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PAPER

Molecular design and synthesis of ruthenium(II) sensitizers for highly efficient dye-sensitized solar cells[†]

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We synthesized hydrophobic ruthenium(II) sensitizers (SY-04 and SY-05) with high molar extinction coefficient by extending the π -conjugation of 3,4- or 3-alkylthiophene-substituted bipyridine ligands. Both dyes displayed a remarkably high molar extinction coefficient of 21.7×10^3 M⁻¹ cm⁻¹ arising from red-shift of their metal-to-ligand charge transfer band when compared to a commonly used N3 sensitizer. The solar-to-electrical energy conversion efficiency (η) of the SY-04 based dye-sensitized solar cell (DSC) was 7.70%, which is 27% higher than that (6.05%) of the N3-based DSC under the same cell fabrication conditions. The increased η was attributed to the increase in life time and recombination half-life measured by electrochemical impedance and transition absorption spectroscopy, respectively. Density functional theory and time-dependent density functional theory calculations of two dyes in both gas phase and solution were performed. The calculated values of the highest occupied and the lowest unoccupied molecular orbitals and absorption spectra are in good agreement with the experimental results.

Introduction

Increasing energy demands and concerns over global warming have led to a greater focus on renewable energy sources. Dye-sensitized solar cells (DSCs) based on the ruthenium(II) dyes have been shown to be very efficient candidates for photovoltaic technology due to their high photon-to-current conversion efficiency, low manufacturing cost, long-term stability, and tunable electrochemical properties covering wide absorption ranges from the visible to the near-infrared (NIR).^{1–7} Although the currently used

† Electronic supplementary information (ESI) available: Synthesis, characterization and optimized structure for ancillary ligands and sensitizers, calculated molecular orbitals/energy-levels, and transition assignments. See DOI: 10.1039/c1jm11760b

DSCs based on N3 and N719 sensitizers combined with a thick mesoscopic titania film and an acetonitrile-based electrolyte show a solar-to-electrical energy conversion efficiency (η) of up to 11.1% under the air mass 1.5 global (AM 1.5G) illumination,⁸⁻¹¹ a further improvement in the efficiency is required for the cost-effective commercial production of DSCs. To achieve this objective, one should increase the absorption at near-infrared wavelengths or the molar extinction coefficient at visible wavelengths.

To enhance both the molar extinction coefficient and red-shift arising from the metal-to-ligand charge transfer (MLCT) band, while maintaining good solubility, various ancillary ligands, such as 2-hexylthiophene (HRS-1), furan, carbazole, dialkylaminobenzene, dipyridylamine, hexylsulfanylphenyl (TG6) and triazole derivatives, have been attached to the bipyridine ligand in the ruthenium dyes.¹²⁻²⁷ Among many ancillary ligands, the thiophene moiety showed high efficiency. Wang and coworkers¹⁴⁻¹⁷ synthesized a series of ruthenium dyes (C101–C107) with extended π -conjugation length by using a single thiophene or furan derivative. Ho and coworkers¹⁹⁻²¹ synthesized bithiophene (CYC-B1) and thiophene-attached carbazole derivatives (CYC-B6S and CYC-B6L) as the ancillary ligands that are attached to bipyridine ruthenium(II) sensitizers. These dyes showed a high molar extinction coefficient and redshift of the MLCT. The η of a dye with thiophene-functionalized ancillary ligands is known to be higher than that of another dye without the ligands.14-27

However, the ancillary ligands of the thiophene derivative in ref. 14–21 were synthesized *via* the Stille coupling reaction of

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4,4'-dibromo-2,2'-bipyridine with corresponding stannane thiophene ligands in the presence of palladium as a catalyst.^{14–21} The yield of the product was relatively low due to the poor solubility of the tin compound in the solvent. Furthermore, since the product might have both *cis* and *trans* isomers, multiple (at least 3 (or possibly 4) times) purifications by using column chromatography should be required to obtain the desirable product (only *cis* isomer). Thus, an efficient synthetic method is of the utmost importance to produce high yields of ruthenium(II) dyes with thiophene ancillary ligands without sacrificing high molar extinction coefficients as well as the red-shift of the MLCT band.

We realize that the stereoselectivity of the Horner–Emmons– Wadsworth (HEW)²⁸ reaction gives only the *E*-form alkene with very high yield. Previously, Grätzel and coworkers^{29,30} synthesized K-series (**K19**, **K77**), ruthenium(II) sensitizers by using alkyloxybenzaldehyde attached-bipyridine ligands *via* the HEW. But the alkyloxybenzaldehyde moieties showed low molar extinction coefficients compared with the thiophene attached ruthenium(II) sensitizers.¹⁴⁻²¹

The amount of a dye sensitizer adsorbed on the TiO₂ surface has a significant influence on the open circuit voltage (V_{oc}) because the Fermi energy level of TiO₂ is influenced by the density of photo-injected electrons. Since the aggregation of a dye on the TiO₂ surface sometimes decreases V_{oc} , the solubility of a dye in the solvent should be increased to enhance the dye adsorption.31 For an ancillary ligand with thiophene, the introduction of alkyl chains increases the solubility. However, the ruthenium sensitizers (C101-C107, and CYC-B1 and CYC-B6S) reported in the literature have the alkyl chain attached to position 2 (or 5) in the thiophene ring.¹⁴⁻²¹ It is noted that the attachment of the alkyl (for instance, n-hexyl) group to position 3 (or 4) of the thiophene ring shows very high solubility compared with the attachment of the alkyl group to position 2 (or 5) of the thiophene ring.^{32,33} Thus, when the alkyl chain could be located at position 3 (or 4) in the thiophene ring attached to the bipyridine ligand (or its ruthenium complexes), the solubility is very much enhanced in common organic solvents (chloroform, tetrahydrofuran, ethanol, toluene, and acetonitrile) compared with other ligands (or their ruthenium complexes) having the alkyl chain attached to other positions (2 or 5) in the thiophene.12-27

Based on the above argument, in this study, we synthesized two heteroleptic ruthenium(II) dyes (SY-04 and SY-05) containing the ancillary ligands of 3,4-dihexylthiophene and 3-hexylthiophene units which were synthesized based on the HEW reaction. We found that the overall yield for the synthesis of the ancillary ligands was very high (more than 85%). Also, the solubility of the dyes in solvents is very good due to the existence of the 3,4-dihexylthiophene or 3-hexylthiophene groups. Because the ligands employed in this study extended the π -conjugation, the dyes increased the absorption coefficients and red-shifted the MLCT band. The solar-to-electrical energy conversion efficiency (η) of the **SY-04**-based DSC was 7.70%, which is 27% higher than that (6.05%) of the N3-based DSC under the same cell fabrication conditions. The effects of the alkyl thiophene ancillary ligands on energy levels and electronic transitions of the sensitizers were discussed by the density functional theory (DFT) and the time-dependent density functional theory (TD-DFT) calculations. The calculated values of the highest occupied and the

lowest unoccupied molecular orbitals (HOMO and LUMO) and absorption spectra are in good agreement with experiment results. Fig. 1 shows the molecular structures of the two sensitizers (SY-04 and SY-05) synthesized in this study and N3 for the reference dye.

Experimental section

General procedures

All reactions were performed under a dried nitrogen atmosphere. Solvents and liquid reagents were transferred by nitrogen flushed syringes or cannula. Reaction mixtures were stirred with Teflon coated magnetic stir bars. Reaction solvents used were HPLC grade, dried further by passage through a column of appropriate desiccants. Commercial reagents were used as such unless otherwise noted. Thin layer chromatography was performed using Merck 60 F524 pre-coated silica gel plates. Subsequent to elution, the plates were visualized by ultra-violet light at 254 nm. Column chromatography was performed using Merck silica gel 60 (230–400 mesh).

UV-Vis spectra were obtained with a Carry 5000 UV-Vis-near infrared double beam spectrophotometer. Photoluminescence (PL) spectra were collected with a laser excitation source instrument. An 800 nm laser beam from a continuous wave Ti/sapphire laser was used as an excitation source. A combination of the monochromator (Oriel 77200), InSb (Judson SP28) or PIN detector (Thorlabs DET410), lock-in amplifier, and mechanical chopper was used to record the photoluminescence of dyes.

The ¹H and ¹³C NMR spectra were measured with a Bruker (¹H 500 MHz and ¹³C, 125 MHz) spectrometer. Chemical shifts are reported in parts per million using the residual solvent peaks as internal reference. The C, H, N contents of the ligands and complexes were carried out using Carlo Erba Elemental analyzer Model 1106 and Haereus CHN rapid analyzer. High resolution mass spectral analysis was performed by using 6224 TOF LC-MS and the value is in the unit of mass to charge (*m/z*). The electrospray ionization (ESI) source was selected for positive voltage for ligands and negative voltage for complexes. Finally, melting points of the ligands were measured on a capillary melting point apparatus (Optimelt/SRS).

The cyclic voltammograms of the sensitizers $(10^{-3} \text{ M in DMF})$ with 0.1 M (n-C₄H₉)₄NPF₆ as a supporting electrolyte were obtained with a CHI600A electrochemical analyzer at a scan rate of 100 mV s⁻¹. The measurements were carried out under oxygen-free conditions using a three-electrode cell in which a carbon electrode was used as a working electrode, a saturated Ag/AgCl electrode as a reference electrode, and platinum wire was used as an auxiliary electrode. The ferrocene/ferrocenium (+1) couple



Fig. 1 The molecular structures of SY-04, SY-05 and N3 dyes.

was used as an internal standard. The half potential $(E_{1/2})$ between the cathodic peak and the anode peak for the ferrocene/ ferrocenium couple is 0.47 V in dimethylformamide (DMF) medium.

Materials

3,4-Dihexylthiophene (1) and 2-bromo-3-hexylthiophene (4) were synthesized according to the literature.^{34,35} Two ancillary ligands (6 and 7) were first synthesized from the HEW reaction²⁸ between 3,4-dihexylthiophene carbaldehyde (2) or 3-hexylthiophene carbaldehyde (5) and 4,4'-bis(diethylphosphonomethyl)-2,2'bipyridine³⁶ (3). Then, a one-pot synthetic procedure developed for heteroleptic polypyridyl ruthenium(II) sensitizer³⁶ was used for the synthesis of **SY-04** and **SY-05**, as shown in Scheme 1. (A detailed synthesis of 1–5 is given in the supporting information.[†])

Synthesis of ligand (6)

A solution of 2 (0.5 g, 1.78 mmol) in dry THF (20 mL) was added dropwise into the solution of 3 (0.4 g, 0.87 mmol) and t-BuOK (0.2 g, 1.78 mmol) in dry THF (30 mL) under dry argon and stirred for 5 h at room temperature. The solvent was evaporated under a vacuum. Aqueous HCl (0.05 M, 20 mL) was added, and the aqueous phase was extracted three times with CH₂Cl₂ (30 mL). The combined organic layers were washed with water and dried over MgSO₄. The solvent was evaporated under a vacuum. The crude product was purified by column chromatography (silica gel with 60-120 mesh size, acetone) to give a light yellow solid (0.54 g). Yield: 87%; mp: 108-109 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.66 (d, J = 5.1 Hz, 2H), 8.46 (s, 2H), 7.59 (d, J = 15.5 Hz, 2H) 7.39 (dd, J = 5.0 Hz, 2H), 6.92 (d, J = 16.0 Hz, 2H) 6.84 (s, 2H), 2.70 (t, J = 8.0 Hz, 4H), 2.52 (t, J = 8.0 Hz, 4H), 1.65 (m, 4H), 1.53 (m, 4H), 1.40–1.35 (m, 24H), 0.93 (t, J = 5.0Hz, 12H). ¹³C NMR (125 MHz, CDCl₃): 156.58; 149.43; 145.93; 143.57; 142.41; 135.88; 125.14; 124.57; 120.45; 119.99; 118.27; 31.76; 31.66; 31.21; 29.67; 29.40; 28.99; 27.06; 22.66; 14.13. LC-MS (ESI, positive mode): Calcd for $C_{46}H_{64}N_2S_2$: [M⁺]: 708.45. Found. [MH⁺]: 709.4586. Anal. Calcd for C₄₆H₆₄N₂S₂: C: 77.91; H: 9.10; N: 3.95. Found. C: 77.98; H: 9.15; N: 3.91%.

Synthesis of ligand (7)

Ligand 7 was synthesized similarly to ligand **6** by using **5** instead of **2**. The crude product was purified by column chromatography (silica gel, acetone) to give as a white solid (0.56 g). Yield: 85%; mp: 127–128 °C; ¹H NMR (500 MHz, CDCl₃): δ 8.67 (d, J = 5.0 Hz, 2H), 8.50 (s, 2H), 7.60 (d, J = 15.5 Hz, 2H), 7.39 (dd, J = 5.0 Hz, 2H), 7.21 (d, J = 5.0 Hz, 2H), 6.94 (d, J = 16.0 Hz, 2H), 6.90 (s, 2H), 2.77 (t, J = 8.0 Hz, 4H), 1.66 (m, 6H), 1.42–1.34 (m, 10H), 0.93 (t, J = 5.0 Hz, 6H). ¹³C NMR (125 MHz, CDCl₃): 156.70; 149.56; 145.96; 143.32; 135.53; 130.08; 125.16; 124.75; 124.70; 120.90;120.72; 31.81; 31.10; 29.17; 28.67; 22.72; 14.19. LC-MS (ESI, positive mode): Calcd for C₃₄H₄₀N₂S₂: [M⁺]: 540.26. Found. [MH⁺]: 541.2709. Anal. Calcd for C₃₄H₄₀N₂S₂: C: 75.51; H:7.45; N: 5.18. Found. C: 75.57; H: 7.52: N: 5.23%.

Synthesis of ruthenium(II) sensitizer (SY-04)

In a nitrogen-flushed three-neck flask, 6 (0.135 g, 0.190 mmol) and dichloro(*p*-cymene)ruthenium(II) dimer (0.059 g, 0.096 mmol) in DMF were heated at 70 °C for 4 h in the dark. Subsequently, 4,4'-dicarboxylic acid-2,2'-bipyridine (8) (0.046 g, 0.190 mmol; Sigma Aldrich Co.) was added and the reaction mixture was heated to 150 °C and reacted at this temperature for 4 h. The solution became dark green. Solid NH₄NCS (0.376 g, 4.94 mmol) was added to this solution and the reaction was carried out for 4 h at 140 °C. DMF was removed on a rotary evaporator under vacuum, and water (200 mL) was added to cause precipitation. The purple solid was filtered off, washed with water and dried under vacuum. The crude compound was dissolved in basic methanol with tetrabutylammonium hydroxide and then purified using the Sephadex LH-20 resin in column chromatography with methanol as eluent. The main band was collected and solution was slowly titrated with acidic methanol (HNO₃) to become pH 5.6. The precipitate was collected on a sintered glass crucible by suction filtration and dried under vacuum. Yield: 65%. ¹H NMR (500 MHz, DMSOd₆): δ 9.35 (d, J = 5.5 Hz, 1H); 9.15 (d, J = 6.0 Hz, 1H); 9.07 (s, 1H); 8.91 (s, 1H); 8.87 (s, 1H); 8.71 (s, 1H); 8.21 (t, J = 6.5 Hz, 2H); 8.06 (d, J = 16.0 Hz, 1H); 7.78 (s,1H); 7.74 (d, J = 5.5 Hz 1H); 7.58 (dd, J = 6.0 Hz 1H); 7.43 (d, J = 6.0 Hz, 1H); 7.31 (d, J = 6.0 Hz, 1H); 7.26 (s, 1H); 7.18 (s, 1H); 7.07 (d, J = 15.5 Hz, 1H); 6.81 (d, J = 15.5 Hz, 1H); 2.83 (t, J = 7.4 Hz, 2H); 2.81 (t, J = 7.4 Hz, 2H); 1.78 (t, J = 7.4 Hz, 2H), 1.63 (t, 2H, 7.4); 1.56 (t, J = 7.4 Hz, 2H); 1.43–1.26 (m, 10H); 0.91 (t, J = 6.0 Hz, 3H); 0.83 (t, J = 7.0 Hz, 3H). ¹³C NMR (125 MHz, DMSO): 165.57; 165.16; 158.62; 158.21; 157.32; 152.39; 151.45; 144.77; 144.06; 143.46; 143.33; 143.25; 135.40; 135.18; 133.89; 133.69; 127.40; 127.18; 125.81; 122.71; 122.40; 122.17; 121.76; 121.69; 119.90; aliphatic carbon: 30.99; 30.95; 30.84; 30.68; 29.20; 19.13; 28.89; 28.49; 28.44; 28.37; 28.16; 28.09; 22.99; 22.01; 21.96; 21.93; 19.11; 13.81; 13.80; 13.79; 13.71; 13.34. LC-MS (ESI, negative mode): Calcd for C₆₀H₇₂N₆O₄S₄: [M⁺]: 1170.35. Found. [MH⁻]: 1169.4049. Anal. Calcd for C₆₀H₇₂N₆O₄S₄: C: 61.56; H: 6.20; N: 7.18. Found. C: 61.63; H: 6.28; N: 7.23%.

Synthesis of ruthenium(II) sensitizer (SY-05)

The synthesis of **SY-05** is similar to that of **SY-04** by using 7 instead of 6. The crude product was purified on the Sephadex



LH-20 resin in column chromatography with methanol as eluent. The main band was collected and solution was slowly titrated with acidic methanol (HNO₃) to become pH 5.6. Yield: 65%. ¹H NMR (500 MHz, DMSO- d6): δ 9.70 (d, J = 6.0 Hz, 1H); 9.28 (d, J = 6.0 Hz, 1H); 9.12 (s, 1H); 8.96 (s, 1H); 8.51 (s, 1H); 8.43 (s, 1H); 8.13 (d, J = 6.0 Hz 2H); 8.06 (s, 1H); 7.83 (d, J = 15.5 Hz 2H); 7.71 (dd, J = 6.0 Hz 1H); 7.56 (d, J = 5.0 Hz 1H); 7.49 (d, J = 5.0 Hz 1H; 7.35 (d, J = 5.0 Hz, 1H); 7.20 (d, J = 6.5 Hz 1H); 7.15 (d, J = 5.5 Hz 1H); 7.09 (d, J = 5.0 Hz, 1H); 7.01 (d, J = 15.5 Hz 1H); 6.82 (d, J = 15.5 Hz, 1H); 2.83 (t, J = 7.4 Hz, 2H); 2.81 (t, J = 7.4 Hz, 2H); 1.78 (t, J = 7.4 Hz, 2H); 1.63 (t, 2H, 7.4); 1.56 (t, J = 7.4 Hz, 2H); 1.43-1.26 (m, 10H); 0.91 (t, J = 6.0 Hz 3H);0.83 (t, J = 7.0 Hz 3H). ¹³C NMR (125 MHz, DMSO): 165.58; 165.19; 158.58; 158.23; 157.30; 157.00; 152.31; 151.57; 152.47; 150.81; 144.68; 144.49; 144.43; 144.32; 143.97; 143.81; 140.75; 140.57; 134.91; 134.69; 133.83; 133.67; 130.32; 130.22; 126.83; 126.61; 126.47; 126.39; 125.81; 125.18; 123.18; 123.06; 122.94; 122.65; 122.39; 122.12; 120.11; 119.78; aliphatic carbon: 31.02; 31.00; 30.95; 30.91; 30.88; 29.72; 29.58; 27.53; 22.98; 22.00; 21.93; 19.11; 13.96; 13.90; 13.89; 13.61; 13.32. LC-MS (ESI): Calcd for C48H48N6O4S4: [M⁺]: 1002.17. Found. [M-H⁻]: 1001.2114. Anal. Calcd for C₄₈H₄₈N₆O₄S₄: C, 57.52; H, 4.83; N, 8.39. Found. C, 57.58; H, 4.86; N, 8.45%.

Electrochemical impedance spectra

Electrochemical impedance spectra (EIS) were obtained in the dark using an SP-200 electrochemical workstation with frequencies ranging from 50 mHz to 100 kHz and potentials from -0.7 to -0.3 V. The obtained impedance spectra were fitted with Z-view software.

Nanosecond transient absorption spectra (TAS)

TAS were obtained by using a nanosecond pulse laser. The 504 nm pulse generated by hydrogen Raman shifting of third harmonic generation (THG, 355 nm) from Q-switched Nd:YAG laser (Continuum, Surelite II, pulse width of 4.5 ns fwhm) was used to excite the samples. A 150 W Xenon Arc lamp (Newport, 70525) was focused on the sample solution as the probe light for the transient absorption measurement. Temporal profiles were measured with a monochromator (DongWoo Optron, Monora 500i) equipped with a photomultiplier (Zolix Instruments Co., CR 131) and a digital oscilloscope (Tektronix, TDS-784D). The whole system was controlled with a computer through a GP-IB interface. Transient absorption spectra were measured by ICCD (Ando Technology, iStar) with the gate time of 2 ns at various time-delays. Reported signals were averages of 500 events.

Computational study

The molecular structure and electronic properties of **SY-04** and **SY-05** were investigated with DFT and TD-DFT calculations.³⁷⁻⁴² The calculations were performed using the B3PW91 exchange correlation functional, as implemented in the Gaussian03 program package.⁴³ The 6-31G* basis set was used for S, N, O, C, and H, and CRENBL ECP basis set for Ru. The geometries, electronic structure and optical absorption spectra of the ruthenium complexes were optimized in the gas phase and in the solvent (ethanol) medium using the polarized continuum model (PCM).⁴³

Device fabrication

Transparent TiO₂ electrodes were prepared by screen printing a paste of TiO₂ nanoparticles (T20/SP; Solaronix) on the FTOcoated glass (8 Ω cm⁻²) and annealed at 500 °C in air for 30 min. Then, a reflecting scattering layer containing ~ 400 nm sized TiO₂ anatase particles (Ti-Nanoxide R/SP; Solaronix) was also prepared by screen printing and sintering at 500 °C for 30 min. The thickness of the TiO_2 electrode was approximately 17 μ m. After cooling to 80 °C the sintered TiO₂ electrode was immediately immersed into the ethanol solution with dyes (SY-04 and SY-05) (0.3 mM) synthesized in this work and kept at room temperature for 24 h. For the comparison, the same TiO₂ electrode was also immersed into ethanol solution with N3 (0.3 mM). The dye-adsorbed TiO₂ electrode was washed in ethanol and dried with nitrogen. A 60 µm thick Surlyn spacer (SX1170-60 from Solaronix) was sandwiched between the photo anode and a platinized FTO counter electrode. Iodide-based redox electrolyte was used in the present work (the details are given in the supporting information[†]).

The photovoltaic performance of the cells was measured with a solar simulator (Newport, USA) equipped with an AM 1.5G filter and a 300 W Xenon light source. The one sunlight intensity of 100 mW cm⁻² was adjusted with a standard calibrated Si solar cell (PV Measurements Inc.). The current–voltage characteristics were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. Incident photon to current conversion efficiency (IPCE) was recorded by using a computerized setup consisting of a xenon arc lamp and a monochromator (PV Measurements Inc).

Results and discussion

Synthesis and structural characterization

The molecular structures of the ligands (6 and 7) and the sensitizers (SY-04 and SY-05) were confirmed by ¹H, ¹³C NMR, HRMS-ESI and elemental analysis. (see Figs. S1~S4[†]). The peaks at 7.59 (J = 15.5 Hz) and 6.92 (d, J = 16.0 Hz) ppm in the ¹H NMR spectra (see Figs. S1a and S2a) suggest that the protons in the vinyl groups of ligand 6 (or 7) are in a trans configuration.⁴⁴ This is because the ancillary ligand 6 (or 7) was synthesized from 2 (or 5) and 3 based on the HEW reaction.¹⁵ The peaks at 8.06, and 7.07 ppm with the coupling constant (J) of $16.0 \sim 15.5$ Hz, (see Figs. S3a and S4a) suggested that the protons in the vinyl groups in the SY-04 and SY-05 dyes are downfield shifted when compared to free ligand and also trans configuration to each other.⁴ ¹³C NMR spectra of SY-04 (Fig. S3b) and SY-05 (Fig. S4b) have resonance signals between 119 and 166 ppm arising from chemically and magnetically non-equivalent carbon atoms in the four pyridyl rings, two thienyl rings, vinyl groups, and carboxylic acid groups. Two peaks displayed at 133.89 and 133.69 ppm are assigned to the carbons of the two NCS ligands of both SY-04 and SY-05, indicating that the nitrogen atom in the NCS ligands coordinated with Ru. This confirms that only coordinated NCS ligands are present in the dye molecules.⁴

The overall yield for **6** and **7** was very high (>85%). This is a great advantage compared to other ancillary ligands synthesized previously.^{14–21} We found that even the efficiency based on synthesized dyes that were purified only one time using column chromatography was essentially the same as that based on the dye purified three (or four) times. This clearly demonstrates that a single isomer (*cis* form) was formed for the synthesis of **SY-04** and **SY-05**.

Optical and electrochemical property

Fig. 2 shows UV-visible spectra of SY-04, SY-05 and N3 in ethanol solution. The absorption spectrum of SY-04 displays three bands at 546 nm, 386 nm, and 312 nm. The band at 312 nm is assigned to the intra-ligand $\pi - \pi^*$ transitions of the bipyridine ligand. The bands at 546 and 386 nm are the characteristic MLCT absorptions bands which are observed in the visible region for heteroleptic polypyridyl ruthenium complexes.45,46 The π - π * transition of dialkylthiophene ancillary ligand attached to SY-04 has a much stronger absorption coefficient compared with N3. The peak at 546 nm for SY-04 and SY-05 is 15 nm red-shifted compared to N3, which represents the low energy MLCT transition absorption peak. The measured molar extinction coefficient (ε) of the MLCT band at a peak at 546 nm of SY-04 and SY-05 is 21.7×10^3 M⁻¹ cm⁻¹, which is higher than that $(14.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1})$ of N3.^{45,46} The enhanced molar extinction coefficient and the red shift are attributed to the extension of π -conjugation in both SY-04 and SY-05 dyes. The red shift of the MLCT band suggests that the band gap between the HOMO and LUMO levels for SY-04 and SY-05 becomes smaller than that of N3. The UV-vis spectrum of HRS-1 sensitizer also showed two absorption peaks at 371 and 542 nm with an ε value of 18.7 \times 10³ M cm⁻¹.¹² The extinction coefficient of SY-04 and SY-05 is slightly higher than that of HRS-1. This is because of the better solubility SY-04 and SY-05 arising from the hexyl groups in the β (or γ) position of the thiophene ring.

The HOMO and LUMO levels of the dyes are estimated from the oxidation potentials and UV-vis absorption data of the dyes, and are given in Table 1. The excitation transition energies (E_{0-0}) of both dyes are estimated to be 1.83 eV (678 nm) by taking the crossing point of the absorption and emission spectra (Fig. S5†).



Fig. 2 Absorption spectra of SY-04 (solid), SY-05 (dotted) and N3 (dashed) dyes.

The electron transfer from the excited state of the dye to the conduction band of the TiO2 electrode was checked by cyclic voltammetry, and the results are given in Fig. S6.[†] The cyclic voltammograms showed that both dyes are redox-active, namely, metal-centered (oxidation) and ligand-centered (reduction) processes. The values of $E_{1/2} = (E_{ox} + E_{red})/2$, where E_{ox} and E_{red} are the oxidation and reduction peak potentials, respectively, are 0.87 V and 0.82 V for SY-04 and SY-05, respectively, while that of N3 is 1.04 V. The value of $\Delta E = (E_{ox} - E_{red}) \times 1000)$ for SY-04 and SY-05 was 130 eV, which indicates that a one-electron quasi-reversible oxidation took place.27 The difference in the oxidation potential between SY-04 and N3 is attributed to the electron donating of the thiophene groups in the ancillary ligands.12 The experimentally determined LUMO values of the two dyes (SY-04 and SY-05) are similar to that of N3. However, the HOMO values of the two dyes are lower than that of N3; thus the band gaps of the two dyes are ~ 0.06 eV smaller than that of N3. This is attributed to the existence of the alkylthiophene unit attached to the bipyridine ligand, which causes an increase in the peak intensity of the MLCT band.

The location of HOMO-LUMO and the electronic properties of SY-04 and SY-05 dyes were theoretically investigated by using DFT and TD-DFT in both gas and solution (ethanol) phase. Fig. 3 shows the isodensity surface contours (interval of 0.02) of LUMO, HOMO, HOMO-1, HOMO-2 for SY-04 (these contours for SY-05 are given in Fig. S7[†]). The HOMO of both SY-04 and SY-05 were localized on the ruthenium metal over NCS units, whereas the LUMOs of both dyes were localized over the 4,4'-dicarboxy-2,2'-bipyridine and thiophene attached ancillary ligands. The HOMO-1 and HOMO-2 for both dyes have a ruthenium excited state (t_{2g}) character in addition to a significant positive charge from the NCS to the bipyridine ligands. A small change of HOMO level for both dyes compared with N3 is mainly due to the Ru 4d orbital, ancillary ligand, and NCS orbital. But, the LUMO of both dyes is almost the same as that of the N3 dye because the LUMO results mainly from the orbital delocalized on the dcbpy ligand. The proper location of the frontier orbitals also accounts the high absorption coefficient of the MLCT band for SY-04 and SY-05 dyes. The energy levels of the HOMO and LUMO of SY-04 and SY-05 match well with the redox potential of I⁻/I⁻₃ and LUMO of TiO₂.¹⁹

The calculated energy level diagram (HOMO and LUMO) of SY-04, SY-05 and TiO₂ is shown in Fig. S8.[†] The band gap of both dyes is 1.68 eV in the gas phase, while the band gaps of SY-04 and SY-05 in ethanol are 2.42, and 2.45 eV, respectively. Because both SY-04 and SY-05 have similar bandgaps, the two dyes have very similar chemical structure. The HOMO-LUMO energy gap of N3 in the solution phase was reported to be 2.60 eV calculated by DFT.²³ The absorption intensity and the energy levels (HOMO and LUMO) of the frontier orbitals are almost the same for both dyes (SY-04 and SY-05), but those are smaller compared to reference N3. The relative intensity predicted by theory is consistent with experiment (cf. Figs. S9 and S10⁺ with Fig. 2). The energy-minimized structures of SY-04 and SY-05 and ancillary ligands are given in Figs. S11~S14.† The transitions between the HOMO and LUMO, the excitation energies, and the detailed origins of the transitions for both dves are listed in the supporting information (Figs. S15~S16 and Tables S1-S3).[†]

$\lambda_{abs}{}^a/nm$	$E_{0-0}{}^{b}/\mathrm{eV}$	$\Delta E^{c}/V$	$E_{\rm ox}/{\rm V}$	HOMO ^d /eV	LUMO ^e /eV	
312, 386, 546	1.83	130	0.88	-5.21	-3.38	
312, 385, 545	1.83	130	0.92	-5.25	-3.42	
311, 385, 530	1.89	240	1.16	-5.36	-3.47	
	$\frac{\lambda_{abs}{}^{a}/nm}{312, 386, 546}$ 312, 385, 545 311, 385, 530	$\lambda_{abs}{}^{a}$ /nm $E_{0-0}{}^{b}$ /eV 312, 386, 546 1.83 312, 385, 545 1.83 311, 385, 530 1.89	$\lambda_{abs}{}^{a}$ /nm $E_{0-0}{}^{b}$ /eV ΔE^{c} /V 312, 386, 546 1.83 130 312, 385, 545 1.83 130 311, 385, 530 1.89 240	$\lambda_{abs}{}^{a}/nm$ $E_{0-0}{}^{b}/eV$ $\Delta E^{c}/V$ E_{ox}/V 312, 386, 5461.831300.88312, 385, 5451.831300.92311, 385, 5301.892401.16	$\lambda_{abs}{}^{a}/nm$ $E_{0-0}{}^{b}/eV$ $\Delta E^{c}/V$ E_{ox}/V HOMO $^{d}/eV$ 312, 386, 5461.831300.88-5.21312, 385, 5451.831300.92-5.25311, 385, 5301.892401.16-5.36	

Table 1Optical, redox and energy level for SY-04, SY-05, and N3

^{*a*} Absorption spectra were measured in ethanol. ^{*b*} E_{0-0} was determined from intersection of absorption and emission spectra in ethanol. ^{*c*} $\Delta E = (E_{ox} - E_{red}) \times 1000$, where E_{ox} and E_{red} are oxidation and reduction peak potentials, respectively. ^{*d*} HOMO = -4.8 - ($E_{ox} - 0.47$). ^{*e*} LUMO = HOMO + E_{0-0} .



Fig. 3 Isodensity surface plot (isodensity contour = 0.02) of the SY-04 molecular orbitals: 294(LUMO), 293(HOMO), 292(HOMO-1) and 291 (HOMO-2).

Photovoltaic data

The current–voltage characteristics of the **SY-04** and **SY-05** along with **N3** under AM 1.5G one sunlight (100 mWcm⁻²) are shown in Fig. 4, and the photovoltaic parameters of the cells are listed in Table 2. The short-circuit photocurrent density (J_{sc}),



Fig. 4 *J–V* curves of DSCs based on the dyes SY-04 (solid), SY-05 (dotted) and N3 (dashed).

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open-circuit voltage (V_{oc}) and fill factor (ff) of the device based on SY-04 are 14.7 mA cm⁻², 0.756 V, and 0.695, respectively; thus, the η was 7.70%. This value is 27% higher than that (6.05%) of the N3-sensitized solar cell under the same cell fabrication conditions. When a mask was used for another solar cell with a larger active area of 0.46 cm² to avoid diffusive lights, η for SY-04 was slightly decreased to 6.5%, but this is again larger than that for N3 (5.1%) (see Table S4[†]). The increase in J_{sc} of the two dyes compared with N3 is due to higher incident photon-tocurrent conversion efficiency (IPCE), as shown in Fig. 5. The IPCE of SY-04 exhibits a high plateau in a broad spectral range from 450 to 650 nm with a maximum 65% at 548 nm. This indicates that the MLCT transition of the sensitizer can be enhanced by attaching thiophene ancillary ligands. Considering the light absorption and scattering loss by the conducting glass,¹⁵ the maximum efficiency for absorbed photon-to-collected electron conversion efficiency (APCE) would be close to unity over a broad spectral range.

Since the dyes synthesized in this study exhibited high molar extinction coefficients, DSCs made of thinner mesoscopic TiO₂ films or lower concentrations of the dyes could maintain higher η . The effect of the TiO₂ film thickness on η of the DSCs based on SY-04, SY-05 and N3 is summarized in Table S5[†] and the absorption spectra of SY-04 on TiO₂ with different film thicknesses are shown in Fig. S17.† In this case, we do not use a reflecting-scattering layer. Even though the TiO₂ film thickness decreased from 12 to 6 μ m, the η of the DSCs prepared by SY-04 and SY-05 was almost maintained, but η decreased at a thickness of 4 μ m. This indicates that the η of the DSCs prepared by SY-04 and SY-05 would be saturated above a TiO₂ thickness of 6 µm. Interestingly, the dye adsorption amount was steadily increasing with increasing TiO₂ thickness, as shown in Fig. S17.[†] These results suggest that with increasing the dye-adsorbed TiO₂ layer, the charge-recombination sites could be increased, which adversely influences the η .⁴⁷ On the other hand, the η of the DSC prepared by N3 decreased up 30% when the film thickness decreased from 12 to 6 µm. We measured the amount of dyes

 Table 2
 Photovoltaic performance of DSCs with different sensitizers under AM 1.5 light illumination (100 mW cm⁻²)

Dyes	$J_{\rm sc}/{\rm mA~cm^{-2}}$	$V_{\rm oc}/{ m V}$	ff	η (%)	Thickness/µm
SY-04 SY-05 N3	14.7 13.6 13.1	0.756 0.750 0.669	0.695 0.694 0.691	7.70 7.08 6.05	$12 + 5^{a}$ $12 + 5^{a}$ $12 + 5^{a}$

 a 400 nm sized TiO₂ anatase scattering layer. The active areas of the cells were 0.250 cm² without a mask.



Fig. 5 IPCE spectra of SY-04 (solid), SY-05 (dotted), and N3 (dashed).

adsorbed on the TiO₂ electrode on the surface by stripping off the dyes with 0.1 M KOH solution in water and ethanol (20 : 80 v/v). From the absorption spectra of the desorbed dye solution with the peak intensity at 546 nm and the Beer–Lambert law, the amounts for **SY-04**, **SY-05**, and **N3** dyes were 6.8×10^{-7} , 6.5×10^{-7} , and 2.4×10^{-7} mmol cm⁻², respectively. The increased adsorption of two dyes compared with the **N3** dye is due to higher solubility arising from hexyl groups located at the 3,4-position of the thiophene, thus the dye agglomeration. The maintenance of higher η even at a 6 µm TiO₂ layer indicates that the absorption amount of **SY-04** and **SY-05** on TiO₂ is greatly increased compared with **N3**, as verified by the higher molar extinction coefficient.

Also, we found that the η of the DSCs prepared by **SY-04** and **SY-05** was almost the same even though the dye concentration decreased by three times (0.3 to 0.1 mM). But, under the same conditions, the η of the N3-based DSC was decreased to 25% (see Table S6†). These results clearly demonstrate the advantage of the sensitizers with higher molar extinction coefficient arising from their metal-to-ligand charge transfer band.

It is also noted in Table 2 that the V_{oc} values of **SY-04** and **SY-05** are similar, because the absorption profile and the energy levels (HOMO and LUMO) of the frontier orbitals are almost the same. On the other hand, the V_{oc} of the two dyes is 87 mV higher than that of **N3**. The V_{oc} depends on many factors such as the electron life-time, the number of protons in the carboxylic groups of the dye, the inherent dye structure, and the conduction band shift in TiO₂.⁴⁷⁻⁵⁰ Among them we consider two main factors: (1) the number of protons in the carboxylic groups of the dye, and (2) the electron life-time.

The increase in the V_{oc} of **SY-04** and **SY-05** compared with **N3** might be due to the fact that only two protons in the carboxylic groups are existent in the present dyes compared with four protons for **N3**. Therefore, the offset between the quasi-Fermi level of the TiO₂ and the redox level of the electrolytes for **SY-04** and **SY-05** increased.^{51,52} To investigate the electron life-time of the sensitizers in the mesoporous titania, we measured the dark electrochemical impedance spectra⁵³ of DSC cells at various bias potentials.

Fig. 6 shows the Bode phase diagram of the DSCs measured under the dark at open circuit voltage conditions for the samples made with **SY-04**, **SY-05**, and **N3**. It contains three characteristic



Fig. 6 Impedance spectra of the (Bode phase diagram) measured under the dark for SY-04 (\bullet), SY-05 (\blacksquare), and N3 (\triangle).

peaks that were assigned in the order of increasing frequency to diffusion impedance of I_3^- ions, electron transport and recombination in TiO₂ electrode, and electron transfer process at counter electrode–electrolyte interface, respectively. The life time (τ) of dyes attached to TiO₂ conduction band is given by *f*,

$$\tau = 1/(2\pi f)$$

where f is the characteristic frequency corresponding to the middle peak in Fig. 6.

The first peak observed between *ca.* 1 and 10 Hz was not distinct due to a small contribution of the electrolyte diffusion to the impedance. The second peak corresponds to the electron transport and recombination in the TiO₂ electrode. From the peak positions (57.50, 35.06, and 32.12 Hz for N3, SY-05, and SY-04, respectively), the life times of these three dyes are calculated to be 2.76, 4.54 and 4.95 ms, respectively. It is generally accepted that a decrease in frequency at the second semicircle (*f*) is correlated with an increase in the V_{oc} of electrochemical impedance spectroscopy.⁵⁴ The increased V_{oc} values for SY-04 and SY-05 compared with that of N3 are well consistent with long life times.

To elaborate the EIS results, transient absorption spectra (TAS) measurements were carried out to find the recombination half-life time $(t_{1/2})$ between the oxidized redox couple and photo-injected electrons in mesoporous TiO₂ having 12 µm thickness with liquid electrolyte.

Fig. 7 shows the decay profiles of the absorption of the dyes. From the profiles, $t_{1/2}$ values for **SY-04** and **SY-05** were 74.4 and 73.2 µs, respectively. These values are higher than that (49.7 µs) of **N3** when measured under identical conditions. Therefore, the increased values of $V_{\rm oc}$ and $J_{\rm sc}$ for the **SY-04** and **SY-05** dyes compared with **N3** might be attributed to the longer recombination half-life time measured by TAS and the longer electron life time measured by EIS.^{55,56}

Conclusions

We synthesized two heteroleptic ruthenium-based sensitizers (**SY-04** and **SY-05**) in which 3,4- or 3-hexylthiophene moieties were incorporated *via* a vinyl group to the bipyridine ligand. Due



Fig. 7 Transient absorbance decay of the dyes obtained by nanosecond laser flash photolysis.

to the employment of the HEW reaction, the yield of ancillary ligands was very high, and the purification of these two dyes was very easy. The functionalization of position 3,4 in the thiophene ancillary ligands increases the molar extinction coefficient considerably. Furthermore, the electron life time adsorbed on TiO₂ and the adsorption amount of these two dyes are larger than those of N3. With increases of both V_{oc} and J_{sc} , the η of the DSC prepared using SY-04 was 7.70%, which is 27% higher than that (6.05%) prepared with N3 under the same cell fabrication conditions. The increased η might be attributed to the increase in electron life time (4.95 ms) measured by electrochemical impedance as well as the increased recombination half-life (74.4 µs) measured by TAS for SY-04 compared with those (2.76 ms and 49.7 µs) of N3.

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