\text{Zn}(\mathbf{1})_2]^{2+}$ , and  $\delta$  8.72 to 7.79 ppm from  $\mathbf{2}$  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 and broad bands with  $\lambda_{\text{max}}$  407 and 420 nm, respectively, which extend well into the visible region (Fig. 2).

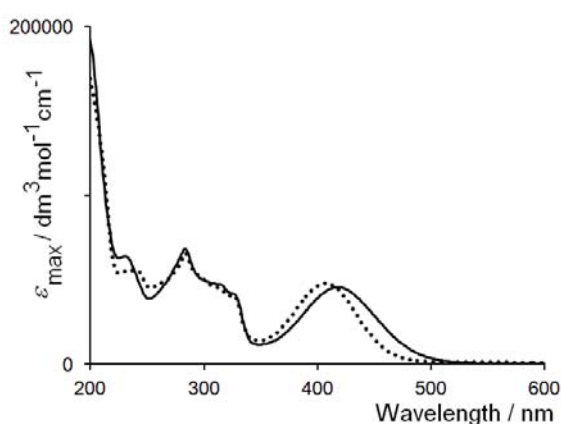


Fig. 2. Electronic absorption spectra (MeCN,  $1 \times 10^{-5}$  mol  $\text{dm}^{-3}$ ) of  $[\text{Zn}(\mathbf{1})_2][\text{PF}_6]_2$  (.....) and  $[\text{Zn}(\mathbf{2})_2][\text{PF}_6]_2$  (—).

We have recently established a sequential method for attaching copper(I)-based dyes to  $\text{TiO}_2$  nanoparticles. Firstly, an anchoring ligand  $\text{L}^{\text{anc}}$  is bound to the surface and then treated with a homoleptic  $[\text{CuL}_2]^+$  complex which exchanges to give the surface-bound (surface- $\text{L}^{\text{anc}}\text{Cu}^{\text{I}}\text{L}$ ) species.<sup>4</sup> We expected that the ligands in  $[\text{ZnL}_2]^{2+}$  complexes ( $\text{L} = 2,2':6',2''\text{-terpyridine}$  or 4'-substituted-2,2':6',2''-terpyridine, 4'-Rtpy) would be labile.  $^1\text{H}$  NMR spectra of mixtures of  $[\text{Zn}(\text{L}^{\text{Me}})_2][\text{PF}_6]_2$  and  $[\text{Zn}(\text{L}^{\text{OMe}})_2][\text{PF}_6]_2$  ( $\text{L}^{\text{Me}} = 4'-(4\text{-methylphenyl})\text{-}2,2':6',2''\text{-terpyridine}$ ,  $\text{L}^{\text{OMe}} = 4'-(4\text{-methoxyphenyl})\text{-}2,2':6',2''\text{-terpyridine}$ ) in  $\text{CD}_3\text{CN}$  solution ( $\approx 10^{-3}$  mol  $\text{dm}^{-3}$ ) provided evidence for exchange of the ligands at room temperature within an hour (Fig. S1). However, the similarity in the aromatic regions of the spectra of the two complexes (Fig. S1a) made monitoring the exchange difficult. In contrast, the signals for protons  $\text{H}^{\text{B3}}$  (Scheme 1) in  $[\text{Zn}(\text{tpy})_2][\text{PF}_6]_2$  and  $[\text{Zn}(\text{L}^{\text{OMe}})_2][\text{PF}_6]_2$  appear at  $\delta$  8.74 and 8.93 ppm, respectively. The  $^1\text{H}$  NMR spectra of a  $\text{CD}_3\text{CN}$  solution containing a 1 : 1 mixture of  $[\text{Zn}(\text{tpy})_2][\text{PF}_6]_2$  and  $[\text{Zn}(\text{L}^{\text{OMe}})_2][\text{PF}_6]_2$  recorded at room temperature were consistent with the formation of a statistical mixture of  $[\text{Zn}(\text{tpy})_2]^{2+}$ ,  $[\text{Zn}(\text{tpy})(\text{L}^{\text{OMe}})]^{2+}$  and  $[\text{Zn}(\text{L}^{\text{OMe}})_2]^{2+}$ , with equilibrium being reached after  $\approx 2$  hours (Fig. S2). Compared to exchange 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  $\text{TiO}_2$  surface was first functionalized with anchoring ligand  $\text{L}^{\text{anc}}$  ( $\text{L}^{\text{anc}} = \mathbf{3},^\dagger \mathbf{4}^{20,21}$  or  $\mathbf{5},^{22}$  Scheme 1) by immersing the anode in a DMSO solution of  $\text{L}^{\text{anc}}$  for 24 hours. This was followed by metallation with  $\text{Zn}(\text{OAc})_2$  or  $\text{ZnCl}_2$ , and subsequent capping with the chromophoric ligand  $\mathbf{1}$  or  $\mathbf{2}$  (Scheme 1) by immersing the anode in a  $\text{CH}_2\text{Cl}_2$  solution of the ligand for 64 hours. Full details of the preparation of the solar cells are given in the ESI.<sup>†</sup> After capping with ligands  $\mathbf{1}$  or  $\mathbf{2}$ , the electrodes were orange (Fig. 3) and the colour was retained after washing the glass slides with  $\text{CH}_2\text{Cl}_2$ . Figure 4 illustrates the solid state electronic absorption spectra of  $\text{TiO}_2$ -anchored ligands  $\mathbf{3}$ ,  $\mathbf{4}$  and  $\mathbf{5}$  after successive treatment with either  $\text{Zn}(\text{OAc})_2$  or  $\text{ZnCl}_2$  and ligand  $\mathbf{2}$ . Values of  $\lambda_{\text{max}}$  lie in the range 425 to 480 nm, red shifted with respect to the 420 nm observed for  $[\text{Zn}(\mathbf{2})_2][\text{PF}_6]_2$  in MeCN (Fig. 1).

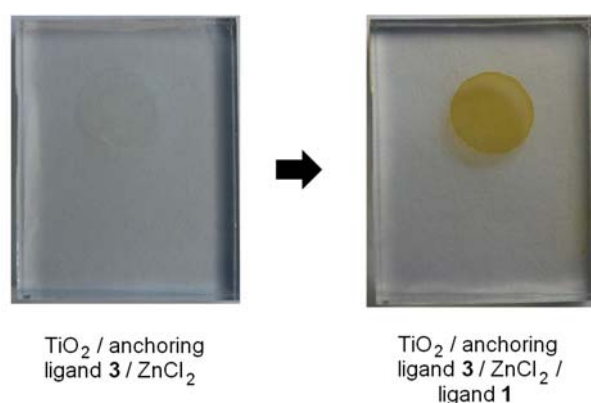


Fig. 3. Photographs taken during the preparation of the anode for a DSC using anchoring ligand  $\mathbf{3}$ ,  $\text{ZnCl}_2$  and capping ligand  $\mathbf{1}$ .

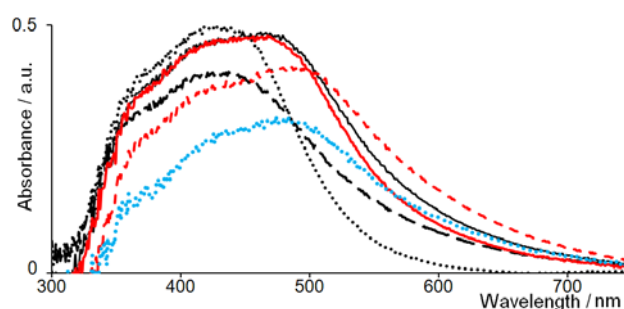


Fig. 4. Solid state electronic absorption spectra of  $\text{TiO}_2$ -anchored ligands  $\mathbf{3}$  (—),  $\mathbf{4}$  (.....) and  $\mathbf{5}$  (---) after addition of  $\text{Zn}(\text{OAc})_2$ ,  $\mathbf{3}$  (—),  $\mathbf{4}$  (.....) and  $\mathbf{5}$  (---) after addition of  $\text{ZnCl}_2$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

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  $\text{Zn}(\text{II})$  complexes assembled on the  $\text{TiO}_2$  surface are stable sensitizers for DSCs.

The efficiencies are surprisingly good for first trials of {Zn(tpy)<sub>2</sub>}-based photosensitizers. To date, we have made no attempt to optimize the performances of the DSCs. A comparison of the data in Table 1 suggest that the (surface-3)Zn<sup>II</sup>(1) system preforms the most efficiently, but the differences between the efficiencies of the different cells are not significant enough to draw clear conclusions.

Table 1. DSC efficiency data compared to standard dye N719 measured under the same conditions.

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

† Electronic Supplementary Information (ESI) available: Experimental details; Figures S1 and S2: NMR spectra for ligand exchange experiments. See DOI: 10.1039/b000000x/

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

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## 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 results 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

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