

Cyclometalated Ruthenium(II) Complexes as Near-IR Sensitizers for High Efficiency Dye-Sensitized Solar Cells**

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Dye-sensitized solar cells (DSSCs) based on nanocrystalline TiO₂ films have attracted considerable attention because of their great potential in terms of low fabrication costs and high solar-light-to-electricity conversion efficiency.^[1] Extensive efforts have been focused on the development of new, highly efficient sensitizers, as they play a critical role in cell performance. Sensitizers exhibiting absorption over a wide range of the solar spectrum and a high molecular extinction coefficient have been investigated for improving the conversion efficiency of DSSCs. Among the most successful of the various sensitizers are complex N3, [Ru(dcbpy)₂(NCS)₂] (dcbpy = 4,4'-dicarboxy-2,2'-bipyridine),^[2] and complexes of the type [Ru(dcbpy)(L1)(NCS)₂], where L1 is a 2,2'-bipyridine with a highly conjugated ancillary group.^[3] However, these sensitizers show insufficient light-harvesting efficiencies in the near-IR region. As the solar spectrum has a large photon flux in the near-IR region above 800 nm, the synthesis of efficient near-IR sensitizers is currently one of the most important issues in the development of solar cells.

The absorption properties of Ru^{II} complexes can be tuned by careful consideration of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels.^[4] The absorption band can be extended into a longer wavelength region by either destabilizing the metal t_{2g} orbital using a strong σ-donating ligand or by introducing a ligand with a low-lying π*-level molecular orbital. Complex N749, (TBA)₃[Ru(tctpy)(NCS)₃] (tctpy = 4,4',4''-tricarboxy-2,2':6',2''-terpyridine; TBA = tetra-*n*-butylammonium),^[5] and complexes of type PRT-11-14, (TBA)₃[Ru(L2)(NCS)₃], where L2 is a 4,4'-dicarboxy-

2,2':6',2''-terpyridine derivative with a highly conjugated ancillary group,^[6] have been reported to exhibit panchromatic sensitization up to 900 nm. Although the introduction of the tctpy ligand improves near-IR sensitization, the main drawbacks of N749 are the inferior incident-photon-to-current conversion efficiency (IPCE) in the shorter wavelength region, and the presence of three NCS ligands. The former problem arises predominantly from the lack of an effective chromophore, whereas the latter is caused by two factors: 1) The linkage isomers of the NCS ligand cause a decrease in the synthetic yield.^[5,7] 2) The stability of the complex decreases owing to dye decomposition by weak Ru–NCS bonding. Although NCS-free Ru^{II} complexes with a conversion efficiency of up to 10% have been reported,^[8] these dyes also show relatively low light-harvesting properties over 800 nm.

We^[9] and others^[10] have examined terpyridyl Ru^{II} complexes of the type [Ru(tctpy)(L3)(NCS)]^z, where L3 is a bidentate ligand and *z* = 0 or +1, in an attempt to optimize near-IR sensitizers. The role of the NCS ligand is to regenerate the sensitizers from the iodine redox.^[10a,11] Among these complexes, cyclometalated Ru^{II} complexes show superior light-harvesting properties in the near-IR region.^[9e] A new absorption band above 700 nm is seen with complex FT3, [Ru(tctpy)(ppy)(NCS)] (ppy = 2-phenylpyridinato). However, the DSSC based on FT3 exhibited a low efficiency, probably because of the insufficient energy difference between the HOMO and iodine redox (Δ*G*₂, see Figure 4). To obtain a sufficient thermodynamic driving force for dye regeneration,^[12] we have investigated the structural modification of the cyclometalating ligand. The modifications to the ligand affect not only its σ-donating ability but also the HOMO energy level of the resulting complexes. Herein, we report Ru^{II} complexes of the type [Ru(tctpy)(L3)(NCS)], where L3 is either a ppym ligand (FT67; ppym = 2-phenylpyrimidinato), or a derivative bearing one CF₃ group (FT57) or two CF₃ groups (FT89). The strongly electron-withdrawing CF₃ group was introduced to further increase Δ*G*₂.

The molecular structures of FT67, FT57, and FT89 are shown in Figure 1. FT67 and FT57 were prepared by a previously described procedure.^[9e] FT89 was synthesized by a modification of the literature procedure (see the Supporting Information for details). These complexes normally exist as mixtures of stereoisomers, but the single isomers depicted in Figure 1 could be obtained by microwave synthesis. The structures of the resulting complexes were identified by nuclear magnetic resonance (NMR) and electrospray-ionization mass spectral (ESI-MS) analyses. The far-

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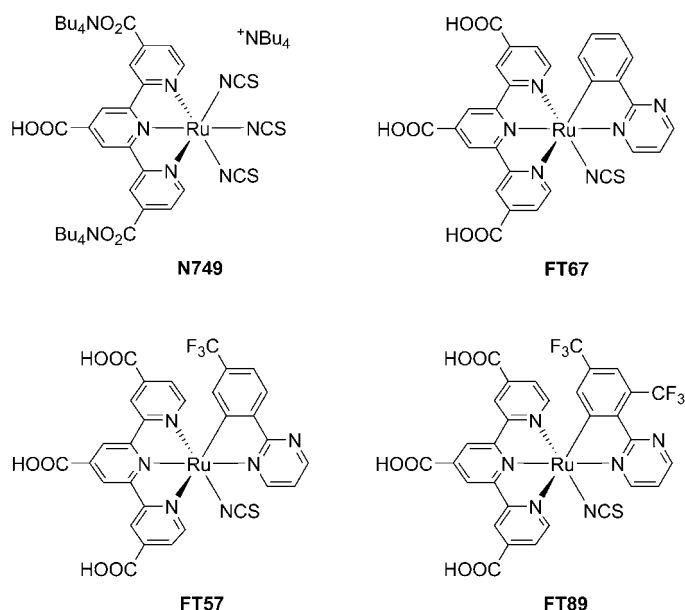


Figure 1. Molecular structures of N749, FT67, FT57, and FT89.

the upfield signal in the aromatic region, which is assigned to the proton in the position *ortho* to the organometallic bond, is a useful spectroscopic reference for evidence of cyclometalation.^[13] In the case of the obtained isomer, the further upfield shift of this proton is induced by the ring current effect of the 2,2':6',2''-terpyridine ligand.^[9e]

The absorption spectra of Ru^{II} complexes in a methanolic solution of tetra-*n*-butylammonium hydroxide (TBAOH) are shown in Figure 2. Strong π - π^* absorptions of the coordinating ligands are observed in the UV region. A broad metal-to-

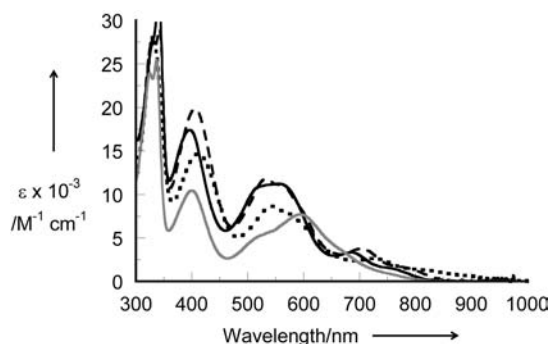


Figure 2. Absorption spectra of FT67 (.....), FT57 (---), FT89 (—), and N749 (—) in a methanol solution of TBAOH (1×10^{-3} M).

ligand charge transfer (MLCT) absorption is observed in the lower energy region. The absorption maxima of FT67, FT57, and FT89 are 542 nm ($\epsilon = 8700 \text{ M}^{-1} \text{ cm}^{-1}$), 532 nm ($\epsilon = 11800 \text{ M}^{-1} \text{ cm}^{-1}$), and 556 nm ($\epsilon = 11200 \text{ M}^{-1} \text{ cm}^{-1}$), respectively. The most notable feature of this FT series of dyes is an absorption band above 650 nm with a distinct shoulder around 750 nm. The enhanced absorption in the lower energy region is probably due to the introduction of a strong

σ -donating cyclometalating ligand. FT57 and FT89 show a higher molecular extinction coefficient than N749, except in the 600–675 nm region.

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations were performed on this system (see the Supporting Information), and the frontier orbitals for FT89 are depicted in Figure 3. As can be seen in Figure S1 (see the Supporting Information), FT67 and FT57 show

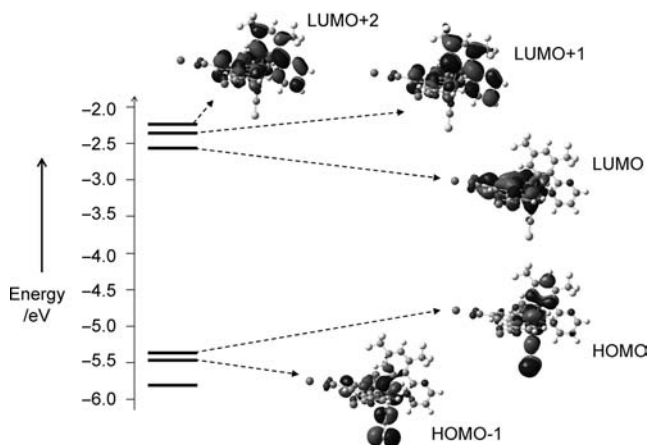


Figure 3. Kohn-Sham orbital energy diagram of FT89.

a similar localization of the HOMO and LUMO. The HOMO is localized on the metal center with the NCS and phenyl group of the cyclometalating ligands, and the LUMO is localized on the tctpy anchoring ligand, whereas the LUMO + 1 and LUMO + 2 are delocalized over the tctpy and cyclometalating ligands. Since these complexes are adsorbed onto TiO₂ through the tctpy anchoring ligand, the presence of a LUMO on the ligand facilitates an effective electron injection from the excited complexes to TiO₂. Figure S2 (see the Supporting Information) shows calculated energy diagrams of the FT dyes. It was anticipated that structural modifications to the cyclometalating ligand would shift the HOMO level to a lower energy in the order FT89 (-5.38 eV) > FT57 (-5.31 eV) > FT67 (-5.21 eV). This shift may be desirable for efficient dye regeneration. The calculated spectra of FT89 and N749 are shown in Figure S3 (see the Supporting Information). TD-DFT calculations predict both the blue shift of the MLCT absorption, as compared with that of N749, and the existence of an absorption in the low-energy region. Since the calculated spectrum of FT89 is in good agreement with the experimental spectrum, TD-DFT may be a useful tool for the synthesis of new, efficient sensitizers in this type of Ru^{II} complex.

The energy level diagrams of Ru^{II} complexes are shown in Figure 4. Cyclic voltammetry was performed to ensure that the HOMO energy levels of the FT dyes were suitable for the dye regeneration process. A quasi-reversible wave for the Ru^{3+/2+} couple between 0.2 and 0.7 V vs. a saturated calomel electrode (SCE) was obtained. The peak potentials of differential pulse voltammograms for FT67, FT57, FT89, and N749 are 0.42, 0.49, 0.52, and 0.66 V vs. SCE, respectively. The order of the HOMO energy levels of the FT dyes is in good

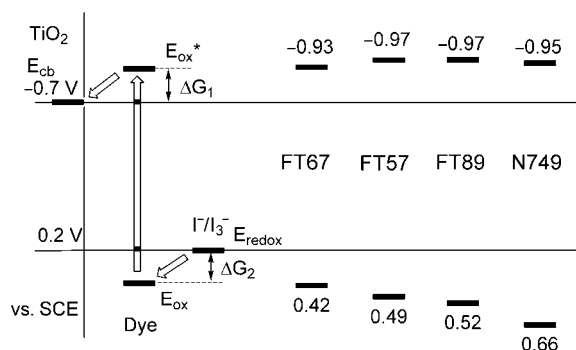


Figure 4. Energy level diagrams of TiO_2 , Ru^{II} complexes, and I^-/I_3^- .

agreement with that obtained by DFT calculation. The redox potentials of the Ru^{II} complexes are strongly affected by the introduction of a cyclometalating ligand and structural modifications. An increase in the number of trifluoromethyl groups improves the ΔG_2 of the FT dyes. The 0–0 transition energies (E_{0-0}) of the Ru^{II} complexes were estimated from the absorption edge, and the calculated LUMO energy levels are sufficiently high for rapid electron transfer from the excited complex to the conduction band of TiO_2 .^[14] It was expected that the LUMO energy levels of FT57 and FT89 would be slightly higher than that of N749.

The DSSC performance of the FT dyes was investigated under AM 1.5 irradiation (100 mW cm^{-2} ; AM = air mass); the results are summarized in Table 1, and current–voltage curves are shown in Figure 5. Although the DSSC based on FT67 has an efficiency of 6.4 %, the cells based on FT57 and FT89 show remarkably high efficiencies of 9.1 % and 10.7 %, respectively. The short-circuit current density (J_{sc}), open-circuit voltage (V_{oc}), and overall conversion efficiency (η) of cells based on the FT dyes are improved with increasing ΔG_2 . The increase in V_{oc} can be correlated with a decrease in the dark current. The dark current of the cell based on FT89 has almost the same value as that of N749. The higher J_{sc} of the cells based on FT89 can be explained by the increase in the molecular extinction coefficient and the improvement of the dye regeneration process. Note that FT89 not only exhibits an efficiency of up to 10 %, but also one that is higher than N749 under the same cell fabrication conditions. Figure 6 shows the photocurrent action spectra of the maximum performance of DSSCs containing FT dyes and N749. The IPCE for each DSSC is plotted as a function of the wavelength. As anticipated from photovoltaic experiments, the cell based

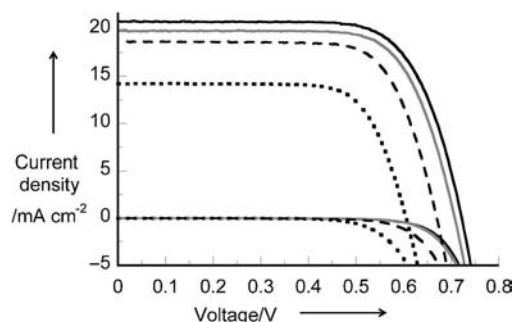


Figure 5. Current–voltage curves of DSSCs based on FT67 (••••), FT57 (---), FT89 (—), and N749 (—). The onsets of the dark current densities of the cells are also shown.

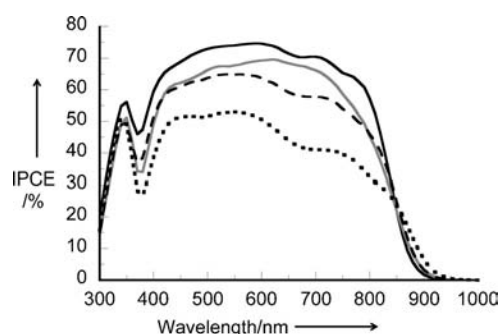


Figure 6. Photocurrent action spectra of DSSCs based on FT67 (••••), FT57 (---), FT89 (—), and N749 (—).

on FT67 shows slightly lower IPCE values. The higher IPCE values of FT89, as compared with those of FT57, can be explained by the improvement in the HOMO energy level, because FT89 and FT57 have similar structure and absorption properties. This result suggests that the rapid dye regeneration does not occur if the HOMO energy level is less than 0.49 V vs. SCE, and if there is a threshold of efficient electron transfer near 0.5 V vs. SCE. It is notable that the cell based on FT89 exhibits efficient panchromatic sensitization over the entire visible wavelength range, extending into the near-IR region. Moreover, even though the HOMO energy level of FT89 is 0.14 eV more negative than that of N749, FT89 exhibits higher IPCE values than N749. This is consistent with the results obtained from photovoltaic experiments, as the DSSC based on FT89 has a higher J_{sc} value than N749. The IPCE values of FT89 and N749 at 800 nm are 57 % and 45 %, respectively.

Table 1: Electrochemical and photovoltaic data of DSSCs based on FT67, FT57, FT89, and N749.^[a]

Dye	E_{ox} [V vs. SCE]	E_{0-0} [eV]	E_{ox}^* [V vs. SCE]	η [%]	J_{sc} [mA cm ⁻²]	V_{oc} [V]	ff	IPCE _{max} [%]	IPCE at 800 nm [%]
FT67	0.42	1.35	−0.93	6.4	14.1	0.62	0.74	53	32
FT57	0.49	1.46	−0.97	9.1	18.7	0.67	0.73	65	46
FT89	0.52	1.49	−0.97	10.7	20.8	0.72	0.71	75	57
N749	0.66	1.61	−0.95	10.1	19.8	0.71	0.72	70	45

[a] All DSSCs were fabricated and measured under the same experimental conditions. The TiO_2 layer thickness is 31 μm , the active area of the cells defined by a black metal mask is 0.175 cm^2 , and the electrolyte solution consists of 1,2-dimethyl-3-propylimidazolium iodide (0.6 M), iodine (0.05 M), lithium iodide (0.1 M), and *tert*-butylpyridine (0.5 M) in acetonitrile.

respectively. Thus, FT89 has superior light-harvesting properties above 800 nm, as well as in the visible wavelength region. The present work provides new possibilities in sensitizer design, because it is important to minimize ΔG for efficient near-IR sensitizers.

In summary, [Ru(tctpy)(L3)(NCS)] complexes, which possess a cyclometalated Ru^{II} center, have been synthesized as near-IR sensitizers. Tuning of the HOMO energy level by structural modification of the cyclometalating ligand greatly influenced efficiency and improved cell performance. The DSSC sensitized with FT89 shows a 10.7% efficiency, which is higher than that of the N749 benchmark (10.1%). To the best of our knowledge, this is the highest efficiency to date among DSSCs based on cyclometalated Ru^{II} sensitizers. The advantage of this type of Ru^{II} complex is that the cyclometalating ligand can be modified in several ways to obtain a higher efficiency and superior light-harvesting properties in the near-IR region. We are currently investigating optimization of the ligand structure and cell fabrication.

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