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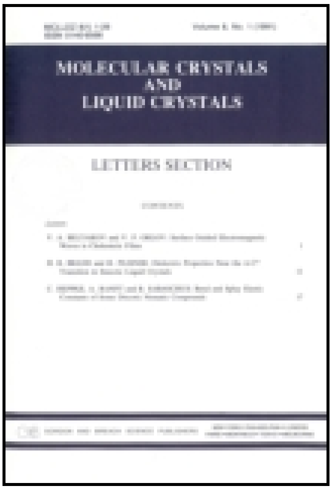

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# Triarylamine-Functionalized Ru Dyes with Different Conjugation Lengths for Highly Efficient Dye Sensitized Solar Cells

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# Triarylamine-Functionalized Ru Dyes with Different Conjugation Lengths for Highly Efficient Dye Sensitized Solar Cells

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*Triarylamine-functionalized ruthenium (Ru) complexes with different conjugation linkage lengths are synthesized and applied to dye-sensitized solar cells (DSSCs). These triarylamine-functionalized Ru complexes show appreciably high extinction coefficients. DSSCs based on the new dye show higher power conversion efficiency than standard N3 dyes under same conditions. Among others, Ru-TP3 dye that has the longest conjugation length shows the highest efficiency of 3.7% under simulated 1 sun illumination (AM 1.5).*

**Keywords** Dye sensitized solar cell; ruthenium complex; triarylamine-functionalized dye; conjugation length

## 1. Introduction

Since highly efficient dye-sensitized solar cells (DSSCs) based on ruthenium (Ru) complex were introduced [1], extensive efforts have been focused on development of new sensitizers to boost the power conversion efficiency [2–4]. Functionalization of photo-sensitizer with extended $\pi$-electron delocalization is one of promising means to increase molar extinction coefficients, to shift the absorption bands to match the solar spectrum, and to enhance redox reversibility and photo-stability [5, 6]. Electron-rich molecules such as triphenylamine and carbazole provide good hole-transporting properties for photovoltaic applications [7–9].

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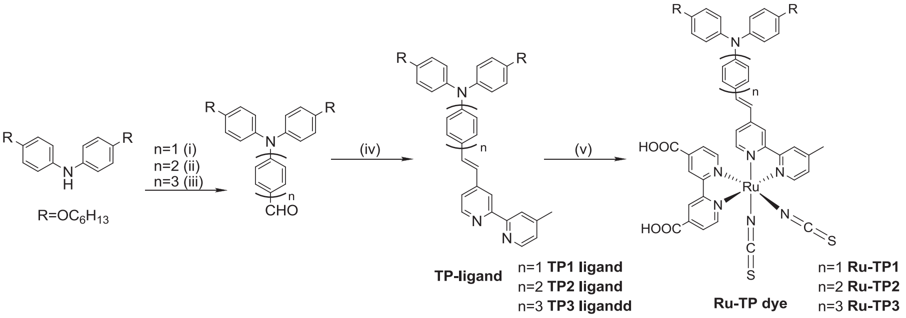
On the basis of this concept, we have designed new Ru dyes with an alkoxy-substituted triphenylamine group that are bridged from bipyridine through extended $\pi$-conjugation of one or more styryl groups, and investigated their properties as a photo-sensitizer in DSSCs. The effects of ligands with different conjugation linkage length on the photophysical properties and on the performance of DSSCs based on the new dyes have been studied.

## 2. Experimental

### *2.1. Synthesis of Ru Dyes*

Three ruthenium dyes, [Ru($H_2$dcbpy)$(NCS)_2$(4-(4-(N,N-di-(p-hexyloxyphenyl)amino) styryl)-4′-methyl-2,2′-bipyridine)] (Ru-TP1), ([Ru($H_2$dcbpy)$(NCS)_2$ (4-(4-(N,N-di-(p-hexyloxyphenyl)amino)biphenyl-4′-yl-ethenyl)-4′-methyl-2,2′-bipyridine)]) (Ru-TP2), and [Ru($H_2$dcbpy)$(NCS)_2$(4-(4-(4-(N,N-di-(p-hexyloxyphenyl)amino)-biphenyl)-4′-yl-styryl)-4′-methyl-2,2′-bipyridine)] (Ru-TP3), were synthesized by following a multi-step pathway according to the previously reported methods with some modification [10, 11], as shown in Scheme 1. Structures of the dyes were confirmed by $^1$H NMR (Varian INOVA spectrometer at 400 MHz using DMSO-$d_6$) and mass spectroscopy (FAB-MS; JMS-700 HRMS).



**Scheme 1.** Preparation of triarylamine-functionalized Ru dyes. (i) 4-bromobenzaldehyde, $PBu^t_3$, NaOBu$^t$, $Pd(dba)_2$, toluene; (ii) 4′-bromobiphenyl-4-carbaldehyde, $PBu^t_3$, NaOBu$^t$, $Pd(dba)_2$, toluene; (iii) (1) 4,4′-dibromobiphenyl, NaOBu$^t$, DPPF, $Pd(OAc)_2$, toluene, (2) 4′-bromobiphenyl-4-carbaldehyde, n-BuLi, $B(OCH_3)_3$, $Pd(OAc)_2$, $K_2CO_3$; (iv) (1) 4,4′-Dimethyl-2,2′-bipyridine, $LiNPr^i_2$, THF, −78°C, (2) conc. AcOH, reflux; (v) [$RuCl_2$(*p*-cymene)$]_2$, $H_2$dcbpy, Excess $NH_4$NCS, DMF.

**Ru-TP1** Yield: 30%, $^1$H-NMR (400MHz, $d_6$-DMSO) $\delta_H$[ppm]: 9.38 (d, 1H), 9.04 (d, 2H), 8.85 (d, 1H), 8.79 (s, 1H), 8.68 (s, 1H), 8.63 (s, 1H), 8.53 (s, 1H), 8.21 (d, 1H), 7.92 (s, 1H), 7.78 (d, 1H), 7.52-7.59 (m, 2H), 7.41 (d, 1H), 7.27 (d, 1H), 7.19 (d, 1H), 7.08 (d, 2H), 7.03 (d, 2H), 6.88-6.94 (m, 4H), 6.76 (d, 1H), 6.69 (d, 1H), 3.90-3.93 (m, 4H), 2.38 (s, 3H), 1.66-1.68 (m, 4H), 1.38-1.4 (m, 4H), 1.2-1.29 (m, 8H), 0.84-0.86 (m, 6H), FAB-MS: m/z for $C_{57}H_{57}N_7O_6RuS_2 = 1101.2$ $[M]^+$.

**Ru-TP2** Yield: 27%, $^1$H-NMR (400MHz, $d_6$-DMSO) $\delta_H$[ppm]: 9.43 (d, 1H), 9.13 (d, 2H), 9.07 (d, 1H), 8.92 (d, 1H), 8.76 (d, 1H), 8.59 (s, 1H), 8.29 (d, 1H), 8.05 (d, 1H), 7.95 (d, 2H), 7.86 (d, 1H), 7.74-7.80 (m, 2H), 7.6 (d, 1H), 7.54-7.62 (m, 2H), 7.39 (d, 1H), 7.33 (d, 1H), 7.25 (d, 1H), 7.05 (m, 4H), 6.92 (m, 4H), 6.83 (m, 2H), 3.94 (m, 4H), 2.43 (s, 3H), 1.69 (m, 4H), 1.40 (m, 4H), 1.31 (m, 8H), 0.88 (m, 6H), FAB-MS: m/z for $C_{63}H_{61}N_7O_6RuS_2 = 1177.2$ $[M]^+$.

**Ru-TP3** Yield: 25%, $^1$H-NMR (400MHz, $d_6$-DMSO) $\delta$H[ppm]: 9.45 (d, 1H), 9.14 (d, 2H), 9.07 (d, 1H), 8.94 (s, 1H), 8.79 (d, 1H), 8.63 (d, 1H), 8.29 (s, 1H), 8.08 (d, 1H), 7.95 (d, 2H), 7.79-7.87 (m, 4H), 7.70-7.77 (m, 3H), 7.55-7.64 (m, 3H), 7.41 (d, 1H), 7.31 (d, 2H), 7.04 (m, 4H), 6.92 (m, 4H), 6.84 (m, 2H), 3.94 (m, 4H), 2.43 (s, 3H), 1.70 (m, 4H), 1.41 (m, 4H), 1.31 (m, 8H), 0.88 (m, 6H). FAB-MS: m/z for $C_{69}H_{65}N_7O_6RuS_2 = 1253.2$ $[M]^+$.

### *2.2. Fabrication of Dye Sensitized Solar Cells*

Sandwich-type DSSCs were fabricated as reported [12]. The devices had 12 $\mu$m-thick $TiO_2$-coated working electrodes and platinum-coated counter electrodes. Ru dyes were adsorbed onto the $TiO_2$ surface by immersing the electrodes in a solution of the dye (0.5 mM) and chenodeoxycholic acid (1 mM) in $CH_3CN/^t$BuOH (1:1) at 70°C for 12 hours. The redox electrolyte consisted of a solution of 0.1 M lithium iodide, 0.1 M iodine, 0.5 M 4-*tert*-butylpyridine, and 0.6 M 1,2-dimethyl-3-propyl imidazolium iodide in acetonitrile.

## 3. Results and Discussion

Triarylamine-functionalized Ru dyes were prepared through a multi-step synthetic route (Scheme 1). Bis(4-hexyloxyphenyl)amine was synthesized via Pd-catalyzed C-N coupling with 4-(hexyloxy)aniline and 1-bromo-4-n-hexyloxybenzene. Next step of the reaction involves N-arylation of bis(4-hexyloxyphenyl)amine with 4-bromobenzaldehyde (TP1-ligand) and 4-bromobiphenyl-4′-carboxaldehyde (TP2-ligand). For TP3-ligand, 4,4′-dibromobiphenyl was employed, which can then be converted to boronic acid by boronation reaction with trimethylborate. This boronic acid derivative was treated with 4-bromobenzaldehyde in a Suzuki coupling reaction to obtain the aldehyde-functionalized molecules. The ligands were synthesized by nucleophilic addition to the benzaldehyde group and dehydration with bimethylbipyridine in reflux acetic acid. Finally, Ru dyes were synthesized with dichloro(p-cymene) ruthenium(II) dimer, $NH_4NCS$, 4,4′-dicarboxy-2,2′-bipyridine ($H_2$dcbpy), and the synthesized TP-ligands, following Grätzel's standard procedure [11].

Figure 1 shows the UV-visible spectra of the Ru-TP dyes in DMF with a concentration of $1.23 \times 10^{-5}$ mol/L. All dyes show absorption peaks at near 300 nm, corresponding to intra-ligand ($\pi \rightarrow \pi^*$) transitions of bipyridines, and at 380 nm and 535 nm, related to metal-to-ligand charge transfer transition (MLCT) [13, 14]. The molar extinction coefficients ($\varepsilon$) of these peaks are 20560, 20600, and 20800 $M^{-1}cm^{-1}$ for Ru-TP,1 Ru-TP2, and Ru-TP3 dye at 526, 529, and 532 nm, respectively. These values are higher than that of reference dye, $[Ru(H_2dcbpy)_2(NCS)_2]$ (N3; 14200 $M^{-1}$ $cm^{-1}$ at 534 nm) [2]. The replacement from $H_2$dcbpy group to styryl-triarylamine-substituted bipyridine led to enhanced light absorption due to enrichment of spectral response by $\pi$-conjugation extension.

There is a slight difference in bandgap of Ru TP dyes which calculated from the onset of absorption spectra. The bandgaps of Ru-TP1, Ru-TP2, and Ru-TP3 are 2.07, 2.06, and 2.05 eV, respectively, which is smaller than that of the reference N3 dye (2.09 eV). We believe that, because the origin of the lowest energy gap of the dyes is not from $\pi$–$\pi^*$ transition of the ligands but from metal-to-ligand charge transfer transition, the change in conjugation length is contributing a small shift of the bandgap of new Ru-TPs. Rather, elongation of the conjugation length has likely resulted in the larger molar extinction coefficient by increased absorption cross-section.

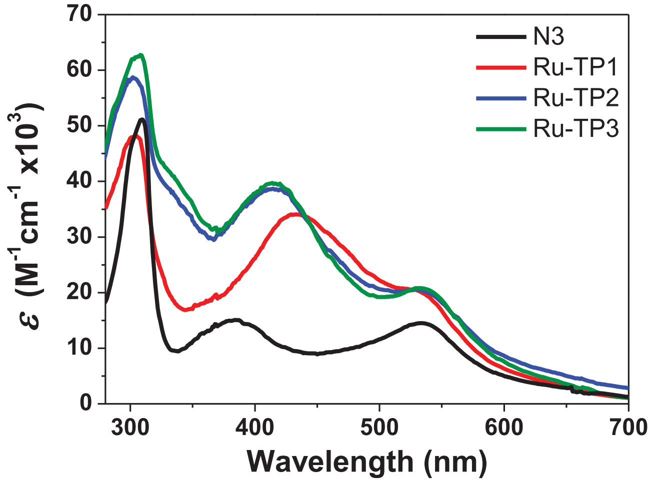


**Figure 1.** Molar extinction coefficient ($\varepsilon$) of triarylamine-functionalized Ru dyes in DMF with a concentration of $1.23 \times 10^{-5}$ M.

The photovoltaic characteristics of DSSCs based on the Ru dyes under standard global AM 1.5 illumination conditions are shown Figure 2 and the parameters are summarized in Table 1. Ru-TP dyes have higher short circuit current density ($J_{SC}$) compared with N3, due to the enhanced light harvesting properties, especially in long wavelength region (>520 nm), as shown in incident photon-to-current conversion efficiency (IPCE) plots (inset of Figure 2). In particular, Ru-TP3-based DSSCs have the power conversion efficiency of 3.69%, which is higher than Ru-TP1 and Ru-TP2 dye-based devices under same conditions. In other words, higher power conversion efficiency was observed when the styryl

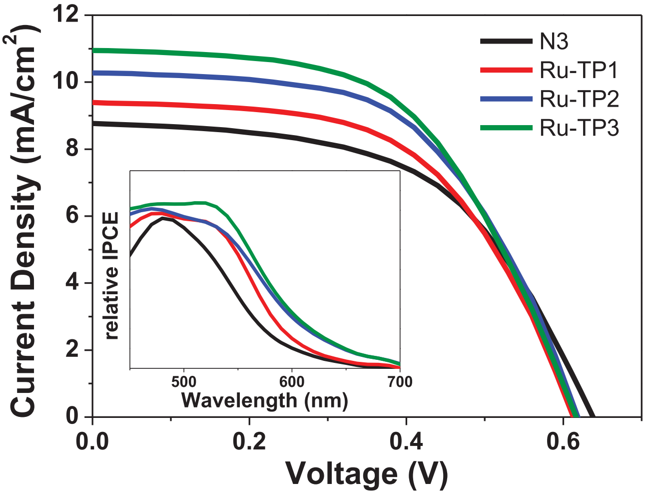


**Figure 2.** Current density versus voltage characteristics for triarylamine-functionalized Ru-dye-based DSSCs under simulated solar light illumination (AM 1.5, 100 mW/cm$^2$) (Inset: incident photon-to-current conversion efficiencies).

**Table 1.** Photophysical properties and photovoltaic performance of DSSCs based on triarylamine-functionalized Ru dyes under simulated solar light illumination (AM 1.5; 100 mW/cm$^2$)

| Dye | $E_g$ [a] [eV] | $\varepsilon$ [b] [$M^{-1}$ $cm^{-1}$] | $J_{SC}$ [mA/cm$^2$] | $V_{OC}$ [V] | FF | $\eta$ [%] |
|---|---|---|---|---|---|---|
| Ru-TP1 | 2.07 | 20,560 | 9.39 | 0.613 | 0.56 | 3.21 |
| Ru-TP2 | 2.06 | 20,600 | 10.25 | 0.619 | 0.56 | 3.52 |
| Ru-TP3 | 2.05 | 20,800 | 10.95 | 0.616 | 0.55 | 3.69 |
| N3 | 2.09 | 14,200 | 9.06 | 0.634 | 0.54 | 3.04 |

[a] Bandgap ($E_g$) was estimated from the onset of absorption spectra.
[b] Molar extinction coefficient ($\varepsilon$) was obtained at the absorption peak near ~530 nm (see text).

conjugation linkage was longer. Better absorptivity of dyes by extended $\pi$-conjugation linkage length results in higher $J_{SC}$ in a solar cell.

## 4. Conclusions

We have studied new ruthenium dyes with conjugated ligands containing hexyloxy-substituted triarylamine units. The dyes have a high molar extinction coefficient that originates from the extended $\pi$-conjugation between the bipyridine and triphenylamine groups in a ligand. Solar cells based on the new dyes showed better photovoltaic performance compared to standard N3 dyes. Our results suggest that the $\pi$-conjugation length in ligands of a dye need to be optimized to achieve good light harvesting ability and enhanced photovoltaic performance in dye sensitized solar cells.

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