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# Synthesis of a Novel Ruthenium Sensitizer Bearing an *ortho*-Dicarboxyphenyl Group as an Anchoring Unit for Dye-sensitized Solar Cells

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A novel ruthenium sensitizer **TUS-20**, which is a structural analog of black dye, bearing an *ortho*-dicarboxyphenylterpyridine as an anchoring unit to $TiO_2$ surface has been synthesized. Adsorption rate of **TUS-20** was much faster, and the maximum amount of dye adsorption was larger than that of black dye. The dye-sensitized solar cell with **TUS-20** exhibited 7.3% conversion efficiency under AM 1.5 ($100\,mW\,cm^{-2}$) irradiation.

Recently, the light-to-electrical energy conversion efficiency of dye-sensitized solar cells (DSCs) has reached more than 11% by employing an efficient sensitizer, such as polypyridyl ruthenium complexes[1] or zinc porphyrins.[2] Extensive efforts have been thus far made to develop highly efficient sensitizers for further improvement of the conversion efficiency of DSCs. On the other hand, for the practical application of DSCs, long-term stability is one of the most important requirements as well as high conversion efficiency. Several reasons for gradual decrease of the conversion efficiency of DSCs have been thus far pointed out. Among them, one of the major reasons is thought to be dye desorption from $TiO_2$ photoelectrode.[3] In this context, various ruthenium-complex sensitizers having hydrophobic alkyl chains, such as Z907[4] and C101,[1c] have been synthesized to suppress dye desorption from $TiO_2$ photoelectrodes. The DSCs with these types of ruthenium sensitizers actually show superior long-term stability than those based on ruthenium dyes without hydrophobic alkyl chains. In these cases, the binding ability of dyes themselves are not improved by the introduction of such functionalized substituents even though dye desorption from the $TiO_2$ photoelectrode was effectively suppressed. Therefore, it is important to improve the binding ability of dyes themselves by the structural modification of their anchoring units. Although a little attention has been thus far paid to improving the binding ability of dyes, it is recently reported that DSC with zinc phthalocyanine dye having an *ortho*-dicarboxyphenyl group as an anchoring unit showed superior long-term stability than that with zinc phthalocyanine dye bearing a carboxyphenyl group.[5] It is also reported that one carboxy group of the *ortho*-dicarboxyphenyl unit binds to $TiO_2$ surface with a bidentate bridge coordination mode and the other carboxy group binds with a monodentate coordination mode.[6] These studies clearly indicate that *ortho*-dicarboxyphenyl is an effective anchoring unit to $TiO_2$ surfaces.

On the other hand, continuous efforts have been made to increase the conversion efficiency of DSCs with black dye analogs.[7] More than 10.5% conversion efficiency was obtained in black-dye-based DSCs in our group,[8] however, relatively inferior long-term stability of these DSCs compared to DSCs with Z907 or C101 is still another subject. In this study, a novel ruthenium sensitizer **TUS-20** (Figure 1), which is a structural analog of black dye and possesses an *ortho*-dicarboxyphenyl unit as an anchoring unit has been synthesized. Although two structural analogs having an *ortho*-dihydroxyphenyl group as an anchoring unit were previously synthesized,[9] **TUS-20** is the first example of a ruthenium sensitizer having an *ortho*-dicarboxyphenyl unit as an anchoring unit. Here we communicate photo- and electrochemical properties and the adsorption behavior of **TUS-20**, together with the performance of DSC based on this novel sensitizer.

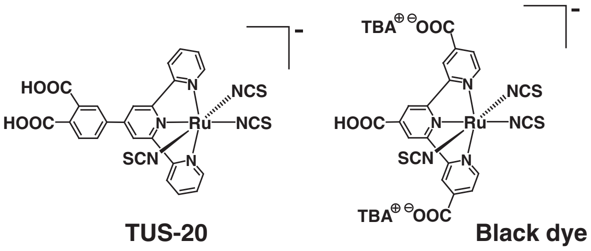

**Figure 1.** Structures of **TUS-20** and black dye.

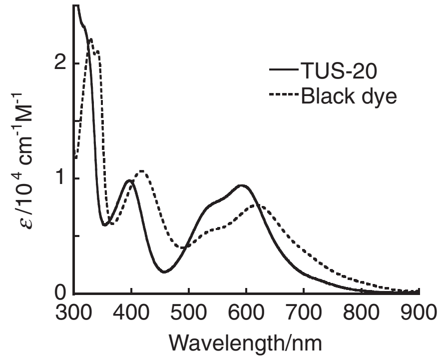

**Figure 2.** Molar absorptivity spectra of **TUS-20** and black dye in ethanol.

A novel *ortho*-dicarboxyphenylterpyridine ligand was prepared by the oxidation of 4′-(3,4-dimethylphenyl)terpyridine, which was synthesized via a Kröhnke-type reaction, using $KMnO_4$. The total synthetic yield for four steps was 31%. 4′-(3,4-Dicarboxyphenyl)terpyridine was reacted with $RuCl_3\cdot 3H_2O$, and further reacted with $[N(C_4H_9)_4]NCS$ in DMF. The crude product was purified on a silica gel column and pure compound **TUS-20** was obtained as a blue powder.

**TUS-20** showed similar absorption to that of black dye although the maximum wavelengths of two MLCT bands were shifted to shorter wavelength by about 30 nm (Figure 2). The onset wavelength of absorption spectrum of **TUS-20** was also shifted to shorter wavelength by about 40 nm compared to that

**Table 1.** Electrochemical properties of **TUS-20** and black dye, and the solar cell performances of DSCs with these dyes[a]

| Dye | $E_{\mathrm{HOMO}}$ /V vs. SCE | $E_{0\text{–}0}$[b] /V | $E_{\mathrm{LUMO}}$ /V vs. SCE | $J_{\mathrm{sc}}$ /mA cm$^{-2}$ | $V_{\mathrm{oc}}$ /V | $FF$ | $\eta$ /% | Amount of dye adsorption /$10^{-7}$ mol cm$^{-2}$ |
|---|---|---|---|---|---|---|---|---|
| **TUS-20** | 0.55 | 1.71 | −1.16 | 16.18 | 0.635 | 0.707 | 7.27 | 3.3 |
| Black dye | 0.66 | 1.61 | −0.95 | 20.40 | 0.704 | 0.726 | 10.42 | 2.3 |

[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. Film thickness and active area of $TiO_2$ film were about 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]$E_{0\text{–}0}$ was estimated from the intersection between absorption and luminescence spectra.

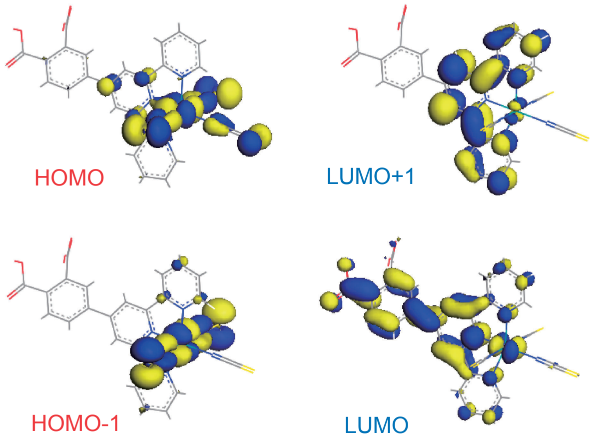

**Figure 3.** Frontier molecular orbitals (occupied and unoccupied MOs) of a fully optimized structure of **TUS-20** in acetonitrile.

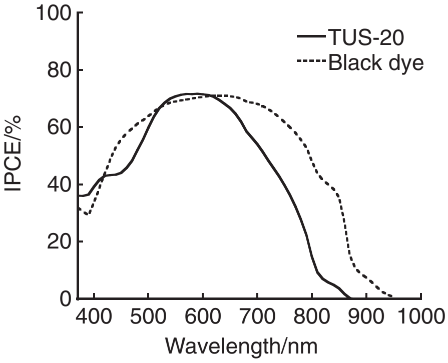

**Figure 4.** IPCE spectra of DSCs with **TUS-20** or black dye.

of black dye. These results suggest that the lowest transition energy of **TUS-20** is larger than that of black dye. Such blue shifts of the maximum wavelengths of MLCT bands and the onset wavelengths of the absorption spectra compared to black dye due to the absence of carboxy groups at the terpyridyl ligand are also reported for two structural analogs ($[Ru(L)(NCS)_3]^-$, L = 4′-carboxyterpyridine or 4′-(4-carboxyphenyl)terpyridine).[10,11] On the other hand, slight increase of the molar absorptivity at the lowest energy MLCT band was observed. This enhancement of the molar absorptivity is presumably due to the extension of the $\pi$-conjugated system of terpyridine ligand by the introduction of an *ortho*-dicarboxyphenyl unit.

The energy level of the HOMO for **TUS-20** (0.55 V vs. SCE, Table 1), corresponding to the filled Ru(II) $t_{2g}$ orbital hybridized with NCS orbitals (Figures 3 and S1[13]), was slightly higher than that for black dye (0.66 V vs. SCE). The lowest transition energy ($E_{0\text{–}0}$) of **TUS-20**, estimated from the intersection between absorption and luminescence spectra, was larger than that of black dye. This result agrees well with the fact that the onset wavelength of absorption for **TUS-20** was shifted to shorter wavelength as mentioned above. The energy level of LUMO for **TUS-20** (−1.16 V vs. SCE) was significantly higher than that for black dye (−0.95 V vs. SCE). It is reported that about 0.53 V vs. SCE is the upper limit of the energy level of HOMO of ruthenium sensitizers for the effective reduction of the one-electron-oxidized form of dye by $I^-$.[12] Therefore, the reduction yield of the one-electron-oxidized form of **TUS-20** might be lower than that of black dye.

DFT calculations for **TUS-20** revealed that the LUMO corresponding to the $\pi^*$ orbital mainly locates at the *ortho*-dicarboxyphenyl unit and the central pyridine of terpyridine ligand, and is largely stabilized by the presence of two carboxy groups (Figures 3 and S1[13]). In addition, LUMO+1 is the $\pi^*$ orbital spread over the terpyridyl unit. Therefore, it is thought that the electron transfer from terpyridyl unit to *ortho*-dicarboxyphenyl unit leading to the electron injection into the conduction band of $TiO_2$ is thermodynamically favorable.

The DSC with **TUS-20** showed 7.3% conversion efficiency under AM 1.5 irradiation, where that with black dye showed 10.4% efficiency (Table 1). This inferior performance for **TUS-20** was mainly attributed to the much lower $J_{\mathrm{sc}}$ value and relatively lower $V_{\mathrm{oc}}$ value. As shown in Figure 4, incident photon-to-current conversion efficiency (IPCE) of DSC with **TUS-20** at wavelength longer than 650 nm was much lower than that for black dye, although the same IPCE value (70%) was obtained the wavelength range between 500 to 620 nm. This result seems to reflect the inferior absorption of **TUS-20** at the wavelength longer than 650 nm. The other possible interpretation for the lower $J_{\mathrm{sc}}$ value is that the electron injection yield to the conduction band of $TiO_2$ was decreased by the introduction of the phenyl spacer between terpyridyl unit and anchoring unit. On the other hand, electron lifetime in the $TiO_2$ photoelectrode for **TUS-20** was found to be much shorter than that for black dye (Figure S2[13]). This shorter electron lifetime must be relevant to the observed lower $V_{\mathrm{oc}}$ value. Interestingly, the amount of dye adsorption for **TUS-20** ($3.3 \times 10^{-7}$ mol cm$^{-2}$, Table 1) was much larger than that for black dye ($2.3 \times 10^{-7}$ mol cm$^{-2}$), even though all adsorbed **TUS-20** could not be completely desorbed from $TiO_2$ photoelectrode under the same conditions for black dye. Adsorption profiles of **TUS-20** and black dye on $TiO_2$ photoelectrode showed that the adsorption rate of **TUS-20** is much faster than that of black dye. In addition, the maximum amount of dye adsorption of **TUS-20** was increased by about 1.8 equivalents to that of black dye after 20 h immersion (Figure S3[13]). Such an effective improvement of the adsorption behavior was also reported for the zinc phthalocyanine dye having an *ortho*-dicarboxyphenyl group as an anchoring unit.[5] These results clearly indicate that *ortho*-dicarboxyphenyl unit can serve as an effective anchoring unit to $TiO_2$ surfaces.

On the other hand, electrochemical impedance spectroscopy measurements under irradiated conditions were conducted to investigate the reasons for observed lower performance of the DSC with **TUS-20**. The R2 resistance of the DSC with **TUS-20** corresponding to the resistance at the $TiO_2$/dye/electrolyte interface was found to be much larger than that for black dye (Figure S4[13]). Since the frequency at the maximum imaginary resistance of R2 semicircle of the DSC with **TUS-20** (10 Hz) was slightly larger than that of black dye (7.9 Hz), it is suggested that the rate of backward electron transfer from the conduction band of $TiO_2$ to the oxidized form of **TUS-20** was larger than that of black dye. This result reasonably explains the observed shorter electron lifetime in the $TiO_2$ photoelectrode for **TUS-20** as mentioned above.

In conclusion, a novel ruthenium sensitizer **TUS-20** bearing an *ortho*-dicarboxyphenyl group as an anchoring unit has been synthesized. The DSC with **TUS-20** exhibited 7.3% conversion efficiency under AM 1.5 ($100\,\mathrm{mW\,cm^{-2}}$) irradiation. This study demonstrated that the adsorption behavior of dyes can be changed by the structural modification of the anchoring unit. Further investigations of the binding ability of dye having an *ortho*-dicarboxyphenyl unit, and the long-term stability of DSCs are now underway in our laboratory.

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