Enhanced light-harvesting capability by phenothiazine in ruthenium sensitizers with superior photovoltaic performance

Jen-Fu Yin, Jian-Ging Chen, Jiann-T'suen Lin, Dibyendu Bhattacharya, Ying-Chan Hsu, Hong-Cheu Lin, Kuo-Chuan Ho and Kuang-Lieh Lu

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This paper reports on the design and synthesis of two new ruthenium dyes [Ru(dcbpy)(potip)(NCS)2] (JF-3, dcbpy = 4,4'-dicarboxylic acid-2,2'-bipyridine, potip = 2-(4-(10H-phenothiazin-10-yl)-5-octythiophen-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline, and [Ru(dcbpy)(dpotip)(NCS)2] (JF-4, dpotip = 2-(4-(N,N-diphenylamino)-5-octythiophen-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline) that contain electron-donating phenothiazine-based or N,N-diphenylamino-based ancillary ligands. The ruthenium dye JF-3, in which an excellent electron-donating phenothiazine is incorporated, shows superior DSC performance (9.1%; compared to 8.8% for N3). A comparison of the electron-donating phenothiazine and N,N-diphenylamino groups utilized in the molecular architecture of ruthenium dyes demonstrates that the phenothiazine group efficiently increases the molar extinction coefficient of band II and also broadens that band in the UV-vis absorption spectrum, reduces device resistance, increases electron lifetime, and enhances power-conversion efficiency. This finding not only clarifies the significance of multifunctionalized design in the molecular architecture of ruthenium dyes, but also represents an alternative route for the introduction of an excellent electron-donating group for improving the light-harvesting characteristics of ruthenium dyes as well as DSC performance.

1. Introduction

Humans require energy for almost any type of activity that they perform. The world annual energy consumption is ca. 4.7 × 1020 J and is expected to grow by about 2% each year for the next 25 years.1,2 However, fossil fuel reserves, such as oil, coal and gas, are rapidly becoming depleted. The development of alternative energy sources to meet our needs has become a significant topic in recent years.3,4 Energy from the sunlight that strikes the earth in 1 hour exceeds all of the energy consumed by humans in an entire year. Furthermore, the energy supplied from the sun is clean and sustainable.6 Photovoltaic technology is one of the most favorable ways to convert solar energy into some forms of usable energy.7 Dye-sensitized solar cells (DSCs) have attracted widespread interest owing to the fact that they are relatively cost-effective, easy to manufacture, and can be readily shaped with flexible substrates to satisfy the demands of various applications.8,9 DSC performance is deeply affected by three crucial components: porous nanocrystalline TiO2 film, photosensitizers, and electrolyte. Since the report of the ruthenium-based photosensitizer, [Ru(dcbpy)2(NCS)2] (N3, where dcbpy = 4,4'-dicarboxylic acid-2,2'-bipyridine), by Grätzel and coworkers in 1993,10 various structural modifications have been proposed to improve its power-conversion efficiency.11–25 Certain light-harvesting chromophores such as thiophene26,27 and carbazole27 that are employed in producing multifunctionalized ruthenium dyes are known to enhance their power-conversion efficiency. In addition, the electron-donating phenothiazine was widely used to enhance the light-harvesting capability of organic dyes.26,27 Its structure is an analogous plane with a slight bending butterfly conformation in the ground state, which can impede the molecular aggregation and the formation of intermolecular excimers.26 However, issues related to how to select a beneficial chromophore to improve the light-harvesting capability of ruthenium dyes, and how it affects ruthenium dyes are still not very clear. Moreover, reports of alternate electron-donating groups that can be used for the structural modification of ruthenium dyes are also rare. In this paper, we address these issues. We introduced an excellent electron-donating phenothiazine for enhancing the light-harvesting capability of ruthenium dyes and applied the concept of multifunctionalized molecular design to the preparation of ruthenium dyes. A ruthenium dye with an electron-donating phenothiazine shows excellent photovoltaic performance greater than that with an N,N-diphenylamino group (Scheme 1). This up and down adjustment for the optimization of DSC efficiency is of fundamental importance. The
origins of these effects can be explained by spectral data, theoretical studies, and device properties.

2. Results and discussion

2.1. Synthesis

2-Bromo-3-(10H-phenothiazin-10-yl)thiophene and 2-bromo-3-(N,N-diphenylamino)thiophene were synthesized through a cross-coupling reaction\[^{28-29}\] of 3-bromothiophene with phenothiazine and N,N-diphenylamine, respectively, followed by bromination with N-bromosuccinimide (NBS) in dimethylformamide (DMF). 3-(10H-Phenothiazin-10-yl)-2-octylthiophene and 3-(N,N-diphenylamino)-2-octylthiophene were obtained by forming the dianion of their 2-bromo-3-substituted thiophene precursors with 1.2 equiv. of n-butyllithium, followed by reaction with 1-bromoocotane. 4-(10H-Phenothiazin-10-yl)-5-octythiophene-2-carbaldehyde and 4-(N,N-diphenylamino)-5-octythiophene-2-carbaldehyde were then prepared using a synthetic procedure similar to that described above, except that N-formylpiperidine was used instead of 1-bromooctane. Eventually, the ancillary ligands, 2-(4-(10H-phenothiazin-10-yl)-5-octythiophene-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (potip) and 2-(4-(N,N-diphenylamino)-5-octythiophene-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (dpotip), were obtained by coupling the corresponding 4-(10H-phenothiazin-10-yl)-5-octythiophene-2-carbaldehyde and 4-(N,N-diphenylamino)-5-octythiophene-2-carbaldehyde with 1,10-phenanthroline-5,6-dione\[^{30}\] and ammonium acetate, which is used as the source of ammonia, in glacial acetic acid, according to protocols reported by Steck and Day.\[^{31}\] Scheme 2 depicts the synthetic routes used in preparing the potip and dpotip ligands. The ruthenium dyes, JF-3 and JF-4 (Fig. 1), were prepared by treating a ruthenium dimer with each of the ancillary ligands, potip and dpotip, in DMF under an argon atmosphere using a typical one-pot synthesis.\[^{32}\] The one-pot synthesis consists of three different temperature regimes: [RuCl_{2}(p-cymene)], reacts with the ancillary ligand at 80 °C, resulting in the formation of a mononuclear Ru(II) complex; the cyanide ligand from the Ru(II) coordination sphere is replaced with cydpy at 160 °C under dark conditions; and the desired ruthenium dye product is obtained by adding excess ammonium thiocyanate at 130 °C.

2.2. Photophysical properties

Fig. 2 shows UV-vis absorption spectra of the free ligands, potip, dpotip and opip (where opip, 2-(5-octythiophen-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline, was used as ancillary ligand for JF-2 in our previous study,\[^{18}\] Fig. 1), in DMF solution. All ligands display an intense absorption band with a shoulder in the UV-vis region. The absorption maxima (\(\lambda_{\text{max}}\)) for all ligands are in the range of 270–290 nm. The \(\lambda_{\text{sh}}\) of dpotip (375 nm) is red-shifted by 35 nm compared to that (340 nm) of opip, and the molar extinction coefficient (\(\varepsilon\)) of the shoulder for dpotip is reduced to half that for opip. However, the \(\varepsilon\) value of potip is doubled at \(\lambda_{\text{sh}}\) and increased slightly at \(\lambda_{\text{sh}}\) compared with that of opip, indicating that the phenothiazine group strengthens the molar extinction coefficient in the UV-vis absorption spectra of opip. The UV-vis absorption spectra of JF-2, JF-3, and JF-4 show three main features, assigned as bands I, II (shoulder), and III with increasing energy order (Fig. 3). The UV-vis absorption data for dyes, JF-2, JF-3 and JF-4, are listed in Table 1.\[^{18}\] The \(\varepsilon\) values (0.99–1.05 \times 10^{4} \text{ M}^{-1} \text{ cm}^{-1}) and positions (520 nm) of the lowest metal-to-ligand charge transfer (MLCT) band I for all dyes are nearly identical. However, the \(\varepsilon\) values of band II are increased in the order JF-4 < JF-2 < JF-3. The order of the absorption band II wavelength for all dyes is consistent with that of \(\lambda_{\text{sh}}\) in their corresponding ancillary ligands, indicating that band II is an ancillary ligand-localized transition. Moreover, the ancillary ligand with an electron-donating phenothiazine group can efficiently increase the molar extinction

\[\text{S} \xrightarrow{a} \text{S} \xrightarrow{b} \text{S} \xrightarrow{c} \text{S} \xrightarrow{d} \text{S} \xrightarrow{e} \text{S} \xrightarrow{f} \]
coefficient of band II and hence result in superior light-harvesting characteristics.

Fig. 4 shows the UV-vis absorption spectra of JF-2, JF-3 and JF-4, when anchored onto the surface of 2.4 μm thick transparent nanocrystalline TiO2 films. The lowest energy MLCT bands of JF-2/TiO2 (513 nm), JF-3/TiO2 (470 nm) and JF-4/TiO2 (510 nm) are blue-shifted by 6, 50 and 10 nm, respectively, compared with their spectra in DMF solution (Fig. 3). This blue-shift of the spectra on TiO2 films can be attributed to π-stacking interactions or the formation of aggregates on the TiO2 surface. In addition, one can see the broader absorption spectrum of JF-3 compared to JF-4 (and also JF-2), suggesting a better molecular planar configuration between thiophene and phenothiazine groups in JF-3 than that of thiophene and the N,N-diphenylamino group in JF-4 (vide infra).

2.3. Electrochemical behaviors

The electrochemical behaviors of dyes, JF-3 and JF-4, were investigated by square-wave voltammetry (Fig. 5) and their oxidation potentials are listed in Table 1. The redox potentials of dyes, JF-3 and JF-4, were unequivocally determined to be 0.35 and 0.33 (V vs. Fe/Fe⁵⁺). The highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) energy levels of JF-2, JF-3 and JF-4 were calculated from their oxidation potentials and their absorption edges obtained from UV-vis absorption spectra (listed in Table 1). The energy levels of the HOMO of JF-2, JF-3 and JF-4 at −5.50, −5.45 and −5.43 eV are more positive than the iodide electron donor. This provides a sufficient driving force for efficient dye regeneration, and the avoidance of geminate charge recombination. Furthermore, the energy levels of the LUMO of JF-2, JF-3 and JF-4 at −3.62, −3.65 and −3.60 eV are more negative than the conduction band of TiO2, ensuring a sufficient driving force for electron injection from the excited dyes to TiO2.

2.4. Molecular modeling

The optimized molecular structures of JF-3 and JF-4 as well as their frontier molecular orbitals of their calculated HOMO and LUMO were computed by density functional theory (DFT), and the data are shown in Fig. 6. The HOMOs of JF-3 and JF-4 are populated from Ru-t₂g to the NCS-π orbital, while their LUMOs are delocalized homogeneously on the anchoring ligand (dcbpy). This spatially directed separation of HOMO and LUMO is an ideal condition for DSCs, which is good for dye regeneration and interfacial electron injection from the excited dye to the conduction band of TiO2. On closer inspection, the dihedral angle between the planes of thiophene and phenothiazine is 80.35°, and the phenothiazine group in the structure of JF-3 is
an analogous plane with a slight bending, however, the \(N, N\)-diphenylamino group in the structure of JF-4 is twisted and non-planar (Fig. 6). Therefore, the phenothiazine group is more highly conjugated than the \(N, N\)-diphenylamino group.

The calculated absorption spectra of JF-3 and JF-4 obtained by computing their optimized structures from time-dependent density functional theory (TDDFT) calculations are shown in Fig. 7. For both dyes, JF-3 and JF-4, the calculated absorption spectra from 420 to 700 nm are not different. However, the intensity of the calculated absorption spectra between 340 and 400 nm for JF-3 is obviously higher than that of JF-4. Overall, the experimental and predicted electronic spectra are in good agreement. Both the calculated results and experimental absorption spectra are consistent with the higher molar extinction coefficient of band II in JF-3 than that in JF-4.

2.5. Photovoltaic performance

As shown in Fig. 8, the short-circuit photocurrent density \(J_{sc}\), open-circuit voltage \(V_{oc}\), and fill factor (ff) of the JF-3-sensitized solar cell under AM 1.5 sunlight (100 mW cm\(^{-2}\)) are 17.1 mA cm\(^{-2}\), 0.74 V and 0.72, respectively, yielding an overall power-conversion efficiency \(\eta\) of 9.1% which is higher than that of JF-2 (8.3%)\(^{18}\) and JF-4 (7.9%). The photophysical data for the ruthenium dyes in solution showed that the \(\epsilon\) values for band II (Fig. 3 and Table 1) are increased in the order JF-4 < JF-2 < JF-3. Moreover, the UV-vis absorption spectra of the dyes on the TiO\(_2\) film (Fig. 4) showed that the \(\epsilon\) values are in the order JF-4 < JF-2 < JF-3, which basically follow the same trend as that in the solution state. These results are consistent with the findings relative to photovoltaic performance, which is increased in the order of JF-4 < JF-2 < JF-3. The incident photon-to-current conversion efficiency (IPCE) of the JF-3-sensitized solar cell exceeds 80% in the spectral range 410–610 nm, reaching

![Fig. 5 Square-wave voltammograms of ruthenium dyes, JF-3 and JF-4.](image)

![Fig. 6 Optimized molecular structures and the frontier orbitals of JF-3 and JF-4 along with isodensity plots for the HOMO and LUMO orbitals. Atoms in yellow, gray, red, cyan and blue color correspond to sulfur, carbon, oxygen, ruthenium and nitrogen, respectively.](image)

<table>
<thead>
<tr>
<th>Dye</th>
<th>(\epsilon) (\times 10^4) M(^{-1}) cm(^{-1})</th>
<th>(\pi - \pi^*)</th>
<th>(\pi - \pi^<em>) or 4d-(\pi^</em>)</th>
<th>4d-(\pi^*)</th>
<th>(E_{ox}) of Ru(^{III/II}) (V vs. Fc/Fc(^+))</th>
<th>(E_{HOMO})/eV</th>
<th>(E_{LUMO})/eV</th>
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<tbody>
<tr>
<td>JF-2</td>
<td>4.76 (298)(^a)</td>
<td>2.17 (358)</td>
<td>0.99 (519)</td>
<td>0.38</td>
<td>-5.50</td>
<td>-3.62</td>
<td></td>
</tr>
<tr>
<td>JF-3</td>
<td>3.59 (298)</td>
<td>3.02 (342)</td>
<td>1.05 (520)</td>
<td>0.35</td>
<td>-5.45</td>
<td>-3.65</td>
<td></td>
</tr>
<tr>
<td>JF-4</td>
<td>4.95 (296)</td>
<td>1.56 (373)</td>
<td>1.02 (520)</td>
<td>0.33</td>
<td>-5.43</td>
<td>-3.60</td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}\) Absorption maxima, \(\lambda_{max}\) (nm). \(^{b}\) The Ag/AgNO\(_3\) reference electrode was calibrated with a ferrocene/ferrocinium (Fc/Fc\(^+\)) redox couple. The electrochemical experiments were carried out in 0.1 M tetrabutylammonium tetrafluoroborate/DMF solution. \(^{c}\) The values of \(E_{HOMO}\) and \(E_{LUMO}\) were calculated with the following formula: HOMO (eV) = \(E_{ox} - E_{Fc/Fc^+}\) + 5.1; LUMO (eV) = HOMO - \(E_g\). \(E_g\) is the absorption onset estimated from the UV-vis absorption spectra of the sensitizers.
a overlap of 88% at 521 nm (Fig. 9). The calculated \( J_{oc} \) from the overlap integral of the IPCE spectrum of the JF-3-sensitized solar cell is 16.0 mA cm\(^{-2}\), and the mismatch factor\(^{34} \) in our device fabrication for the calculated and measured photocurrent density is less than 1.07. Data related to the photovoltaic performance for JF-3- and JF-4-sensitized solar cells are summarized in Table 2.

### 2.6. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) provides useful information for the realization and characterization of the photovoltaic parameters in DSCs. EIS was mainly applied to DSCs to study the resistance of the charge transfer at the counter-electrode, the resistance at the dye-adsorbed TiO\(_2\)/electrolyte interface together with electron transport in the TiO\(_2\) network, and the resistance of the triiodide to diffusion in the electrolyte.\(^{35-38} \) Fig. 10 shows EIS data for JF-3- and JF-4-sensitized solar cells in the form of a Nyquist plot (i.e., minus the imaginary part of the impedance \( Z' \) vs. the real part of the impedance \( Z'' \) when sweeping the frequency). The radius of the middle semicircle in the Nyquist plot for JF-3 is smallest amongst the three dyes (Fig. 10). This indicates that the overall resistance at the TiO\(_2\)/electrolyte interface and the TiO\(_2\) network of the JF-3-sensitized solar cell is smaller and follows the following trend: JF-4 < JF-2 < JF-3. We were also able to clarify two important factors from EIS data, namely, electron lifetime (\( \tau \)) and effective diffusion length (\( L_d \)), both of which affect DSC performance.\(^{39-43} \) The electron lifetime was calculated by \( \tau = 1/(2\pi\omega_{\text{min}}) \), where \( \omega_{\text{min}} \) is the angular frequency at the midfrequency peak in the EIS Bode plot, see Fig. 11, and the \( \tau \) value expresses the electron recombination in TiO\(_2\) films. The effective diffusion length was calculated by \( L_d = L(R_{ct}/R_i)^{1/2} \), where \( L \) is the thickness of TiO\(_2\) films, \( R_{ct} \) and \( R_i \) are the charge transfer resistance at the dye/TiO\(_2\)/electrolyte interface and are related to electron recombination and electron transport resistance in the TiO\(_2\) film, respectively, and \( L_d \) describes the competition between charge collection and recombination. The values of \( L_d \) for JF-3 and JF-4 are 29.2 and 31.6 \( \mu \)m, respectively. The effective diffusion lengths for both dyes in the cells are larger than the thickness of the TiO\(_2\) films, indicating that all photogenerated electrons will be collected efficiently. Moreover, the values of \( \tau \) for the JF-2-, JF-3- and JF-4-sensitized solar cells are 6.4, 6.4 and 4.3 ms, respectively, indicating that the electron transport efficiency follows the order JF-3 > JF-2 > JF-4. Based on the above analysis of the Nyquist plots and Bode plots, we can conclude that the EIS

### Table 2 Photovoltaic performance and parameters for JF-3 and JF-4

<table>
<thead>
<tr>
<th>Dye</th>
<th>( J_{oc} ) mA cm(^{-2})</th>
<th>( V_{oc} ) V</th>
<th>( \eta ) (%)</th>
<th>( \tau ) ms</th>
<th>( L_d ) ( \mu )m</th>
</tr>
</thead>
<tbody>
<tr>
<td>JF-3</td>
<td>17.1 (16.0)(^b)</td>
<td>0.74</td>
<td>0.72</td>
<td>9.1</td>
<td>6.4</td>
</tr>
<tr>
<td>JF-4</td>
<td>16.1 (15.1)</td>
<td>0.71</td>
<td>0.69</td>
<td>7.9</td>
<td>4.3</td>
</tr>
</tbody>
</table>

\(^{b}\)The cell performance data of JF-3 and JF-4 are the average of four measurements, and the power-conversion efficiency of N3-sensitized solar cell (where N3 is [Ru(dcbpy)\(_2\)(NCS)\(_2\)]) measured by the same device fabrication process is 8.8%. \(^{b}\)The values in parentheses were the average of four measurements.
A comparison of the phenothiazine and electron-donating phenothiazine group, exhibits superior device performance. The dye JF-3 shows enhanced ruthenium dye harvesting capability of ruthenium dyes as well as DSC performance. The resistance adjustment provides an alternative route for improving the light-power conversion efficiency. This finding of up and down resistances, increase electron lifetime, and therefore enhance coefficient in the UV-vis absorption spectrum, reduce device efficiently broaden band II and increase its molar extinction coefficient in the UV-vis absorption spectrum.

In conclusion, we report on the design and synthesis of two new ruthenium dyes, JF-3 and JF-4, containing ancillary ligands with electron-donating groups. The dye JF-3, which contains an electron-donating phenothiazine group, exhibits superior device performance. A comparison of the phenothiazine and N,N-diphenylamino groups utilized in molecular engineering for ruthenium dyes demonstrates that the phenothiazine group can efficiently broaden band II and increase its molar extinction coefficient in the UV-vis absorption spectrum, reduce device resistances, increase electron lifetime, and therefore enhance power-conversion efficiency. This finding of up and down adjustment provides an alternative route for improving the light-harvesting capability of ruthenium dyes as well as DSC performance via a multifunctionalized design of the ancillary ligand.

3-(10H-Phenothiazin-10-yl)thiophene

To a two-necked flask containing 3-bromothiophene (1092.4 mg, 6.7 mmol), phenothiazine (1335.1 mg, 6.7 mmol), Pd(dba)₂ (80.5 mg, 0.14 mmol) and sodium tert-butoxide (1105.3 mg, 11.5 mmol) were added a solution of tri-tert-butylphosphine in toluene (0.5 M, 0.25 mL) and 35 mL of anhydrous toluene under an argon atmosphere. The mixture was refluxed for 90 min. The hot reaction mixture was filtered to remove insoluble solids. The filtrate was concentrated under reduced pressure to give a yellow powder. The crude product was purified by chromatography using CH₂Cl₂/hexane (2 : 8) as the eluent to afford 3-(10H-phenothiazin-10-yl)thiophene as pure white solid. ¹H NMR (400 MHz, DMSO-d₆, δ): 7.88 (d, J = 8.0 Hz, 1H), 7.75 (s, 1H), 7.21 (d, J = 8.0 Hz, 1H), 7.09 (d, J = 7.2 Hz, 2H), 6.99 (d, J = 6.8 Hz, 2H), 6.88 (d, J = 6.8 Hz, 2H), 6.32 (d, J = 7.2 Hz, 2H); EIMS (m/z): 281.1 [M⁺].

3-(N,N-Diphenylamino)thiophene

The compound 3-(N,N-diphenylamino)thiophene was synthesized following a similar procedure to that described for the 3-(10H-phenothiazin-10-yl)thiophene, except that N,N-diphenylamine was used in place of phenothiazine. The crude product was purified by chromatography using CH₂Cl₂/hexane (2 : 8) as the eluent to afford 3-(N,N-diphenylamino)thiophene as a pure white solid (yield 70%). ¹H NMR (400 MHz, DMSO-d₆, δ): 7.51 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 7.6 Hz, 4H), 6.99 (m, 6H), 6.84 (d, J = 5.6 Hz, 2H); EIMS (m/z): 251.2 [M⁺].
2-Bromo-3-(10H-phenothiazin-10-yl)thiophene

NBS (979.3 mg, 5.5 mmol) in 20 mL of DMF was added dropwise under darkness to a solution of 3-(10H-phenothiazin-10-yl)thiophene (1407.9 mg, 5.0 mmol) in DMF at 0 °C. The reaction mixture was stirred at room temperature for another 10 h before being poured into water. The organic layer was separated, and the aqueous layer was extracted with methylene chloride. The organic layers were collected, dried over anhydrous MgSO4 and the removal of the solvent gave the crude product. The crude product was purified by chromatography using CH2Cl2/hexane (2 : 8) as the eluent to afford 1447.5 mg (4.02 mmol, yield 80%) of 2-bromo-3-(10H-phenothiazin-10-yl)thiophene as pure white solid. 1H NMR (400 MHz, DMSO-δ6, δ): 7.98 (d, J = 5.2 Hz, 1H), 7.28 (d, J = 5.2 Hz, 1H), 7.07 (d, J = 8.4 Hz, 2H), 6.99 (t, J = 7.6 Hz, 2H), 6.88 (t, J = 7.6 Hz, 2H), 6.17 (d, J = 8.4 Hz, 2H); EIMS (m/z): 359.0 [M⁺].

2-Bromo-3-(N,N-diphenylamino)thiophene

The compound 2-bromo-3-(N,N-diphenylamino)thiophene was synthesized following a similar procedure to that described for 2-bromo-3-(10H-phenothiazin-10-yl)thiophene, except that 3-(N,N-diphenylamino)thiophene was used in place of 3-(10H-phenothiazin-10-yl)thiophene. The crude product was purified by chromatography using CH2Cl2/hexane (2 : 8) as the eluent to afford 1432.5 mg (3.4 mmol, yield 68%) of 4-(10H-phenothiazin-10-yl)-5-octylthiophene-2-carbaldehyde as light yellow liquid. 1H NMR (400 MHz, DMSO-δ6, δ): 9.96 (s, 1H), 8.31 (d, J = 2.8 Hz, 1H), 7.12 (d, J = 7.6 Hz, 2H), 7.01 (t, J = 7.6 Hz, 2H), 6.91 (t, J = 7.2 Hz, 2H), 6.31 (d, J = 8.0 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 1.52 (m, 2H), 1.33 (m, 10H), 0.98 (t, J = 8.0 Hz, 3H); EIMS (m/z): 421.3 [M⁺].

4-(10H-Phenothiazin-10-yl)-5-octylthiophene-2-carbaldehyde

The compound 4-(N,N-diphenylamino)-5-octylthiophene-2-carbaldehyde was synthesized following a similar procedure to that described for 4-(10H-phenothiazin-10-yl)-5-octylthiophene-2-carbaldehyde, except that 3-(N,N-diphenylamino)-3-(10H-phenothiazin-10-yl)-3,4-dihydro-2H-imidazo[4,5-f][1,10]phenanthroline (potip) was used as the eluent to afford potip (355.3 mg, 0.581 mmol, 58%) as yellow solid. 1H NMR (400 MHz, DMSO-δ6, δ): 9.02 (d, J = 6.4 Hz, 3H); EIMS (m/z): 393.3 [M⁺].

3-(N,N-Diphenylamino)-2-octylthiophene

The compound 3-(N,N-diphenylamino)-2-octylthiophene was synthesized following a similar procedure to that described for 3-(10H-phenothiazin-10-yl)-2-octylthiophene, except that 2-bromo-3-(N,N-diphenylamino)thiophene was used in place of 2-bromo-3-(10H-phenothiazin-10-yl)thiophene. The crude product was purified by chromatography using hexane as the eluent to afford 3-(N,N-diphenylamino)-2-octylthiophene as colorless liquid (yield 62%). 1H NMR (400 MHz, CD2Cl2, δ): 7.25 (t, J = 8.0 Hz, 4H), 7.18 (d, J = 5.6 Hz, 1H), 7.03 (d, J = 8.0 Hz, 4H), 6.96 (t, J = 7.2 Hz, 2H), 6.82 (d, J = 5.6 Hz, 1H), 2.49 (t, J = 8.0 Hz, 2H), 1.89 (m, 2H), 1.34 (m, 10H), 0.95 (t, J = 6.4 Hz, 3H); EIMS (m/z): 363.3 [M⁺].

4-(10H-Phenothiazin-10-yl)-5-octylthiophene-2-carbaldehyde

A mixture of 1,10-phenanthroline-5,6-dione (210.5 mg, 1.0 mmol), 4-(10H-phenothiazin-10-yl)-5-octylthiophene-2-carbaldehyde (422.3 mg, 1.0 mmol), ammonium acetate (1550.0 mg, 20.1 mmol) and glacial acetic acid (30 mL) was refluxed for 2 h. After the reaction, the mixture was poured into 200 mL of cool water and the resulting precipitate was isolated by filtration. The crude products were washed with water and purified by chromatography using CH2Cl2/hexane/MeOH (5 : 5 : 1) as the eluent to afford potip (355.3 mg, 0.581 mmol, 58%) as yellow solid. 1H NMR (400 MHz, DMSO-δ6, δ): 9.02 (d, J = 4.0 Hz, 2H), 8.80 136 | J. Mater. Chem., 2012, 22, 130–139
d, \(J = 7.6\) Hz, 2H), 7.95 (s, 1H), 7.81 (s, 2H), 7.11 (d, \(J = 8.0\) Hz, 2H), 7.04 (d, \(J = 6.4\) Hz, 2H), 6.91 (t, \(J = 7.6\) Hz, 2H), 6.47 (d, \(J = 8.0\) Hz, 2H), 2.76 (t, \(J = 7.2\) Hz, 2H), 1.56 (m, 2H), 1.17 (m, 10H), 0.85 (m, 3H); FABMS (\(m/z\)): 612.2 [M + H]+.

2-(4-(N,N-Diphenylamino)-5-octylthiophene-2-yl)-1H-imidazo[4,5-f][1,10]phenanthroline (dpotip)

The compound dpotip was synthesized following a similar procedure to that described for potip, except that 4-(N,N-diphenylamino)-5-octylthiophene-2-carbaldehyde was used in place of 4-(10H-phenothiazin-10-yl)-5-octylthiophene-2-carbaldehyde. The crude products were washed with water and purified by chromatography using CH2Cl2/hexane/MeOH (5:5:1) as the eluent to afford dpotip (yield 57%) as brown solid. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): 8.99 (d, \(J = 2.4\) Hz, 2H), 8.78 (d, \(J = 8.4\) Hz, 2H), 7.78 (dd, \(J = 6.0, 8.4\) Hz, 2H), 7.65 (s, 1H), 7.30 (d, \(J = 5.8\) Hz, 2H), 6.99 (m, 6H), 2.78 (t, \(J = 7.6\) Hz, 2H), 1.61 (m, 2H), 1.24 (m, 10H), 0.85 (t, \(J = 6.4\) Hz, 3H); FABMS (\(m/z\)): 582.3 [M + H]+.

\([\text{Ru(dcbpy)}(\text{potip})(\text{NCS})_2]\) (JF-3)

\([\text{RuCl}_2(\text{p-cymene})]\) (306.4 mg, 0.5 mmol) and potip (582.5 mg, 1.0 mmol) were added to dry DMF (20 mL). The reaction mixture was heated at 80 °C under N\(_2\) for 4 h and then dcbyp (4,4'-dicarboxylic acid-2,2'-bipyridine; 244.3 mg, 1.0 mmol) was added. The reaction mixture was refluxed at 160 °C for another 4 h in the dark. Excess NH\(_4\)NCS was added to the reaction mixture and heated at 130 °C for 5 h. After the reaction, the solvent was removed by a rotary evaporator. The product was collected and washed with water and diethyl ether. The crude product was dissolved in methanol and then passed through a column using methanol as the eluent to afford dpotip (yield 57%) as brown solid. \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): 9.50 (m, 2H), 9.12 (s, 1H), 9.02 (s, 1H), 8.93 (s, 1H), 8.69 (d, \(J = 6.4\) Hz, 1H), 8.27 (d, \(J = 8.0\) Hz, 2H), 7.65 (m, 2H), 2.75 (t, \(J = 6.8\) Hz, 2H), 1.23 (m, 10H), 0.86 (t, \(J = 6.8\) Hz, 3H); FABMS (\(m/z\)): 1073.2 [M+]. Anal. Calcd for \(\text{C}_{52}\text{H}_{41}\text{N}_8\text{O}_7\text{Ru}_3\text{S}_5\): 570.5, H 3.85, N 11.75, S 11.95; found: C 56.67, H 3.74, N 11.49, S 11.68%.

\([\text{Ru(dcbpy)}(\text{dpotip})(\text{NCS})_2]\) (JF-4)

The photosensitizer JF-4 was synthesized following a similar procedure to that described for JF-3, except that dpotip was used in place of potip. The crude product was dissolved in methanol and then passed through a column using methanol as the eluent. The main band was collected and concentrated, and a black solid was obtained as the product (yield 32%). \(^1\)H NMR (400 MHz, DMSO-\(d_6\)): 9.50 (m, 2H), 9.12 (s, 1H), 9.02 (s, 1H), 8.93 (s, 1H), 8.66 (s, 1H), 8.32 (d, \(J = 4.8\) Hz, 2H), 7.81 (d, \(J = 4.0\) Hz, 1H), 7.71 (d, \(J = 4.8\) Hz, 1H), 7.65 (d, \(J = 4.8\) Hz, 1H), 7.56 (d, \(J = 5.2\) Hz, 1H), 7.44 (d, \(J = 5.2\) Hz, 1H), 7.27 (m, 4H), 6.99 (m, 6H), 2.77 (t, \(J = 6.8\) Hz, 2H), 1.59 (m, 2H), 1.28 (m, 10H), 0.85 (t, \(J = 6.8\) Hz, 3H); FABMS (\(m/z\)): 1043.2 [M+]. Anal. Calcd for \(\text{C}_{52}\text{H}_{41}\text{N}_8\text{O}_7\text{Ru}_3\text{S}_5\): 525.3, C 52.30, H 3.93, N 11.49, S 11.56; found: C 52.11, H 3.85, N 11.27, S 11.57%.

**Molecular modeling**

The geometrical properties of the dyes, JF-3 and JF-4, were studied with density functional theory (DFT) and time-dependent density functional theory (TDDFT) calculations using the Gaussian 03 (G03) program package, employing the DFT method with Becke’s three-parameter hybrid function and Lee–Yang–Parr’s gradient corrected correlation function (B3LYP). The LanL2DZ effective core potential was used for the ruthenium atom and the split-valence 6-31G** basis set was applied for hydrogen, sulfur, carbon, oxygen and nitrogen atoms. The ground-state geometries of the dye molecules were optimized in the gas phase. Molecular orbitals were visualized using ‘Gauss View 3.09’. TDDFT calculations for JF-3 and JF-4 were performed using the conductor-like polarizable continuum model method (C-PCM) with dimethylformamide (DMF) as the solvent. The empirical solvent data, molecular radius and dielectric constant, employed in C-PCM are 2.647 Å and 36.71, respectively.

**Preparation of TiO\(_2\) electrode**

Preparation of the TiO\(_2\) precursor and electrode fabrication were carried out based on previous reports. The TiO\(_2\) film, serving as the photoanode, was prepared by the general sol–gel method. The precursor solution was prepared according to the following procedure: to 430 mL of a vigorously stirred 0.1 M nitric acid solution, 72 mL of Ti(C\(_2\)H\(_4\))\(_4\) was slowly added dropwise to form a mixture. After hydrolysis, the mixture was heated at 85 °C in a water bath and stirred vigorously for 8 h in order to achieve peptization. When the mixture was cooled to room temperature, the resulting colloid was filtered, and then heated in an autoclave at a temperature of 240 °C for 12 h to permit the growth of the TiO\(_2\) particles. After cooling the colloid to room temperature, it was ultrasonically vibrated for 10 min. The TiO\(_2\) colloid was concentrated to 13 wt% and 30 wt% (with respect to TiO\(_2\) weight) of poly(ethylene glycol) (PEG, \(M_w = 20 000\) and 200 000) was added to prevent the film from cracking during drying. To fabricate the TiO\(_2\) electrode, TTIP (titanium(IV) isopropoxide) was vigorously mixed with ME (2-methoxyethanol) (in the weight ratio of 1:3) to form a metalorganic solution. The metalorganic solution was then spin-coated onto clean conducting fluorine-doped tin oxide (FTO) glasses with a sheet resistivity of 13 Ω per square, followed by annealing at 500 °C for 30 min to form a compact, thin TiO\(_2\) layer. A TiO\(_2\) paste was applied thrice to the top of this compact film using a glass rod to produce the appropriate thickness. For the first coating (paste 1), the TiO\(_2\) colloid mixed with PEG having a molecular weight of 200 000 was used. The second coating used a TiO\(_2\) paste (paste 2) containing a TiO\(_2\) colloid and PEG with a molecular weight of 20 000. Paste 2 mixed with the light scattering particles of TiO\(_2\) (300 nm, 30 wt% in total TiO\(_2\)) was used for the third (final) coating to reduce light loss by back scattering.

**Device fabrication of dye-sensitized solar cells**

The TiO\(_2\) film electrode with a 0.4 [\(\mu\)m dye sensitizers. A platinized FTO was used as a counter-electrode and had an
active area of 0.16 cm², produced by adhering a polyester tape with a thickness of 60 μm. The dye-sensitized photoanode was rinsed with acetonitrile and air-dried. After filling the spacer with electrolyte, the photoanode was placed on top of the counter-electrode and was then tightly clipped to form a cell. The electrolyte was composed of 0.6 M butylmethylimidazolium (BMII), 0.1 M LiI, 0.5 M 4-tert-butylpyridine, 0.03 M I₂, and 0.5 M guanidinium thiocyanate (GuSCN) dissolved in acetonitrile. The photovoltaic characterizations of the solar cells with a mask (0.5 cm², 0.1 M LiI, 0.5 M 4-tert-butylpyridine, 0.03 M I₂, and 0.5 M guanidinium thiocyanate) were carried out using a 150 W Peccell solar simulator (PEC-L11). Light intensity attenuated by a neutral density filter (Oriel, 078–0360) at the measuring (cell) position was calibrated to be 100 mW cm⁻² according to the reading from a radiant power meter (Oriel, 70260) connected by means of a thermopile probe (Oriel, 70263). Photoelectrochemical measurements (photocurrent density–voltage curves) of the solar cells with a mask (0.5 cm², 0.1 M LiI, 0.5 M 4-tert-butylpyridine, 0.03 M I₂, and 0.5 M guanidinium thiocyanate) were recorded using a potentiosstat/galvanostat (PGSTAT 30, Autolab, Eco-Chemie, The Netherlands).

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References


