



Effect of different auxiliary ligands and anchoring ligands on neutral thiocyanate-free ruthenium(II) dyes bearing tetrazole chromophores for dye-sensitized solar cells



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ARTICLE INFO

Article history:

Received 15 December 2016

Received in revised form

21 January 2017

Accepted 22 January 2017

Available online 26 January 2017

Keywords:

Dicarboxyterpyridine

Ruthenium dye

Tetrazole

Thiocyanate-free

Thiophene

ABSTRACT

Four new bistridentate Ru(II) complexes having a combination of ligands, 4,4'-dicarboxy-2,2':6,2''-terpyridine or its 2-hexylthiophene-substituted derivative as the anchoring ligand on one hand and one of tetrazolylpyridine-based ligands having a N⁺N⁺N⁺ coordination pattern or C⁻N⁺N⁺ coordination pattern as the auxiliary ligand on the other are reported as sensitizers for dye-sensitized solar cells (DSSCs), along with their spectroscopic, electrochemical, and theoretical characterizations. For the anchoring ligand, the introduction of 2-hexylthiophene unit leads to narrower spectral response and lower molar extinction coefficients and a smaller driving force for dye regeneration. For the ancillary ligand, the cyclometalating Ru–C bond induces a red shift in absorption compared with a Ru–N bond and thus affords a photocurrent generation at wavelengths of up to 950 nm. Further, the overall efficiencies of DSSCs are higher with the N⁺N⁺N⁺ complexes than with the C⁻N⁺N⁺ complexes, mainly due to higher open-circuit voltages (V_{oc}). Overall, the DSSC based on the bistetrazolate dye without the hexylthiophene unit for the anchoring ligand and having the N⁺N⁺N⁺ coordination pattern for the auxiliary ligand exhibited the highest efficiency of 5.9% when employing 0.5 M *t*-butylpyridine in the electrolyte.

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1. Introduction

Since dye-sensitized solar cells (DSSCs) based on modified nanocrystalline TiO₂ surfaces first appeared in a quarter century ago [1], bidentate 4,4'-dicarboxy-2,2'-bipyridine and tridentate 4,4',4''-tricarboxy-2,2':6,2''-terpyridine were extensively employed as the typical anchoring ligand in thiocyanate (NCS) based [2–10] and NCS-free [11–18] ruthenium complexes. In comparison with Ru(II) dyes with the bidentate structure, those with the tridentate structure exhibited superior absorption response in the near IR region.

It has been recently demonstrated that only two carboxy groups each substituted on a pyridine ring in the terpyridine-based anchoring ligand are sufficient for stable adsorption of the complex on TiO₂ surface [19]. For the dicarboxyterpyridine anchor, the two carboxy groups can be substituted on the terminal pyridine rings [20] leaving the central pyridine ring open or one on the terminal and the other on the central pyridine ring leaving a terminal ligand open [5,21–23]. In these two molecular designs, the remaining pyridine group without the carboxy group becomes available for further functionalization. The Ru(II) complexes with the former anchoring ligand substituted with dicarboxy groups on the terminal pyridine rings showed higher fill factor values but achieved only moderate efficiencies even if functional units were introduced on the middle pyridine ring to provide electron donating abilities and expand the π -conjugation system [20]. In the latter molecular design, functional units have been attached to the 3, 4, 5, and 6-positions of the terminal pyridine unit of 4,4'-dicarboxy-2,2':6,2''-terpyridine, such as

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thiophene, benzene, triphenylamine, and their combined substituents [4,5,21,23–25]. Wu et al. reported a new series of bis-tridentate Ru(II) sensitizers in which a 2-hexylthiophene unit was strategically introduced at the 5- or 6-position of the dicarboxyterpyridine-derived ligand [21]. By comparison, the 6-substituted derivative exhibited a higher conversion efficiency of 9.21%. Subsequently, Ozawa et al. demonstrated the advantages of using a 2-hexylthiophene unit at the 5-position of the dicarboxyterpyridine-derived ligand compared with 4-substituted derivatives in NCS-based Ru(II) complexes [26]. On account of these results, the 6-position, rather than 5- or 4-positions, on pyridine seemed to be the most favorable position of introducing a π -conjugated thiophene substituent to offer an efficient Ru(II) dye sensitizer.

For the auxiliary ligand, it has been demonstrated that the NCS unit is not a complete necessity in designing efficient Ru(II) sensitizers since a high-efficiency dye based on cyclometalated Ru(II) complex was reported in 2009 [27]. We recently reported a bis-tridentate Ru(II) complex with a dianionic bis(tetrazolyl)pyridine unit as the auxiliary ligand (BTP dye), which recorded a comparatively good solar cell efficiency of 6.1% [11]. Continuous efforts have been devoted in our group to develop a novel class of tricarboxyterpyridine Ru(II) complexes possessing 2-X-6-(*ortho*-methoxyphenyl)pyridine as the auxiliary ligands, where X = 3-trifluoromethyl-1,2-pyrazol-5-yl (PYZ dye), 3-trifluoromethyl-1,2,4-triazol-5-yl or 2-trifluoromethyl-1,3,4-triazol-5-yl (TRZ dye), and 1,2,3,4-tetrazol-5-yl (TEZ dye) [28,29]. DSSCs based on these three complexes had broad light-absorption properties extending close to 1000 nm. Especially, the tetrazolate Ru(II) derivative produced the conversion efficiency of 6.44% under the standard air-mass (AM) 1.5G conditions. Prompted by these previous promising results, we have combined the motifs of dicarboxyterpyridine or its 2-hexylthiophene derivative and bis(tetrazolyl)pyridine or 2-(1,2,3,4-tetrazol-5-yl)-6-(*ortho*-methoxyphenyl)pyridine for the design of a new series of bis-tridentate Ru(II) sensitizers, as shown in Fig. 1. Herein, we report the synthesis, photochemical properties, computational chemistry, and photovoltaic properties of these four novel Ru(II) sensitizers (BTDC, OTDC, BTTHDC and OTTHDC dyes).

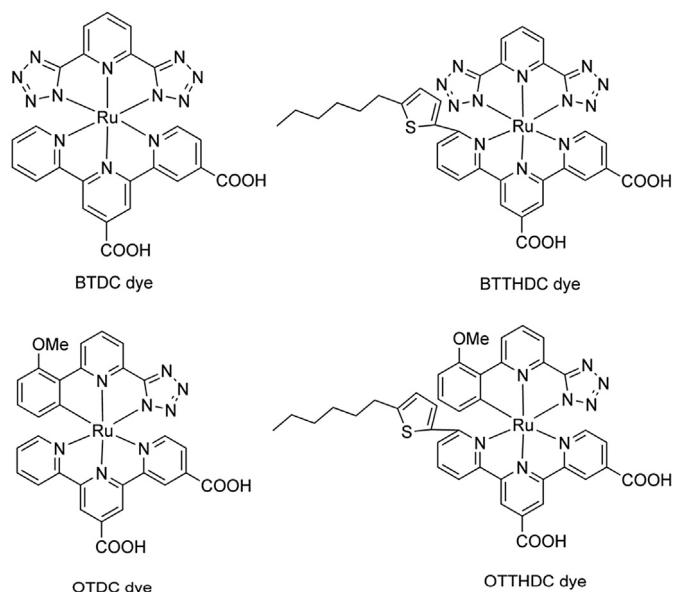


Fig. 1. Molecular structures of the four sensitizers.

2. Results and discussion

2.1. Synthesis

The synthetic route of these four dyes is described in Scheme 1. Terpyridine derivatives **1a** and 6-bromo-terminated terpyridine (**1b**) were obtained by procedures reported recently [22], which began with 2-acetyl-6-bromopyridine and went through Aldol condensation, Krohnke reaction, oxidation reaction by KMnO_4 and final esterification with ethanol under acidic conditions. The hexylthiophenyl terpyridine **1c** was synthesized by the Suzuki-coupling reaction of **1b** and 2-(5-hexylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane [30]. The auxiliary ligand 2,6-di(1*H*-tetrazol-5-yl)pyridine and 2-(2-methoxyphenyl)-6-(1*H*-tetrazol-5-yl)pyridine were synthesized as reported in our previous study [28]. The reaction of **1a** or **1c** and RuCl_3 was carried out prior to the reaction with the auxiliary ligand. Finally, deprotection of two ethoxycarbonyl groups of **3a–3d** was carried out to obtain the four ruthenium dyes.

2.2. Materials and methods

^1H and ^{13}C NMR spectra were recorded on a JOEL JNM-ECX 400 instrument. Electrospray ionization (ESI) mass spectra were recorded on an Agilent LC/MSD TOF 1100 spectrometer. Elemental analysis was performed by the Center for Creative Materials Research, the College of Science and Technology, Nihon University. Spectral properties of the four dyes in DMF solution and on TiO_2 films were measured on a JASCO V-770 spectrophotometer at 298 K. Their fluorescence spectra were measured on a FP-8600 spectrofluorometer at 298 K. Cyclic voltammetry of the four dyes (1 mM) were carried out on a Hokuto Denko HZ-3000 electrochemical analyzer in DMF solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF_6) as supporting electrolyte. The solutions were purged with nitrogen and the scan rate was 100 mV s^{-1} . A platinum disk, a platinum wire, and a silver wire were employed as the working, counter, and pseudo-reference electrodes, respectively. The potentials were calibrated with internal ferricinium/ferrocene reference and converted to the corresponding values with respect to the normal hydrogen electrode (NHE) by addition of 0.63 V [31]. The current–voltage (J – V) curves of the fabricated solar cells were measured with an active area of 0.25 cm^2 under AM1.5G illumination. The IPCE (monochromatic incident photon-to-current conversion efficiency) spectra were measured with a monochromatic incident light. The IMVS (intensity-modulated photovoltaic spectroscopy) measurements were performed with the frequency range from 10^{-1} – 10^6 Hz at an open-circuit condition. The CEM (charge extraction method) was carried out from an open-circuit condition to a short-circuit condition. TA (transient absorption) spectra were obtained by an Edinburgh Photonics LP920 laser flash spectrometer.

2.2.1. Synthesis of **3a**

A solution in toluene (18 mL) and DMF (18 mL) of 2,6-di(1*H*-tetrazol-5-yl)pyridine (60 mg, 0.28 mmol), **2a** (167 mg, 0.28 mmol), and KOAc (300 mg, 3.05 mmol) was refluxed for 24 h. After removing the solvent under reduced pressure, the residue was purified by silica gel column chromatography (chloroform/methanol = 10/1) to afford **3a** (135 mg, 0.20 mmol, 70%). ^1H NMR (400 MHz, $\text{DMSO-}d_6$): δ ppm: 9.39 (s, 1H), 9.25 (s, 1H), 9.10 (s, 1H), 8.93 (d, 1H, $J = 8.4$ Hz), 8.48 (d, 2H, $J = 6.2$ Hz), 8.43 (t, 1H, $J = 6.4$ Hz), 7.94 (t, 1H, $J = 8.0$ Hz), 7.58 (d, 2H, $J = 6.0$ Hz), 7.36 (d, 1H, $J = 5.6$ Hz), 7.28 (t, 1H, $J = 5.6$ Hz), 4.46 (quartet, 2H, $J = 7.2$ Hz), 4.25 (quartet, 2H, $J = 7.2$ Hz), 1.38 (t, 3H, $J = 7.2$ Hz), 1.18 (t, 3H, $J = 7.2$ Hz). ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$): δ ppm: 164.4, 163.6, 162.8, 159.1,

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