Inorganic Chemistry

Efficient Ruthenium Sensitizer with an Extended π-Conjugated Terpyridine Ligand for Dye-Sensitized Solar Cells

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Ⓢ *Supporting Information*

ABSTRACT: A ruthenium sensitizer with an extended π-conjugated terpyridine (**TUS-42**) has been synthesized for dye-sensitized solar cells (DSCs). Upon extension of the π-conjugated system of the terpyridine ligand, the conversion efficiency of the DSC with **TUS-42** improved successfully to 10.7%, which is almost comparable to that of one of the most efficient ruthenium sensitizers (Black dye). Interestingly, an extremely large short-circuit current density (J_{sc}) value (22.7 mA/cm^2) was obtained in the DSC with **TUS-42** even though the amount of dye adsorption to the TiO_2 photoelectrode is relatively small.

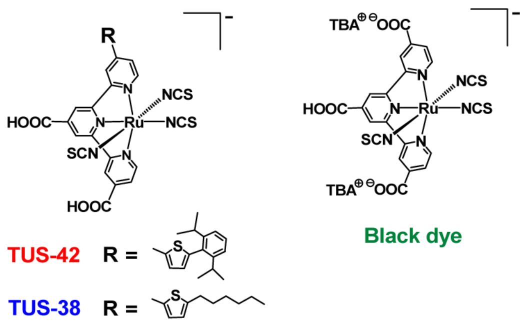

Figure 1. Molecular structures of **TUS-42**, **TUS-38**, and Black dye.

Recently, the light-to-electrical energy conversion efficiency of dye-sensitized solar cells (DSCs) has reached 13% by developing highly efficient molecular sensitizers, such as zinc porphyrin sensitizers.[1] One of the advantages of such highly efficient porphyrin sensitizers is large molar absorption coefficients at the Q band (at around 660 nm), which is approximately 5 times larger than those at the metal-to-ligand charge-transfer (MLCT) band (at around 600 nm) of conventional ruthenium-complex sensitizers. On the other hand, one of the weak points of porphyrin sensitizers is a lack of absorption at the wavelength range above 750 nm, whereas the MLCT band of efficient ruthenium sensitizers covers the solar light until the near-IR region. Therefore, it is considered that a conversion efficiency higher than that for efficient porphyrin sensitizers can be achieved by increasing the molar absorption coefficients at the MLCT band of ruthenium sensitizers. In this regard, a large number of ruthenium sensitizers possessing a chromophore unit, such as carbazole, triphenylamine, and stylenyl units, have been developed so far to increase the molar absorption coefficients at the MLCT band.[2] We have also developed several ruthenium sensitizers with a hexylthiophene-modified terpyridine derivative ligand.[3] These studies demonstrated that the introduction of a 2-*n*-hexylthiophene unit to the 4 position of the terpyridine derivative ligand (i.e., extension of the π-conjugated system of the terpyridine ligand) is an effective method to increase the molar absorption coefficients at the MLCT band, and hence the conversion efficiency of the DSC can be improved by this structural modification.[3] For example, the molar absorption coefficients at the MLCT band of **TUS-38** (Figure 1), which possesses a terpyridine ligand having a 2-*n*-hexylthiophene unit at the 4 position, are larger than those of a structurally analogous ruthenium sensitizer. The DSC with **TUS-38** showed 10.3% conversion efficiency, which is higher than that for the structurally analogous sensitizer. However, this value is still slightly lower than that for Black dye (10.8%), which is well-known and one of the most efficient ruthenium sensitizers (Figure 1).[3b] It is considered that the obtained slightly lower conversion efficiency for **TUS-38** is dominantly attributed to the promoted backward electron transfer of injected electrons in the TiO_2 photoelectrode to the oxidized forms of the sensitizers and/or to I_3^- in the electrolyte solution.[3b] In this study, a novel ruthenium sensitizer with an extended π-conjugated terpyridine ligand (**TUS-42**; Figure 1) has been synthesized as an improved model sensitizer for **TUS-38**. It is expected that the molar absorption coefficients at the MLCT band of **TUS-38** are increased further by replacing the *n*-hexyl chain at the thiophene ring into the 2,6-diisopropylphenyl unit. In addition, it is also expected that access of I_3^- to the sulfur atom of the thiophene ring of the **TUS-42**, which promotes the above-mentioned backward electron transfer, is blocked sterically by the two isopropyl groups at the phenyl unit. Here we communicate the solar cell performance of the DSC with a novel improved model sensitizer (**TUS-42**).

As reported recently, the molar absorption coefficients at the two MLCT bands of **TUS-38** centered at around 450 and 630 nm are obviously larger than that of Black dye (Figure 2).[3b] Upon replacement of the *n*-hexyl chain at the thiophene ring of **TUS-38** into the 2,6-diisopropylphenyl unit, the molar absorption coefficients at the lower-energy MLCT band increased slightly without changing the onset wavelength of the absorption spectrum (ca. 840 nm). This result indicates that further extension of the π-conjugated system of the terpyridine

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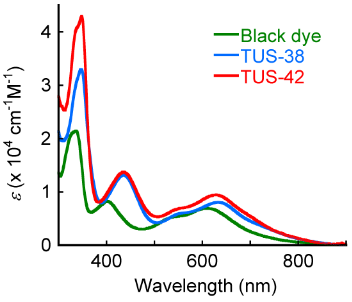

Figure 2. Molar absorption spectra of **TUS-42**, **TUS-38**, and Black dye in *N*,*N*-dimethylformamide.

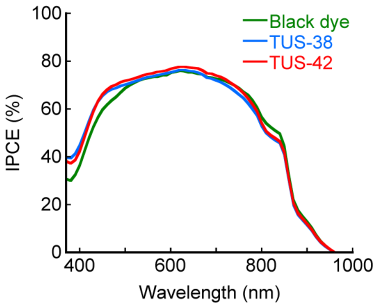

Figure 3. IPCE spectra of the DSC with **TUS-42**, **TUS-38**, and Black dye.

derivative ligand is an effective method to increase the molar absorption coefficients at the lower-energy MLCT band.

On the other hand, the energy levels of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **TUS-42** are almost consistent with those of **TUS-38** (Table 1). It is reported that higher-energy HOMOs (HOMO and HOMO−1) of **TUS-38** locate at the ruthenium atom and the two axial NCS ligands and lower-energy LUMOs (LUMO, LUMO+1 and LUMO+2) of **TUS-38** populate dominantly at the two carboxypyridine rings of the terpyridine ligand.[3b] Therefore, structural modification of the substituent at the thiophene ring does not affect the electrochemical property of **TUS-38**. The important point is that the LUMO of **TUS-42** still populates dominantly at the two carboxypyridine rings (Figure S2) and has a sufficient potential for effective electron injection into the conduction band of the TiO_2 photoelectrode, which are responsible for the higher conversion efficiency.

The solar cell performance of the DSC with **TUS-42** was evaluated at first by using an our standard electrolyte solution [an acetonitrile solution containing 0.05 M I_2, 0.1 M LiI, 0.6 M 1,2-dimethyl-3-*n*-propylimidazolium iodide (DMPImI), and 0.3 M 4-*tert*-butylpyridine (TBP)]. As summarized in Table 1, the DSC with **TUS-42** showed 10.7% conversion efficiency, which is higher than that of **TUS-38** (10.3%) and almost comparable to that of Black dye (10.8%), under AM 1.5 (100 mW/cm^2) irradiation. Interestingly, an extremely large short-circuit current density (J_{sc}) value (22.7 mA/cm^2) was obtained in the DSC with **TUS-42** even though the amount of dye adsorption to the TiO_2 photoelectrode was smaller than those of **TUS-38** and Black dye (Table 1). It is emphasized here that an efficient ruthenium sensitizer showing a J_{sc} value larger than 22 mA/cm^2 is still extremely rare even though numerous ruthenium sensitizers have been synthesized so far.[4] IPCE values of the DSC with **TUS-42** below 500 nm are higher than those of Black dye as well as **TUS-38** (Figure 3). Moreover, IPCE values of **TUS-42** at the wavelength range between 480 and 780 nm are slightly higher than those of **TUS-38**. These results indicate clearly that the superior photosensitizing ability of **TUS-42** reflects improved photochemical properties, which is attributed mainly to the further extension of the π-conjugated system of the terpyridine derivative ligand. On the other hand, such an improvement in the photosensitizing ability was not observed for several structurally analogous sensitizers, which have a terpyridine derivative ligand modified with the 2-*tert*-butylthiophene or 4-*tert*-butylphenyl unit at the 4 position (the details of these results will be reported separately elsewhere). These results indicate clearly that introduction of the 2-phenylthiophene unit (i.e., extension of the π-conjugated system) is essential to improving the photosensitizing ability.

The electron lifetime in the TiO_2 photoelectrode of the DSC with **TUS-38** is reported to be much shorter than that for Black dye, suggesting that charge recombination of the injected electrons and oxidized forms of the sensitizers and/or backward electron transfer of the injected electrons to I_3^- is promoted.[3b] It is known that I_2 (or I_3^-) interacts with a sulfur atom of thiophene, which affords a charge-transfer complex.[5] Therefore, it is likely that I_2 (or I_3^-) in the electrolyte solution interacts with the thiophene unit of **TUS-38**, resulting in an increment in the local concentration of I_3^- at the TiO_2 surface. Under such a condition, backward electron transfer from the conduction band of the TiO_2 photoelectrode to I_3^- would be promoted. In this study, the 2,6-diisopropylphenyl unit is introduced instead of the *n*-hexyl chain in expectation of the blocking effect of two isopropyl groups for access of I_3^- to the sulfur atom of the thiophene ring of **TUS-42**. The electron lifetime of **TUS-42** improved actually; however, it is still shorter than that of Black dye at the matched V_{oc} values (Figure 4), indicating that access of I_3^- is not retarded perfectly by two isopropyl groups. Therefore, introduction of the other substituents with a more bulky structure is considered to be required for developing highly efficient ruthenium sensitizers.

Next, the solar cell performance of **TUS-42** was evaluated by using an electrolyte solution with a modified composition [an acetonitrile solution containing 0.05 M I_2, 0.1 M LiI, 0.6 M 1-ethyl-3-methylimidazolium iodide (EMImI), and 0.3 M TBP]. As we reported recently, the diffusion resistance of the redox

Table 1. Electrochemical Properties of TUS-42, TUS-38, and Black Dye and the Solar Cell Performances of DSCs with These Sensitizers[a]

sensitizer	E_{HOMO} (V vs SCE)	E_{0-0}[b] (eV)	E_{LUMO} (V vs SCE)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	η (%)	amount of dye adsorption (×10^{-7} mol/cm^2)
TUS-42	0.63	1.63	−1.00	22.7	0.666	0.707	10.7	1.6
TUS-38[c]	0.63	1.62	−0.99	22.4	0.660	0.695	10.3	1.8
Black dye[c]	0.66	1.61	−0.95	21.7	0.705	0.708	10.8	2.0

[a] The electrolyte was an acetonitrile solution containing 0.05 M I_2, 0.1 M LiI, 0.6 M DMPImI, and 0.3 M TBP. The film thickness and active area of the TiO_2 photoelectrode were 40 μm and 0.26 cm^2, respectively. Irradiation was carried out by using a solar simulator (AM 1.5, 100 mW/cm^2). [b] E_{0-0} was estimated from the intersection wavelength between absorption and luminescence spectra. [c] Date taken from ref 3b.

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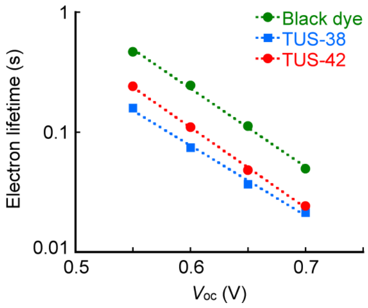

Figure 4. Electron lifetimes in the TiO_2 photoelectrodes as a function of V_{oc} in the DSCs with **TUS-42**, **TUS-38**, and Black dye.

couple in the electrolyte solution between two electrodes can be reduced effectively by using EMImI instead of conventional DMPImI because of the relatively lower viscosity of EMImI.[6] As a result, the conversion efficiency of the cosensitized DSC with Black dye and D131 was improved from 11.1% to 11.5% by using the electrolyte solution containing EMImI.[6] For comparison, the conversion efficiency of the DSC with **TUS-42** was not increased at all by using this electrolyte solution. This result implies that redox-couple diffusion in the electrolyte solution is not a rate-determining step in the DSC with **TUS-42**. As discussed above, backward electron transfer from the conduction band of the TiO_2 photoelectrode to I_3^- is still promoted in the DSC with **TUS-42**; therefore, this result suggests again that backward electron transfer must be suppressed to improve the conversion efficiency.

In summary, an improved model ruthenium sensitizer (**TUS-42**) has been synthesized. Upon replacement of the *n*-hexyl chain into the 2,6-diisopropylphenyl unit, the conversion efficiency of the DSC with **TUS-42** was increased successfully up to 10.7%, which is almost comparable to that of Black dye. Moreover, an extremely large J_{sc} value could be obtained in the DSC with **TUS-42**. This study demonstrates that further extension of the π-conjugated system of the terpyridine ligand is an effective method to develop efficient ruthenium sensitizers for DSCs.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01640.

Experimental procedures, synthetic methods, DFT calculations, and photoelectrochemical measurements (PDF)

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Notes

The authors declare no competing financial interest.

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