

Cyclometallated Iridium Complexes as Sensitizers for Dye-Sensitized Solar Cells

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Dedicated to the 150th anniversary of Japan–UK diplomatic relations

Dye-sensitized solar cells (DSSCs) are considered as being the most promising solution for harnessing the energy of the sun and converting it into electrical energy owing to the low-cost, easy processing, and high performance of the DSSCs.^[1] By using ruthenium complexes, champion cells reaching 11% power-conversion efficiency under AM1.5 conditions have been obtained.^[2] Without a doubt, ruthenium complexes have been the most studied family of sensitizers.^[3] Other metal complexes as well as metal-free organic dyes have also been tested.^[4] It is only recently that iridium complexes have started to be used as sensitizer for DSSCs.^[5] Iridium complexes have been very successful as phosphorescent material in organic light-emitting devices (OLEDs),^[5a,6] biological labelling agents,^[7] oxygen sensors,^[8] and photocatalysts for hydrogen production.^[9] More appropriate for DSSCs, they have also shown good performance for photo-induced charge separation, either as an electron relay^[10] or as the photoactive center.^[11] A particularly appealing point for iridium complexes is the larger d-orbital splitting compared with ruthenium. This is likely to improve the stability of the sensitizer owing to less-accessible metal-centered (MC) states. Indeed, such MC states have been advantageously used for photo-driven molecular machines based on ruthenium owing to their anti-bonding character.^[12] In the case of iridium, such de-coordinating MC states, when acces-

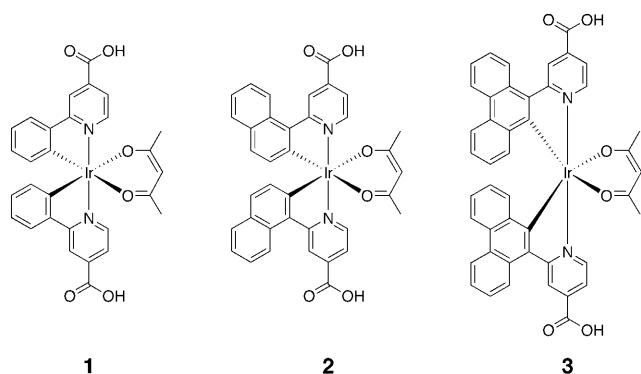
sible at room temperature, are a real issue only for blue-emitting materials.^[13] As sensitizers for DSSCs deal mostly with the red to near-infrared part of the spectra, it is anticipated that iridium complexes would exhibit better stability than their ruthenium counterpart in the long term. However, prior to tackling stability issues, it is important to obtain efficient sensitizers based on this new family of dye; this requires understanding of the dynamics of the photo-induced processes triggered by these new dyes. The aim of the paper is to present the basic dynamics of these new systems.

It is well established that tuning the emitted wavelength in cyclometallated iridium complexes can be achieved by introducing various donor or acceptor groups on the ligand.^[14] HOMO and LUMO energy levels can be almost independently tuned as the HOMO is mostly localized on the carbon-coordinating part of the ligand and the LUMO is mostly localized on the nitrogen-coordinating part of the ligand.^[15] Concomitantly, the absorption maxima can be tuned with the same approach. To tune the absorption toward the red part of the visible spectrum, introduction of an acceptor group on the nitrogen-coordinating part of the ligand will stabilize the LUMO energy level more than the HOMO energy level, leading to a reduced HOMO–LUMO gap observed as a red-shifted absorption. We have achieved this by using an acid carboxylic group on the pyridine. Compared with the parent iridium(phenyl-pyridine)₂(acac) complex, which absorbs up to about 450 nm (yellow color), complex **1** (Scheme 1) with the acid carboxylic group absorbs up to 590 nm (orange-red color). Additionally, as it is important to have directionality in the photoinduced electron transfer, it is advantageous to have the anchoring group directly attached to the group where the LUMO orbital is mainly localized.

Preliminary results using this complex as a dye for DSSCs have recently been partially reported.^[5a] Surprisingly for such a simple molecule, we observed efficiency approaching 1.9%. This first trial looked very promising and we there-

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Scheme 1. Molecular structures of the dyes **1**, **2**, and **3**.

fore further studied this new class of dyes for DSSCs. We prepared two new sensitizers with the aim to improve the light collection by going from phenyl to naphthyl to phenanthrene.

Synthesis of dyes **1**, **2**, and **3** has been achieved by hydrolysis of ester-substituted complexes by using tetrabutyl ammonium hydroxide (TBAOH) in methanol followed by protonation with hydrochloric acid. The ester-substituted complexes have been obtained by using the usual two-step strategy, based on a previously reported method,^[16] that is synthesis of a chloro-bridge dimer in ethoxyethanol followed by reaction with acetylacetonate in the presence of TBAOH as a base in dichloromethane as the low-boiling solvent.

The UV/Vis and emission spectra of dyes **1**, **2**, and **3** measured in dimethylformamide (DMF) are shown in Figure 1. Owing to the intra-ligand (π - π^*) transition, the absorption

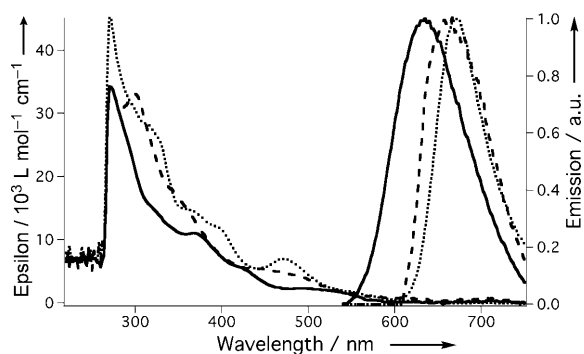


Figure 1. UV/Vis absorption (left) and emission (right) spectra of **1** (—), **2** (---), and **3** (.....) in DMF solutions.

spectra display bands in the UV region between 270 and 400 nm with an intensity higher than $10\,000\text{ L mol}^{-1}\text{ cm}^{-1}$. In the visible region, as anticipated, **3** is the strongest absorber with a band at 472 nm and an absorption coefficient of about $7000\text{ L mol}^{-1}\text{ cm}^{-1}$ and a shoulder at 554 nm extending up to 630 nm. Dye **2** exhibits a broad shoulder at 472 nm, similar to dye **3**, however, with a much lower absorption coefficient of about $4700\text{ L mol}^{-1}\text{ cm}^{-1}$ extending up to 630 nm. Finally, **1** exhibits a band at 500 nm with absorption coefficient of about $2200\text{ L mol}^{-1}\text{ cm}^{-1}$ extending up to 590 nm.

These bands originate from metal-to-ligand charge transfer transitions (MLCT). When excited at 298 K within the ligand (π - π^*) and MLCT absorption bands, the complexes show emission with maxima at 634, 662, and 671 nm for **1**, **2**, and **3**, respectively.

Cyclic voltammetry has been used to measure oxidation potential in DMF (Table 1). The complexes **1**, **2**, and **3** exhibit reversible oxidation at 0.500, 0.475, and 0.406 V versus

Table 1. Photophysical and electrochemical properties of the dyes.

	λ_{em} [nm] ^[a]	E_{ox} [V] ^[b]	E_{0-0} /eV ^[c]	HOMO ^[d]	LUMO ^[e]
1	634	0.500	2.23	-5.30	-3.07
2	662	0.475	2.07	-5.26	-3.19
3	671	0.406	2.00	-5.17	-3.17

[a] In DMF. [b] In DMF, 0.1 M TBAPF₆, reported compared with ferrocene. [c] From the edge of emission. [d] HOMO = $-1.4 \times E_{\text{ox}} - 4.6$.^[17] [e] LUMO = HOMO + E_{0-0} . TBAPF₆ = tetrabutylammonium hexafluorophosphate.

ferrocene, respectively. Hence the HOMO energy level of the complexes is destabilized as the aromatic group is extended. By using the photophysical results to calculate the energy of the 0-0 transitions, it is possible to obtain an approximate energy level for the LUMO of the complex. The energy level of the conduction band of titanium dioxide is about -3.5 eV and the HOMO energy level of the couple I^-/I_3^- is around -4.4 eV. One can see that the energy levels of the dyes are therefore correctly placed relative to TiO₂ and to iodine for testing as a DSSC.

The photovoltaic performances of dyes **1**, **2**, and **3** are shown in Figure 2 and Table 2. The DSSCs based on 9- μm TiO₂ transparent films show a power conversion efficiency of 2.23, 1.96, and 2.04%, respectively, under standard global AM 1.5 solar conditions. The short-circuit current density (J_{SC}) follows the sequence dyes **3** (5.78 mA cm^{-2}) > **2** (5.11 mA cm^{-2}) > **1** (4.6 mA cm^{-2}), which is consistent with the UV/Vis absorption result. Hence, the enhancement in J_{SC} is attributed to an optical red response. In incident photo-to-current efficiency (IPCE; see Figure S1a in the Supporting Information), a red shift of the photoresponse

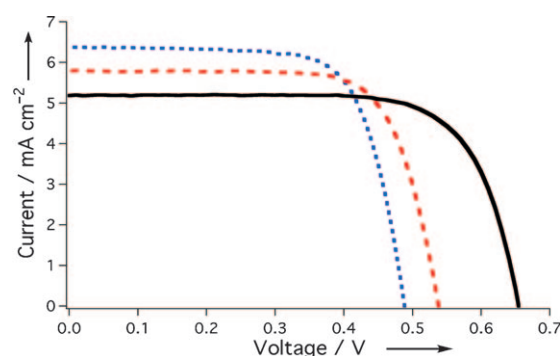


Figure 2. J - V characteristics of dyes **1** (—), **2** (---), and **3** (.....) sensitized solar cells based on 9+5- μm TiO₂ films under 1 sun. The applied electrolyte consists of 0.6 M *N*-methyl-*N*-butyl imidazolium iodide, 0.05 M iodine, 0.1 M LiI, and 0.05 M *tert*-butylpyridine in 15:85 (v/v) mixture of valeronitrile and acetonitrile.

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Table 2. J - V characteristics at 1 sun of dyes, **1**, **2**, and **3** sensitized solar cells with 9- μm transparent TiO_2 films and 9+5- μm TiO_2 films (See Table S1 in the Supporting Information for full details).

	TiO_2 [μm]	J_{SC} [mA cm^{-2}]	V_{OC} [mV]	FF ^[a]	Efficiency [%]
1	9	4.60	670	0.724	2.23
	9+5	5.19	654	0.730	2.51
2	9	5.11	539	0.712	1.96
	9+5	5.79	538	0.729	2.31
3	9	5.78	491	0.719	2.04
	9+5	6.38	488	0.713	2.25

[a] Fill factor (FF) in the context of solar cell performance is defined as the ratio of the maximum obtainable power ($V_{\text{mp}} \times J_{\text{mp}}$) to the theoretical power ($J_{\text{sc}} \times V_{\text{oc}}$).

was observed where dyes **1**, **2**, and **3** showed maximum values, 47, 50, and 53% at 460, 470, 480 nm, respectively. To increase the light-harvesting efficiency, a scattering layer composed of big TiO_2 particles (400 nm) was applied on the transparent TiO_2 layer. With 9+5- μm TiO_2 films, a more than 10% increase in the J_{SC} was observed (see Figure S1 b in the Supporting Information) and thus, the power-conversion efficiencies increased to 2.51, 2.31, and 2.25% for dyes **1**, **2**, and **3**, respectively. The power-conversion efficiencies are not directly proportional to the change in J_{SC} because the open-circuit voltage (V_{OC}) shows opposite inclination which follows the sequence dye **1** > **2** > **3**. The lower V_{OC} values of dyes **2** and **3** are plausibly attributed to faster recombination than that of dye **1** (see below).

To elucidate the different V_{OC} values, photovoltage and photocurrent transients have been performed. Figure S2 in the Supporting Information shows the electron lifetime, which is the reciprocal of the recombination rate for the injected electrons and leads to a change in electron density in TiO_2 and then a subsequent change in the V_{OC} of DSSCs. The electrons injected into the conduction band from optically excited dyes can traverse the TiO_2 network and can be collected at the transparent conducting glass or can react either with an oxidized dye molecule or with the oxidized redox couple, that is, triiodide. The electron lifetime of dyes **2** and **3** are shorter than that of dye **1**, and dye **3** shows the shortest electron lifetime at a fixed charge density. Hence the decreased V_{OC} of dyes **2** and **3** are mainly caused by a faster recombination process. Interestingly, dye **3** shows different electron-lifetime dependence with the charge density than dyes **1** and **2**. The apparent electron lifetime in the device using **3** approaches that of dye **2** at relatively lower charge density. At a fixed charge density of $3 \times 10^{17} \text{ cm}^{-3}$, the dye **3** shows a six times shorter electron lifetime, which is by contrast 1.7 times shorter at a density of $2 \times 10^{16} \text{ cm}^{-3}$ than dye **2**. This different dependence should have an influence on the photovoltaic performance and a difference between V_{OC} of dye **2** and **3** of 26 mV was indeed observed at 0.1 sun, which is less than the difference of 50 mV at 1 sun. The semi-logarithmic plot in Figure S3 in the Supporting Information compares the light-intensity dependence of V_{OC} for DSSCs as dyes. The slopes of dyes **1** and **2** from the linear dependence of the logarithm of the light intensity against V_{OC} were approximately 93 mV/decade, however, it

changed to approximately 69 mV/decade for dye **3**. The light-intensity dependence of V_{OC} is consistent with the photovoltaic results mentioned above. The different slopes may indicate different electron-transfer dynamics. The high slope probably indicates that electron transfer also occurs through additional surface states.^[18] The elimination of additional surface states could be considered because those are the route for the leakage of electrons, however, in this work, the dyes **1** and **2** with high slopes showed the longer electron lifetime. A full understanding of the dynamics of this system is under study, however, this preliminary result shows how meticulous tuning of molecules for application to solar cells is fundamental.

The absorbed photon-to-current conversion efficiency (APCE) can be obtained by known IPCE and light-harvesting efficiency (LHE). Both the quantum yield of the injection yield (η_{inj}) and the charge-collecting efficiency (η_{c}) contribute to the APCE.^[19] Figure 3 shows the LHE and APCE of dyes **1**, **2**, and **3** in which the LHE are obtained by dye-stained 9- μm TiO_2 films. All these dyes have a much lower molar extinction coefficient than ruthenium complexes, hence, the relatively low performance is ascribed to the low light-harvesting efficiency over the visible light range. Moreover, as it turned out, dyes **1** and **2** have lower molar extinction coefficients than dye **3**. Dyes **1** and **2** show the highest APCE, above 80%, compared with less than 60% for dye **3**, albeit the IPCE and current of dye **3** are the highest. This indicates that the lower performance of the dyes **1** and **2** is mainly owing to low LHE. By contrast, the low performance of dye **3** is attributed to low APCE as well as the LHE over the range of visible light. This may indicate a lower η_{inj} owing to a low excited-state potential of the dye and/or the relaxation time of the excited electron. As mentioned above, three dyes show a suitable position of the LUMO leading to a driving force that is sufficient enough to induce electron injection. Hence, the fast relaxation time of the excited electron is probably one reason for the lower APCE of dye **3**. Another parameter is η_{c} , which is mainly governed by the structure of the mesoporous film. As the same colloidal TiO_2 was used, it cannot be used to explain the different behaviors observed. The electron-lifetime dependence with dyes was elucidated, and dye **3** showed the shortest electron

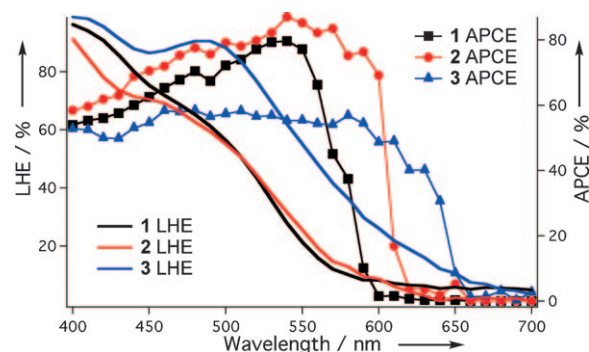


Figure 3. Light-harvesting efficiency (LHE) and absorbed photon-to-current conversion efficiency (APCE) of dyes **1** (black), **2** (red), and **3** (blue) based on 9- μm TiO_2 films.

lifetime. However, the electron lifetime did not influence the APCE because dye **2**, which shows a shorter electron lifetime than dye **1**, exhibits a high APCE above 80%, which is similar to dye **1**. Hence, the foremost reason of the low APCE of dye **3** is plausibly attributed to lower η_{inj} , mainly owing to the fast relaxation time of excited electrons, which still requires further study. This result indicates that the possible current and IPCE of dye **3** could be twice the presented values if the low APCE is overcome.

In conclusion, we report the full data for DSSCs using new cyclometallated iridium complexes as the sensitizers. Despite poor absorption properties compared with commonly used ruthenium dyes, such as low absorption coefficient and an absorption that does not extend far into the red part of the visible spectrum, those dyes performed surprisingly well reaching 2.5% efficiency under full sun. We have shown that the poor light-harvesting properties of the dyes are the main reasons for these efficiencies. A first step to improve the absorption properties will be achieved by replacing the innocent acetylacetonate ancillary ligand with a more-light-absorbing ligand. Interestingly, dye **3**, which as expected harvests more photons than dyes **1** and **2**, exhibits poor APCE. This suggests an additional and different mechanism for the electron relaxation, a mechanism that is detrimental to the final efficiency. Finally, by comparing energy levels of the dyes, the electrolyte, and the titanium oxide, one can see that there is still plenty of room for improvement by tuning those energy levels.

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Keywords: cyclometallation • iridium • charge transfer • sensitizers • solar cells

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