

# Cyclometalated iridium(III)-sensitized titanium dioxide solar cells†

Elizabeth I. Mayo,<sup>a,b</sup> Kristine Kilså,<sup>‡a</sup> Timothy Tirrell,<sup>b</sup> Peter I. Djurovich,<sup>a</sup> Arnold Tamayo,<sup>a</sup> Mark E. Thompson,<sup>a</sup> Nathan S. Lewis<sup>b</sup> and Harry B. Gray<sup>b</sup>

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Ir(III) dyes used as sensitizers in dye-sensitized solar cells produced quantum yields approaching unity for conversion of absorbed photons to current under simulated air mass 1.0 sunlight, with current production resulting from ligand-to-ligand charge-transfer states, rather than the typical metal-to-ligand charge-transfer states in ruthenium-based cells.

Dye-sensitized nanocrystalline TiO<sub>2</sub> solar cells (DSSCs) have attracted attention because they use inexpensive absorber materials for the conversion of sunlight into electricity.<sup>1,2</sup> Efficiencies in excess of 10% have been documented in “champion” devices of this type.<sup>3</sup> Although the quantum yield for photocurrent production is close to unity for light absorbed by the dye (typically >1.7–2.0 eV), the photovoltage is only 0.7–0.9 V under 1 sun air mass (AM) 1.0 illumination.<sup>3,4</sup>

Efficient sensitization has been achieved with a variety of species, including organic chromophores<sup>5</sup> and porphyrins<sup>6</sup> as well as Fe(II)-bipyridyl,<sup>7</sup> Pt(II) polypyridyl,<sup>8</sup> and Re(I)-diimine complexes.<sup>9</sup> The most efficient reported devices use Ru(II)-bipyridyl derivatives,<sup>3</sup> whose lowest excited states have metal-to-ligand charge transfer (MLCT) character.<sup>4,10</sup> An increased spatial separation (*r*) of the dye cation from the electrode surface results in a decrease in the deleterious recombination dynamics.<sup>11</sup> However, increased distances between the absorbing species and the TiO<sub>2</sub> surface can also result in decreased injection efficiencies.<sup>12</sup> Alternatively, if injection occurs from a ligand-to-ligand charge-transfer (LLCT) state, increased *r* values may be obtainable without significantly affecting the injection efficiencies.

To this end, we have investigated the use of Ir(III) complexes as sensitizers in TiO<sub>2</sub>-based photoelectrochemical cells. Cyclometalated Ir(III) compounds have recently found a wide variety of uses as photoreductants,<sup>13</sup> sensors,<sup>14</sup> biological labeling reagents,<sup>15</sup> and organic light-emitting diodes (OLEDs).<sup>16</sup> The combination of cyclometalating ligands with a third-row metal ion results in enhanced mixing of the singlet and triplet excited states via spin-orbit coupling, resulting in reduced Stokes shifts between absorption ( $\lambda_{\text{abs}}$ ) and emission ( $\lambda_{\text{em}}$ ) maxima in complexes in which the lowest excited state is MLCT or LLCT in character.<sup>16,17</sup> Additionally, through variation in the nature of the ligand, members of this family of Ir(III) dyes have been shown to span a wide range of the visible spectrum.<sup>14,16</sup>

We report results for two representative Ir(III) dyes, [Ir(ppz)<sub>2</sub>(dcbpy)]<sup>+</sup> and [Ir(ppz)<sub>2</sub>(dcbq)]<sup>+</sup> (where ppz = phenylpyrazolyl, dcbpy = 4,4'-dicarboxybipyridine and dcbq = 4,4'-dicarboxy-2,2'-biquinoline) (Fig. 1) with PF<sub>6</sub><sup>-</sup> counterions. The synthesis of these dyes has been reported previously.<sup>17</sup> These dyes have spectroscopic and electrochemical properties (Table 1) that are quite similar to those of a Ru(II)-bipyridyl analog, [Ru(bpy)<sub>2</sub>(dcbpy)]<sup>2+</sup> (where bpy = bipyridine; with PF<sub>6</sub><sup>-</sup> counterions) (Fig. 1), which has previously been shown to sensitize TiO<sub>2</sub> (Table 1).<sup>18</sup>

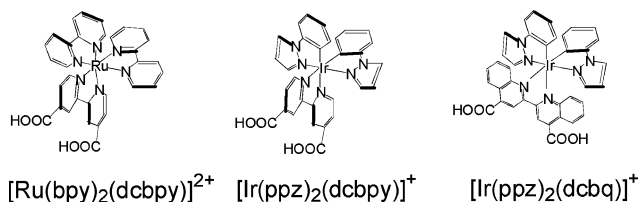


Fig. 1 Structures of the investigated dyes.

Both Ir(III) dyes exhibit a ligand-based ( $\pi$ - $\pi^*$ ) absorption at relatively high energy (380 nm) as well as a weak band in the visible region of the spectrum. Density functional theory (DFT) calculations indicate that the weak absorption is attributable to a LLCT transition from the cyclometalating ligand to the bipyridine or biquinoline ligand, rather than a MLCT band as in the Ru(II)-bipyridyl dye.<sup>17</sup> The LLCT assignment is consistent with the diminished extinction coefficient for these particular dyes. While the low extinction coefficient ( $\epsilon$ ) can be disadvantageous for a DSSC photosensitizer, the LLCT excited state produces a very large spatial separation between the hole and electron, which in turn can facilitate charge injection into TiO<sub>2</sub>. LLCT states have been previously observed to inject electrons into TiO<sub>2</sub>.<sup>19</sup> Consistently, our work describes the use of an Ir-based sensitizer with charge production from a LLCT state.

These Ir(III) complexes have excited-state lifetimes ( $\tau_{\text{em}}$ ) and emission quantum yields ( $\phi_{\text{em}}$ ) in solution comparable to those of the reference Ru(II) complex. Additionally, all of the complexes have ground-state formal reduction potentials ( $E^\circ$ ) that are sufficiently positive to oxidize the I<sub>3</sub><sup>-</sup>/I<sup>-</sup> redox couple. Furthermore, the excited-state formal reduction potentials ( $E^{\circ,*}$ ) of the iridium dyes are quite similar to the ruthenium analog, indicating that these complexes should readily inject electrons into TiO<sub>2</sub>. The emission decays for the dyes adsorbed onto TiO<sub>2</sub> were multiexponentials (Fig. 2). Although the majority of the decay was faster than the instrument response (10 ns), a system-limited lower bound on the injection rate can be determined from the fraction that injected with rates less than  $1.0 \times 10^9 \text{ s}^{-1}$ .<sup>20</sup> Average lower-bound quenching rate constants of  $1.0 \times 10^8 \text{ s}^{-1}$  and

<sup>a</sup>Department of Chemistry, University of Southern California, Los Angeles, California, 90089

<sup>b</sup>Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California, 91125

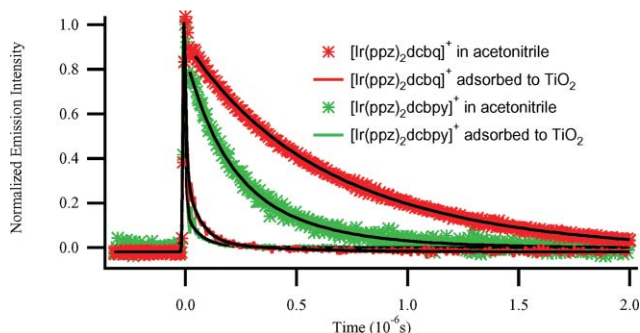
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‡ Present address: Department of Chemistry, University of Copenhagen, Universitetsparken 5, 2100 Copenhagen Ø, Denmark

**Table 1** Spectroscopic and electrochemical data

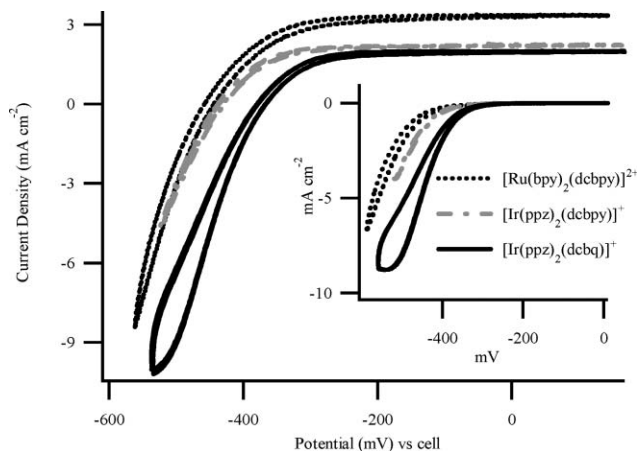
Dye	$\lambda_{\text{abs}}/\text{nm}$	$(\epsilon/10^3)/\text{M}^{-1}\text{cm}^{-1}$	$\lambda_{\text{em}}/\text{nm}$	$\phi_{\text{em}}(\%)$	$\tau_{\text{em}}/\mu\text{s}$	$E_{00}^a/\text{V}$	$E^{\circ,b}/\text{V}$	$E^{\circ,*b,f}/\text{V}$
$[\text{Ir}(\text{ppz})_2(\text{dcbq})]^+$	~495	(1.3)	644	10	0.7	2.17	1.42 <sup>c</sup>	-0.8
$[\text{Ir}(\text{ppz})_2(\text{dcbpy})]^+$	~455	(0.7)	604	12	0.3	2.46	1.35 <sup>d</sup>	-1.1
$[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$	~469	(14)	676	5	0.8	2.00	1.09 <sup>e</sup>	-0.9

<sup>a</sup> Estimated from the intersection of the absorption and emission spectra. <sup>b</sup> Reported *versus* a saturated calomel electrode (SCE); all waves were electrochemically reversible. <sup>c</sup> Estimated from the cyclic voltammetric (CV) measurement of the non-carboxylated dye,  $[\text{Ir}(\text{ppz})_2(\text{dcbq})]^+$  (where bq = biquinoline) in acetonitrile with 0.1 M tetrabutylammonium hexafluorophosphate. <sup>d</sup> Determined from CV measurements in acetonitrile with 0.1 M tetra(*n*-butyl)ammonium hexafluorophosphate. <sup>e</sup> Determined from differential pulse voltammetry measurements in buffered ethanol containing pyridine and pyridium triflate (1 mM each). <sup>f</sup>  $E^{\circ,*} = E^{\circ} - E_{00}/q$  (where  $E_{00}$  is the energy of the 0-0 transition and  $q$  is the charge on an electron).

**Fig. 2** Emission decays of the Ir(III) dyes in acetonitrile solution and after adsorption to  $\text{TiO}_2$ .

$3.8 \times 10^7 \text{ s}^{-1}$  for  $[\text{Ir}(\text{ppz})_2(\text{dcbpy})]^+$  and  $[\text{Ir}(\text{ppz})_2(\text{dcbq})]^+$ , respectively, were obtained.

Fig. 3 shows the current density vs. potential curves obtained when all photoelectrodes were fabricated to have the same absorbance,  $0.7 \pm 0.1$ , at the MLCT or LLCT maximum, to control for differences in extinction coefficients among the various dyes. Hence, the amount of adsorbed Ru complex was kept sufficiently low to produce a similar maximal absorbance on  $\text{TiO}_2$  to that obtained for the more weakly absorbing Ir complexes. Due to the diminished extinction coefficient in the visible region for these Ir(III) dyes, the corresponding nanocrystalline  $\text{TiO}_2$ -based photoelectrochemical cells would be expected to display lower energy conversion efficiencies under solar-simulated illumination than the analogous  $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$ -sensitized cells. However, the quantum yield for conversion of absorbed photons to current for DSSCs was nearly unity for  $[\text{Ir}(\text{ppz})_2(\text{dcbpy})]^+$  and was 0.6 for  $[\text{Ir}(\text{ppz})_2(\text{dcbq})]^+$ . Overall, the short-circuit current density,  $J_{\text{sc}}$ , the open-circuit voltage,  $V_{\text{oc}}$ , and the shapes of the current density-potential curves (Fig. 3) for the two Ir(III) dyes were comparable to

**Fig. 3**  $J$ - $E$  characteristics of dye-sensitized  $\text{TiO}_2$  under AM 1.0 illumination and in the dark (inset).

the corresponding properties of the Ru(II)-bipyridyl analog under these test conditions (Table 2).

The back reaction that determines  $V_{\text{oc}}$  in sensitized  $\text{TiO}_2$  systems is electron transfer from reduced nanocrystalline  $\text{TiO}_2$  to the oxidized species in the  $\text{I}_3^-/\text{I}^-$  electrolyte solution.<sup>4</sup> Trends in the rate of this back reaction were evaluated from the forward-bias potential necessary to produce a fixed amount of cathodic dark-current density ( $0.1 \text{ mA cm}^{-2}$ ) at the  $\text{TiO}_2$ -solution interface (Fig. 3, inset), where a less negative potential is indicative of more facile electron transfer between  $\text{TiO}_2$  and the  $\text{I}_3^-/\text{I}^-$  electrolyte.

Interestingly, the magnitudes of these potentials were similar for  $[\text{Ir}(\text{ppz})_2(\text{dcbpy})]^+$  and  $[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$ , with almost a 100 mV difference towards a more facile back reaction for  $[\text{Ir}(\text{ppz})_2(\text{dcbq})]^+$ . All three of these dyes should bind in a similar fashion to the  $\text{TiO}_2$  surface,<sup>21</sup> and thus the enhanced electron transfer between the  $\text{TiO}_2$  and the redox couple for the

**Table 2** Photoelectrochemical data<sup>a</sup>

Dye	$J_{\text{sc}}/\text{mA cm}^{-2}$	$V_{\text{oc}}/\text{mV}$	ff <sup>b</sup>	Eff <sup>c</sup> (%)	$\Phi^d$ (%)	$E_{\text{dark}}^e/\text{V}$
$[\text{Ir}(\text{ppz})_2(\text{dcbq})]^+$	1.99	-380	0.66	0.5	60	-386
$[\text{Ir}(\text{ppz})_2(\text{dcbpy})]^+$	2.24	-438	0.67	0.65	100	-436
$[\text{Ru}(\text{bpy})_2(\text{dcbpy})]^{2+}$	3.35	-458	0.65	1.0	100	-476

<sup>a</sup> Acetonitrile with 0.50 M LiI, 0.040 M  $\text{I}_2$ , 20 mM pyridine, 20 mM pyridinium triflate under simulated AM 1.0 conditions. <sup>b</sup> The fill factor (ff) is calculated as  $P_{\text{max}}/(J_{\text{sc}} V_{\text{oc}})$ , where  $P_{\text{max}}$  is the most negative value of  $J V$ . <sup>c</sup> The efficiency (Eff) is calculated as  $(-J_{\text{sc}} V_{\text{oc}} \text{ff } 100\%)/I_s$ , where  $I_s = 100 \text{ mW cm}^{-2}$ .

<sup>d</sup> The integrated quantum yield ( $\Phi$ ) was determined by comparing the experimentally measured value of  $J_{\text{sc}}$  with the maximum calculated  $J_{\text{sc}}$  assuming a unity quantum yield when the measured absorbance of the dyes on  $\text{TiO}_2$  electrodes were convoluted with the spectral irradiance of the solar simulator between 1100 and 360 nm. <sup>e</sup> Potential vs. the Nernst potential of the cell required to drive a cathodic current density of  $-0.1 \text{ mA cm}^{-2}$  in the dark.

[Ir(ppz)<sub>2</sub>(dcbq)]<sup>+</sup> sensitizer is noteworthy. It is possible that the increased dark current is due to the metal complex-mediated back electron transfer from TiO<sub>2</sub> to I<sub>3</sub><sup>-</sup>,<sup>22</sup> although there is evidence that bq ligands should work effectively in DSSCs.<sup>23,24</sup>

In summary, Ir(III) dyes have been used to sensitize TiO<sub>2</sub> in a functional DSSC producing quantum yields approaching unity for conversion of absorbed photons to current under simulated AM 1.0 sunlight. The ability to fine tune the spectral overlap between the Ir(III) dye and the solar spectrum could lead to greatly improved energy conversion efficiency. Furthermore, these cells provide examples of solar converters in which current production is based solely on injection from LLCT-based states, indicating that it may be possible to design a single complex for dual sensitization by incorporating injection from both MLCT and LLCT states.

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