Cyclometalated ruthenium complexes for sensitizing nanocrystalline TiO_2 solar cells†

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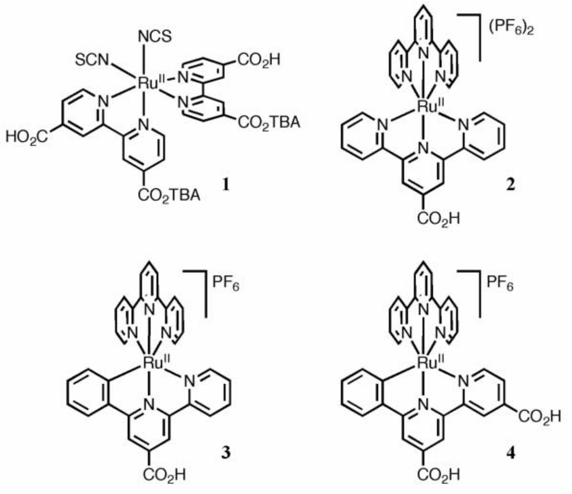
Cyclometalated ruthenium complexes of [Ru(C^N^N)(N^N^N)] configuration are a promising new class of molecular sensitizers for dye-sensitized solar cells, as a result of their broad and red-shifted visible absorption in comparison to the analogous [Ru(N^N^N)$_2$] type coordinative complexes.

Dye-sensitized solar cells (DSSC's) have been extensively investigated since Grätzel and co-workers showed that by sensitizing large bandgap semiconductors, cheap and efficient solar cells can be obtained with energy power conversion efficiencies (η_{sun}) of up to 10%.[1] In these solar cells, the process of light absorption and charge separation is performed by a sensitizer attached to a large bandgap semiconductor, which takes care of charge transport.[2] The electrochemical and photophysical properties of the dye are crucial for the long term stability[3] and the light harvesting efficiency of the solar cell. Coordination complexes of ruthenium and osmium have received wide-spread attention as photosensitizers,[4–6] the most well-known being the N719 dye [Ru(NCS)$_2$(dcbpy)$_2$] (dcbpy = 4,4′-dicarboxy-2,2′-bipyridine) (**1**) and the black dye [Ru(NCS)$_3$(tctpy)] (tctpy = 4,4′,4″-tricarboxy-2,2′:6′,2″-terpyridine). Although the highest efficiencies have been obtained with the black dye[7] it could not replace N719 as commercial standard, because of its difficult synthesis, relatively low extinction coefficient and troublesome cell manufacturing. Organic compounds[8–10] as well as porphyrins[11] have also been used as photosensitizers, but do not reach the same conversion efficiencies as ruthenium complexes. Recently, quantum dots have been applied as the photosensitizer in a hybrid organic–inorganic solar cell.[12] Thus far, cyclometalated compounds[13] have not been explored as a sensitizer for solar cells. Replacing a hetero donor atom by a carbon atom in a multidentate ligand containing additional hetero donor atoms dramatically changes its electronic properties.[14,15] Moreover, cyclometalation itself has a strong effect on the photophysical properties of the resulting complexes.[16] Here we report the first use of cyclometalated ruthenium complexes as efficient sensitizers for TiO_2 semiconductor electrodes. We compare the photocurrent action spectra for the cyclometalated dyes to those obtained for the non-cyclometalated analogues as well as to the standard **1**. Also note that so far the overall solar cell performance has not been optimized.

Complexes **2–4** (Scheme 1) are synthetically easily accessible, can be handled and stored in air and have high extinction coefficients. The synthesis and full characterization of these complexes will be reported elsewhere. Complex **2** is a true ruthenium coordination complex with two tpy ligands (tpy = 2,2′:6′,2″-terpyridine), one of which is functionalized with a carboxyl group for anchoring to TiO_2. Replacing a nitrogen donor atom with a carbon atom in one of the outer pyridine moieties of the functionalized ligand, results in the cyclometalated congener, complex **3**. Complex **4** contains an additional carboxylic acid moiety for more efficient grafting to the TiO_2 surface.

The molecular geometry of **3** as obtained by single crystal X-ray structure determination is depicted in Fig. 1. The carboxyl substituted cyclometalated ligand is coordinated in a meridional fashion to the ruthenium, and is oriented perpendicular to the tpy ligand, resulting in a distorted octahedral coordination environment. The nitrogen to ruthenium bonds lengths in the latter are typical for coordination of this ligand to ruthenium,[17] 2.057(3) Å and 2.068(3) Å for the nitrogens in the outer rings and 1.950(3) Å for the central ring. In the cyclometalated ligand, the carbon to ruthenium σ bond (2.062(3) Å) has a pronounced *trans* effect, elongating the opposite nitrogen to ruthenium bond to 2.158(3) Å, whereas the central nitrogen to ruthenium bond is 2.024(2) Å. In the solid state **3** forms hydrogen bonded dimers *via* very strong



Scheme 1 Molecular structure of dyes **1**, **2**, **3** and **4** (TBA = tetrabutylammonium).

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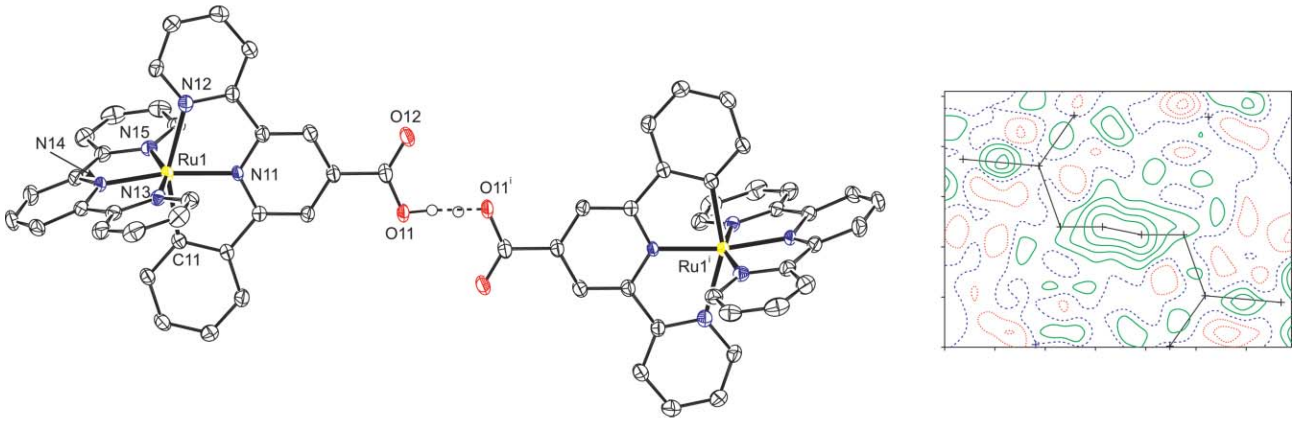

Fig. 1 Displacement ellipsoid plot (50% probability level) of one of two independent hydrogen bonded dimers of **3** in the crystal. The bridging O–H hydrogen atom is close to an inversion center and only half occupied. The second dimer is located on the second independent inversion center of space group $P\bar{1}$. C–H hydrogen atoms, solvent molecules and the PF_6^- counteranion have been removed for clarity. Selected bond lengths (Å) and angles (°): C11–Ru1 2.062(3), N11–Ru1 2.024(2), N12–Ru1 2.158(3), N13–Ru1 2.057(3), N14–Ru1 1.950(2), N15–Ru1 2.068(3), C11–Ru1–N12 156.20(11), N13–Ru1–N15 158.27(10), C11–Ru1–N11 79.74(11), N11–Ru1–N12 76.46(10), O11–O11i 2.467(3). Symmetry operation i: $1 - x$, $-y$, $1 - z$. Inset: difference electron density map in the plane of the carboxylic acid (hydrogen atom omitted). Green contours correspond to positive values with a contour level of 0.1 e Å^{-3}.‡

acid bridges, where two carboxyl groups share one proton. The remaining positive charge is compensated for by one PF_6^- ion.

For the photovoltaic experiments, DSSC's were produced on so called master plate devices, according to previously published procedures.[18] A master plate consisted of two SnO_2:F coated glass plates (7.5 × 10 cm, LOF tec 8) one of which contained five electrically isolated anatase TiO_2 photoelectrodes (4 cm^2) deposited by screen printing.§ The other glass plate contained five platinum counter electrodes.

The active layers are dried and fired at 570 and 450 °C for TiO_2 and Pt, respectively, to remove all organic components and to establish sufficient inter-particle contacts between the TiO_2 particles. A typical film thickness of 13 μm TiO_2 was obtained after firing. The two glass plates comprising the photo- and counter-electrodes were laminated together using Surlyn as a hotmelt foil. All the dyes were adsorbed by staining the electrodes in an 1 mM dye solution in methanol : acetonitrile (3 : 1, v/v). A device containing **1** stained from ethanol has been included in the comparison, because ethanol is the most optimal staining solvent for **1**. The electrolyte contained 0.5 M LiI, 0.05 M I_2 in γ-butyrolactone.

IPCE measurements have been carried out as follows. A 1000 W xenon lamp (Osram XBO/HS OFR) was used as the light source in combination with small band pass filters (Schott, FWHM = 6–10 nm) to generate monochromatic light. The monochromatic light was passed through a chopper wheel to create a small, modulated signal on top of a constant signal originating from 0.3 sun bias illumination. The resulting modulated current was analyzed by a lock-in amplifier.

Fig. 2 shows the absorption spectra of **2–4** in acetonitrile solution as well as the spectrum of **1** for reference. The spectrum of **2** is dominated by an intense and sharp metal to ligand charge transfer (MLCT) transition (λ_{max} = 487 nm, $\varepsilon = 18.0 \times 10^3$ M^{-1} cm^{-1}) typical for substituted Ru(tpy)$_2$ complexes.[19] As can be seen, cyclometalation resulted in a clear broadening and red shift of the absorption features. Unlike **2**, the spectrum of **3** (λ_{max} = 523 nm, $\varepsilon = 15.8 \times 10^3$ M^{-1} cm^{-1}) and **4** (λ_{max} = 552 nm, $\varepsilon = 15.8 \times 10^3$ M^{-1} cm^{-1}) displayed a number of shoulders presumably resulting from the presence of a multiplicity of electronic transitions. Grafting of the dye onto TiO_2 again resulted in both a slight broadening and a small red shift which was considered desirable as it increases the overlap with the solar spectrum and should lead to larger photocurrents.

Fig. 3 shows the photocurrent action spectra for cells using the sensitizers **2–4** and **1** as reference. It must be noted that it was not the aim of this study to maximize the power conversion efficiency of these cells but rather to show the potential of these dyes as molecular sensitizer in DSSC's. For this reason, a more convenient electrolyte was used consisting of LiI (0.5 M) and I_2 (0.05 M) in γ-butyrolactone, instead of a high efficiency electrolyte that increases voltage and fill factor at the expense of the photocurrent.

It is clear from Fig. 3 that the photocurrent action spectrum of **2** in the TiO_2 solar cell displays the same characteristics as the absorption spectrum of **2** in solution, peaking at an incident photon to current conversion efficiency (IPCE) of 35% around

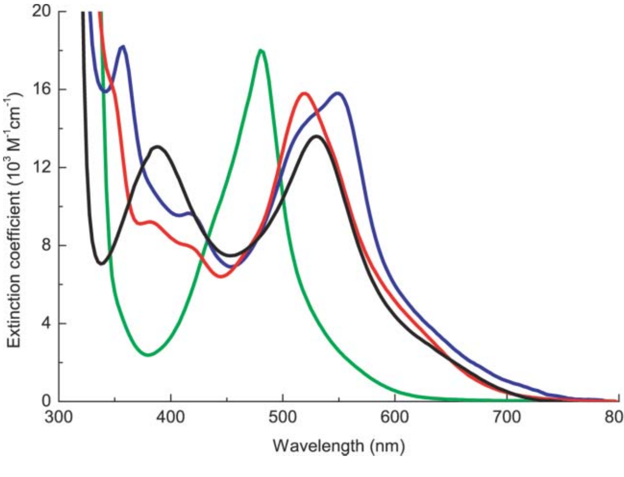

Fig. 2 UV-Vis spectra of **1** (black), **2** (green), **3** (red) and **4** (blue) in acetonitrile solution.

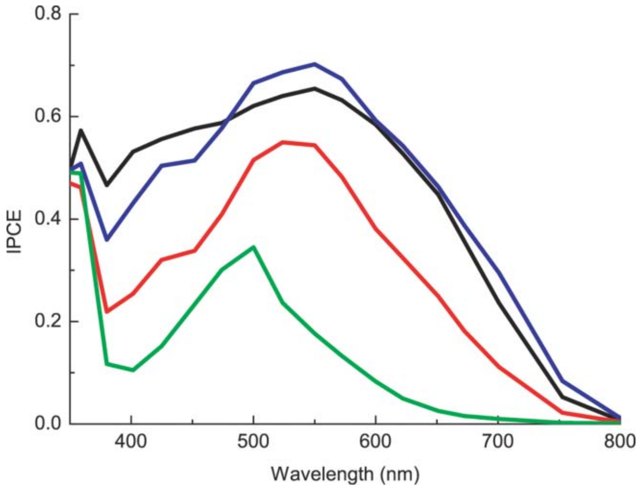

Fig. 3 Photocurrent action spectra of **1** (black), **2** (green), **3** (red), **4** (blue) in a TiO_2 solar cell using 0.5 M LiI and 0.05 M I_2 in γ-butyrolactone as the electrolyte.

500 nm with an onset around 650 nm. For the cyclometalated Ru-complexes **3** and **4**, the photocurrent action spectra show a clear red shift compared to **2** in agreement with the respective absorption spectra. In addition, a substantial enhancement of the maximum IPCE is observed for the cyclometalated dyes **3** and **4**, peaking at resp. 55% around 530 nm and 70% around 550 nm. The higher IPCE for **4** can be explained by a more intimate contact of this sensitizer with TiO_2 due to presence of two anchoring moieties. Interestingly, it is also seen that the spectral features of the photocurrent action spectra of the solar cells sensitized by the cyclometalated dye **4** and the reference dye **1** are very similar, both show an IPCE onset around 800 nm. Moreover, the photocurrent for **4**, derived by taking the spectral overlap of the action spectra and the AM1.5 spectrum, is somewhat higher than for the **1** sensitized reference system (12 *vs.* 11.5 mA cm^{-2}), stained from the acetonitrile–MeOH solvent mixture but somewhat lower when **1** is stained from ethanol solution (13 mA cm^{-2}).¶

In conclusion, [Ru(C^N^N)(N^N^N)] type cyclometalated ruthenium complexes have been used for the first time as a sensitizer in DSSC's. The sensitizing properties of the cyclometalated complexes **3** and **4** are superior to the coordination complex **2**. It has been shown that a device sensitized by **4** is able to achieve short circuit currents comparable to that of the standard ruthenium dye **1** when a γ-butyrolactone based electrolyte is used. The improved anchoring capability of **4** allows the use of higher-performance electrolytes to optimize the efficiency, which is subject of further investigation. Finally, the broad and red-shifted absorption properties of the cyclometalated complexes renders these as a promising new class of compounds capable of sensitizing DSSC's.

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Notes and references

‡ Compound **3**. $[C_{64}H_{43}N_{10}O_4Ru_2](F_6P)\cdot 3(C_2H_3N)$, M = 1486.36, triclinic, a = 9.5350(1), b = 15.4639(2), c = 21.5139(3) Å, α = 97.2304(4), β = 96.0597(5), γ = 92.7702(6)°, V = 3123.27(7) $Å^3$, T = 110(2) K, space group $P\bar{1}$, Z = 2, $\mu(MoK\alpha)$ = 0.590 mm^{-1}, 57455 reflections measured, 14126 unique (R_{int} = 0.0477). $R1$ = 0.0362, w$R2$ = 0.0878 ($I > 2\sigma(I)$). CCDC 640013. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b703636a

§ TiO_2 particles with a size of ∼30 nm were prepared following standard procedures. The colloidal particles were transferred from an aqueous suspension into a mixture of terpineol and ethylcellulose to prepare a screen printable paste. N719 dye was purchased from Solaronix and used as received.

¶ Values obtained for V_{oc}, ff (fill factor) and η_{sun} are 0.42 V, 0.46 and 2.1% respectively for **4**, and 0.45 V, 0.44, 2.3% for **1**.

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