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Three is not a crowd: efficient sensitization of TiO_2 by a bulky trichromic *tris*heteroleptic cycloruthenated dye[†]

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A cyclometalated Ru dye bearing two triphenylamine groups to augment light absorption exhibits a power conversion efficiency (PCE) in excess of 7% in the dye-sensitized solar cell despite having a large molecular footprint on TiO_2 .

The dye-sensitized solar cell (DSSC) has attracted significant attention as a potential alternative to crystalline-silicon and thin-film devices for urban and indoor applications on account of the low embodied energy and relative indifference to the angle and intensity of the incident light.^{1–3} A particularly attractive feature of the DSSC is that the light absorption and charge-transport processes^{4–6} are reasonably well-understood thereby rendering it possible to make efficiency and stability gains through the rational design of molecular components.^{7–13}

We¹⁴ and others^{15,16} have a longstanding interest in developing organometallic Ru sensitizers devoid of labile NCS⁻ groups. Replacing these labile¹⁷ monodentate ligands with chelating cyclometalating ligands such as 2-phenylpyridine (e.g., 1)provides the opportunity to utilize the chelate effect to potentially enhance dye stability, and gain acute control of the HOMO energy level through judicious chemical modification of the anionic ring.^{14,18} This feature is particularly important in view of the apparent need for DSSC dyes to have a HOMO level positioned at ca. > 0.9 V vs. NHE to be regenerated by I^{-} ,^{20,21} which is consistent with the relevant redox couple for the electrolyte being defined by $E^{\circ\prime}$, $I_2^{\bullet-}/I^- = 0.8 \pm 0.1$ V vs. NHE in MeCN.¹⁹ Importantly, the scaffold of 1 also lends itself to the modification of one of the dcbpy ligands with electron-rich aromatic substituents, such as alkylthiophenes (e.g. 2^{22}), to render higher extinction coefficients and PCEs.²³ We have also recently demonstrated that triphenylamine (TPA) groups (which are effective light-harvesting units for metal²⁴⁻²⁸ and metal-free^{29,30} DSSC dyes) conjugated to tridentate chelating ligands produce remarkably high efficiencies for bistridentate complexes.31

We therefore set out to unite these concepts to furnish the first *trichromic* trisbidentate cyclometalated Ru dye in the form of **3**,

Department of Chemistry, University of Calgary and the Institute for Sustainable Energy, Environment & Economy, University of Calgary, 2500 University Drive N.W., Calgary, Canada T2N-1N4. E-mail: cberling@ucalgary.ca; Tel: +1-403-220-3856 † Electronic supplementary information (ESI) available: Synthesis and characterization details. See DOI: 10.1039/c2cc00136e where one of the bidentate bpy ligands bears two TPA groups to further enhance the light absorption relative to that of **2**. It is shown herein that the cyclometalating ligand and TPA groups of **3** collaborate to produce a PCE of >7% in the DSSC.

Complex **3** was formed by the addition of the cyclometalating ligand to the metal prior to the synchronous addition of the two polypyridyl ligands. The TPA-functionalized chelating ligand **P3** was formed using a Suzuki cross-coupling reaction of 4,4'-dibromo-2,2'-bipyridine with proligand **P2** (Scheme S1). Addition of **P3** and 4,4'-diethylester-2,2'-bipyridine (deeb) to $[Ru(CH_3CN)_4(ppy-(CF_3)_2)]PF_6$ (**P4**) in an ABS EtOH/CHCl₃ (3:1) solvent mixture yielded the ester derivative of **3**, **P5**. **P3** is soluble in CHCl₃, but the formation of undesired byproducts is observed in this solvent thus lowering the overall reaction yields (~52.5%). The constitution of **P5** was established by ¹H NMR spectroscopy, high-resolution mass spectrometry and elemental analysis. The deprotection of the ester groups of **P5** to produce **3** was achieved overnight in refluxing DMF/H₂O/NEt₃ (3:1:1).

Dye 3 is insoluble in most polar organic solvents (e.g. MeOH, MeCN, DMSO)-even with the addition of NaOH-but is readily soluble in DMF. Dye 3 can be easily constituted in low-polarity organic solvents (e.g. CH₂Cl₂, CHCl₃, acetone, Et₂O), thus indicating that the solubility of the complex is governed by P3. The ¹H NMR spectrum of 3 in d_8 -DMF displayed broad, poorly resolved signals (Fig. S1, ESI⁺), which we attribute to slow molecular tumbling on the NMR timescale arising from the large size of the complex. Elevated temperatures (e.g., 373 K) yielded a nominal improvement in spectral resolution. Notwithstanding, ESI-MS and elemental analysis supported the identity of 3. The isomer shown in Fig. 1 is based on the structural determination of a related complex, [Ru(bpy)(deeb)(ppy)]PF₆ (4; Fig S2, ESI⁺). Note that this result provides the first structural confirmation of the absolute configuration of a tris-heteroleptic Ru dye related to 1; namely, the Ru-C bond is positioned *trans* to the electron-deficient deeb.

The UV-vis spectrum of **3** (Fig. 2) reveals a relatively intense band centred at 580 nm $(3.3 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$ ascribed to a "metal"-to-ligand charge transfer (MLCT) transition from the Ru-aryl fragment to the dcbpy ligand.¹⁴ The large intensity of the band centred at 465 nm $(6.7 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1})$ arises from intraligand charge-transfer (ILCT) bands emanating from



Fig. 1 Structural drawing of 1, 2, 3 and P3. Counteranion for 1 and 3 is PF_6^- .



Fig. 2 UV-vis absorption spectra of P3, 2 and 3 recorded in DMF. Inset: Cyclic voltammagrams of P3, 2 and 3 recorded in DMF at 200 mV s⁻¹ with 0.1 M NBu₄BF₄ supporting electrolyte.

the TPA groups to complement the MLCT bands.³¹ Excitation of **3** at $\lambda = 580$ nm in degassed DMF generates an emission peak at $\lambda = 797$ nm with a lifetime of 46 ns.

The cyclic voltammogram (CV) of 3 recorded in DMF reveals a quasi-reversible oxidation process at +0.97 V vs. NHE (Fig. 2, inset). The large peak separation ($\Delta E_{\rm p} \sim 170 \text{ mV}$) is rooted in the nearly coincident Ru and TPA oxidation processes; e.g., the first oxidation waves of P3 and 2 in DMF are observed at +0.96 V and +0.99 V, respectively (Fig. 2, inset). The oxidation potential of 3 is not anticipated to deviate significantly from that of 2 because the HOMO is confined to the metal and the aryl ring. (Efforts to resolve the individual redox processes of 3 by square-wave voltammetry were not successful.) An irreversible or quasi-reversible TPA oxidation process superimposed with the ostensibly reversible Ru^{III}/Ru^{II} redox couple presumably causes the larger cathodic signal in the CV of 3. The quasi-reversible reductive wave at -1.17 V is assigned to the anchoring dcbpy ligand of 3. The E_{0-0} energy of 1.76 eV determined from the intersection of the absorption and emission curves corresponds to an $E(S^+/S^*)$ of ca. -0.79 V (assuming the metal-based HOMO resides at +0.97 V), which is suitable for efficient electron injection into TiO₂.^{4,32}

The absorption properties and ground- and excited-state energy levels of **3** were poised for sensitizing TiO_2 in the DSSC. Cells were therefore constructed by immersing TiO_2 photoelectrodes (12 µm active + 3 µm scattering layer) in absolute ethanol solutions of **3** with and without chenodeoxycholic acid (CDCA) present (Supporting Information). Prior to sealing, the cells were filled with an electrolyte containing 0.6 M



Fig. 3 IPCE traces for 3 with (Entry 5, Table 1) and without chenodeoxycholic acid (Entry 6). Inset: J-V curves for 3 with (Entry 5) and without chenodeoxycholic acid (Entry 6).

Table 1 Device characteristics for cells containing 2 and 3

Entry	Dye	Active area (cm ²)	Coadsorbent ^a	$\stackrel{V_{\rm oc}/}{\rm V}$	$J_{\rm sc}/{ m mA} m cm^{-2}$	FF	η^b (%)
1	2	0.28	Yes	0.68	15.8	0.60	6.4
2	2	0.28	No	0.63	13.0	0.64	5.3
3	2	0.13	Yes	0.66	16.3	0.68	7.3
4	2	0.13	No	0.60	13.7	0.67	5.6
5	3	0.28	Yes	0.65	14.6	0.62	5.9
6	3	0.28	No	0.66	15.7	0.60	6.2
7	3	0.13	Yes	0.59	15.0	0.64	5.7
8	3	0.13	No	0.63	17.1	0.67	7.3

^{*a*} Coadsorbent is chenodeoxycholic acid (0.0025 M). ^{*b*} Performance of DSSCs measured under AM1.5 light conditions at 1 sun intensity using 12 μ m active + 3 μ m scattering TiO₂ layers. All cells were filled with an electrolyte consisting of 0.6 M 1-butyl-3-methylimidazolium iodide (BMII), 0.06 M I₂, 0.1 M NaI, 0.5 M 4-tertbutylpyridine and 0.1 M guanidinium thiocyanate.

1-butyl-3-methylimidazolium iodide (BMII), 0.06 M I₂, 0.1 M NaI, 0.5 M 4-tertbutylpyridine and 0.1 M guanidinium thiocyanate. The photocurrent density-voltage diagrams for 3 are depicted in the inset of Fig. 3 along with performance parameters listed in Table 1. The performance is effectively the same at full active area (Entries 5 and 6) with marginal differences observed in $V_{\rm oc}$ ($\Delta = 0.01$ V) and FF ($\Delta = 0.02$). A more significant difference is evident with the $J_{\rm sc}$ ($\Delta = 1.1 \text{ mA cm}^{-2}$). Overall, the performances with and without coadsorbent are 5.9 and 6.2% respectively. The incident-photon-to-currentefficiency (IPCE) trace for 3 shows an onset of current at nearly 790 nm and the curve plateaus between 65-70% in the region of 450-600 nm (Fig. 3). A minimal enhancement is observed from 350-600 nm for devices without CDCA present, presumably a consequence of better dye loading in these devices (vide infra). One possible cause of the low IPCE values is a normalized diffusion length (L_n) that was calculated to be less than the film thickness at $V_{\rm oc}$, both in the presence $(0.6L_n)$ and absence of coadsorbent $(0.8L_n)$. This condition would effectively reduce the charge collection efficiency, as well as $V_{\rm oc}$ and $J_{\rm sc}$.

The larger photocurrent observed in the absence of CDCA is attributed to a higher dye loading on the surface of TiO₂. This claim is supported by dye desorption studies indicating a surface concentration of **3** on TiO₂ as 5.7 and 4.2×10^{-8} mol cm⁻² in the absence and presence of the coabsorbent, respectively.

Surprisingly, an opposite trend was observed for **2**: a higher dye loading $(8.1 \times 10^{-8} \text{ mol cm}^{-2})$ was found for substrates with CDCA compared to those without $(5.4 \times 10^{-8} \text{ mol cm}^{-2})$. Despite these differences, the disparities in cell performance for **2** and **3** were nominal (Entries 1 and 5).

Further insight into the performance of DSSCs composed of 2 and 3 was obtained from electrochemical impedance spectroscopy (EIS) data (Fig. S3, ESI⁺), which was fit to the transmission line model (Fig. S4, ESI[†]). Fig. S3A shows that the R_{ct} values of **3** are the same with and without the coabsorbent, while it is higher for 2 without CDCA. This result suggests that 2 is better than 3 at protecting the surface of TiO₂, presumably due to less space between the dyes and/or better packing between the hexyl chains closer to the surface. The transport resistance (R_t) is effectively the same with or without CDCA in devices sensitized by 3, but in the case of 2 it is higher without CDCA thereby offsetting the advantage of the increased R_{ct} (Fig. S3B). L_n values are therefore approximately equivalent for devices sensitized by 2 and 3 that do not contain CDCA. The charge-transfer capacitance (C_{ct}) , which can be used as a metric for the electron concentration in TiO₂,³³ is the only parameter to significantly differ (Fig. S3C, ESI⁺): the highest value was observed for 3 without CDCA (Entry 6). This result is consistent with the larger J_{sc} for the device containing 3 without coadsorbent (Entry 6) compared to that of 2 without CDCA (Entry 2).

The device results for **3** are unique in that CDCA does not improve V_{oc} and/or J_{sc} . A similar observation for the organic dye **D35** reported by Jiang *et al.*³⁴ was rationalized by a highly ordered dye arrangement on the surface limiting the uptake and effect of CDCA. This scenario could also be the case for **3**, which is indirectly supported by the similarity in dye loading for **D35** and **3**. Regardless, the highest efficiency for **3** was observed in the case with the highest dye loading, which was achieved in the absence of CDCA. A PCE of 6.2% at full active area (0.28 cm²) and 7.3% with a reduced mask size (0.13 cm²) were recorded.

This work provides the first example of a trichromic cyclometalated Ru dye—a strategy inspired by the precedent for TPA-functionalized Ru dyes bearing two or three NCS⁻ ligands in the literature.^{24,25} A particularly relevant example to this work is dye **IJ-1** reported by Ko *et al.*, which has two NCS⁻ ligands in place of the cyclometalating ligand and yields a PCE of 10.3%.²⁶ The inferior performance of **3** may be due to the lower driving force for intramolecular electron-transfer (*i.e.* reduction of the photo-oxidized Ru site by the TPA) relative to **IJ-1** because the two NCS⁻ groups do not raise the HOMO energy to the same extent as a ppy⁻ ligand (although differences in cell fabrication cannot be excluded). Studies are underway to directly examine these intramolecular and interfacial electron-transfer processes.

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