Neutral, panchromatic Ru(II) terpyridine sensitizers bearing pyridine pyrazolate chelates with superior DSSC performance[†]

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A new series of neutral, panchromatic Ru(II) terpyridine sensitizers (PRT1–PRT4) exhibit much higher molar extinction coefficients at 400–550 nm and superior DSSC performance in terms of conversion efficiency ($\eta = 10.05$ for PRT4) and stability.

Dye-sensitized solar cells (DSSCs) have received considerable attention due to their versatility and low cost of manufacture.¹ Typical DSSCs consist of a dyed semiconductor TiO₂ photoelectrode, a Pt counter electrode and a redox electrolyte. Among various organic/inorganic dves, the most successful charge transfer sensitizers should be credited to Ru(H₂dcbpy)₂(NCS)₂ and [Ru(Htctpy)(NCS)₃](TBA)₃, referred to as N3 and black dye, respectively, where H₂dcbpy is 4,4'-dicarboxy-2,2'-bipyridine; H₃tctpy denotes 4,4',4''-tricarboxy-2,2':6',2''-terpyridine and TBA represents the tetra-n-butylammonium counter cation.^{2,3} Progress in optimization of the dye component has been made through increasing the optical absorption cross section and expanding the light absorption capability.⁴⁻¹⁹ With regard to the former, DSSCs could be made thinner and thus more efficient because of reduced transport losses in the nanoporous environment.²⁰ With regard to the latter, dyes are designed to harvest solar energy across the entire visible and even NIR regions of the spectrum with the aim of improving the short-circuit current J_{sc} .

To achieve the above goal, as shown in Scheme 1, we report here the strategic design and syntheses of a new series of panchromatic Ru(II) terpyridine sensitizers **PRT1–PRT4**, which possess pyridine pyrazolate (pypz) chelates. By using bidentate pypz in substitution for two thiocyanates, these heteroleptic sensitizers exhibit significantly higher molar extinction coefficients at 400–550 nm *versus* their parent complex, *i.e.* black dye which shows only reduced absorptivity. This enhancement, together with the extension of the absorption onset to the longer wavelength region > 800 nm and panchromatic configuration, leads to superior light-harvesting cross-sections and hence better DSSC performance.

To establish their basic structure, we have grown single crystals of an analogue, namely **PRT0**, without both carboxylic groups and the functionalized appendage. This complex crystallized in the triclinic space group $P\bar{1}$ with two DMSO solvates (see ESI†), and showed a slightly distorted octahedral coordination mode that is governed by three nitrogen donors from the terpyridine, two nitrogen donors of the pypz chelate and one nitrogen donor of an isothiocyanate ligand (see Fig. S1 in the ESI†). As expected, the Ru–N separation to the central N(5) atom of the neutral terpyridine and the N(2) atom of anionic pyrazolate gives the shortest and second shortest Ru–N distances within the entire molecule.^{21,22}

The absorption spectra of our **PRT** dyes in DMF solution are depicted in Fig. 1 together with that of the parent black dye for a fair comparison. Their pertinent photophysical and electrochemical properties are summarized in Table 1. These PRT dyes show an intense UV absorption band around 330 nm, which is assigned to the ligand centred π - π * transition of the H₃tctpy ligand.^{23,24} They are very different from black dye in that they all exhibit intense and broad electronic absorption with two peaks centred at about 430 and 520 nm and a distinct shoulder around 700 nm extending to 850 nm, which are assigned to metal-to-ligand charge-transfer (MLCT) transitions. The MLCT band at 520 nm is blue-shifted compared to black dye (600 nm). This is mainly due to the replacement of two thiocyanato anions by a single chelating pypz anion in PRT, which stabilizes the ground state by providing less electron donation to the Ru centre, causing a decrease in the energy of the t_{2g} metal orbitals and thus a significant blue-shift of the lowest energy MLCT band.²⁵

Nevertheless, introduction of a pypz chelate also drastically increases the molar extinction coefficient, especially in the wavelength range 400–550 nm, manifesting the contribution of the extending π -conjugation from the pypz chelate, such that the light-harvesting ability is significantly enhanced. The design concept of such a highly π -conjugated organic system is akin to the molecular co-sensitization for efficient panchromatic DSSCs that employ both zinc carboxyphthalocyanine and an organic sensitizer.²⁶ It is notable that the designed organic



Scheme 1 Molecular structures of the PRT dyes.

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Fig. 1 Absorption spectra of **PRT** dyes recorded in DMF. Inset: some key frontier orbitals of **PRT1**.

light-absorbing fragment is anchored directly on the donor segment of the panchromatic Ru(II) sensitizer. Consequently, these fragments will not interfere with the adsorption sites on the TiO₂ photoelectrode, and hence reveal the benefit of combining two dyes with complementary absorption spectra to achieve higher light harvesting efficiencies than that of each individual dye.

Prior to making the solar devices, cyclic voltammetry was performed to ensure that the LUMOs of the complexes are suited for injecting electrons into the conduction band of TiO₂ and whether their HOMOs match the energy level of the redox electrolyte. The E_{ox} values of the dyes adsorbed on a 6 µm thick TiO₂ nanocrystalline film on FTO glass were measured (see Table 1). The results reveal that the redox potential of I^-/I_3^- (*ca.* 0.4 V *vs.* NHE) is more negative than the HOMO and is able to regenerate the dye from electron donation. The LUMO levels

 Table 1
 Photophysical, electrochemical and photovoltaic data of various

 PRT dyes

Dye	$\begin{array}{c} \lambda_{abs}/nm,\\ \epsilon/M^{-1}cm^{-1} \end{array}$	$E_{\mathrm{ox}}{}^{a}/\mathrm{V}$	$E_{0-0}{}^b/\mathrm{V}$	$rac{V_{ m oc}}{ m mV}$	$_{\rm mA~cm^{-2}}^{J_{\rm sc}/}$	FF (%)	$\eta^c(\%)$
PRT1	333, 41 000 432, 17 000 520, 10 600	0.60	1.64	687	20.3	65.4	9.14
PRT2	335, 47 600 423, 19 600 517, 12 300	0.70	1.65	668	21.7	64.4	9.33
PRT3	336, 40 700 427, 15 800 519, 11 500	0.70	1.66	720	20.4	65.3	9.59
PRT4	328, 46 400 424, 16 600 519, 12 200	0.71	1.66	714	21.6	65.2	10.05
Black dye	322, 18 100 396, 9440 594, 7660	_		684	19.8	67.0	9.07

^{*a*} Oxidation potential of dyes deposited on TiO₂ was measured in CH₃CN with 0.1 M TBAP and with a scan rate of 50 mV s⁻¹ (*vs.* NHE). ^{*b*} E_{0-0} was determined from the intersection of absorption and emission spectra. ^{*c*} The electrolyte consists of 0.6 M dimethylpropylimidazolium iodide, 0.1 M I₂, 0.1 M LiI, and 0.5 M *tert*-butylpyridine in acetonitrile.

are also sufficiently more negative than the conduction band edge of the TiO₂ electrode (*ca.* -0.5 V vs. NHE at pH 7).

The inset of Fig. 1 shows selected MOs of the prototypical complex PRT1 deduced from density functional theory (DFT) calculations. The results clearly indicate that the LUMO is mainly ascribed to the H₃tctpy ligand with a considerable amount of π back-donation from the t_{2g} orbitals. Moreover, the LUMO has sizable contributions from the carboxylic groups, thus facilitating the electron injection from the excited PRT1 to the TiO₂ conduction band. The electron density distribution of the HOMO in **PRT1**, similar to other Ru(II) sensitizers, is mainly located on the metal centre and NCS ligands. It is also noteworthy that a highly allowed transition (e.g. $S_0 \rightarrow S_4$) was calculated to involve HOMO - 2 and LUMO + 3 orbitals in which the electron density of HOMO -2 is located at the metal centre, NCS ligand and pyrazole ring, whereas that of LUMO + 3 is contributed to mainly by pyridine moieties (see inset of Fig. 1), supporting our original design strategy.

The incident photon-to-current conversion efficiencies (IPCEs) of these DSSC dyes are shown in Fig. 2A. They exhibited efficient sensitization of nanocrystalline TiO₂ solar cells over the entire visible range extending into the NIR region. The onsets of the IPCE spectra are all close to \sim 910 nm, and excellent IPCE performance was observed from 400 to 770 nm, **PRT2** and **PRT4** with a maximum of 84% at 500–530 nm. In contrast, black dye affords a maximum of 76% at 600 nm under identical conditions. The results reveal that these modified PRT sensitizers exhibit better light harvesting capability than black dye, especially in the 400–600 nm range.

Fig. 2B shows the photocurrent density-voltage curve of the devices employing PRT or black dye under AM 1.5 G simulated sunlight at a light intensity of 100 mW cm^{-2} , while pertinent performance data are summarized in Table 1. The black dye solar cells were made according to the optimized parameters of the literature.³ The short-circuit current density (J_{sc}) , open-circuit voltage (V_{oc}), fill factor (FF) and overall conversion efficiency (η) of black dye are 19.8 mA cm⁻², 684 mV, 0.670 and 9.07%, respectively. It is notable that this conversion efficiency is lower than that of black dye (*i.e.* $\eta \ge 10\%$) documented in the literature, which maybe attributed to some unknown defects produced during the fabrication of the TiO₂ photoelectrode.³ Despite this deficiency, compared with our black dye reference cell, the newly designed PRT dyes were endowed with about 1.02-1.10-fold increases in current density. These results coincide with the UV-visible absorption and incident photonto-current conversion efficiencies spectra. The PRT2 sensitized solar cell gives $J_{\rm sc} = 21.7$ mA cm⁻², $V_{\rm oc} = 668$ mV, and FF = 0.644, corresponding to an overall $\eta = 9.33\%$. Compared with PRT2, n-octyl substituted PRT3 shows slightly lower current density, 20.4 mA cm⁻², which may be due to its large molecular volume which reduces its loading onto the TiO₂ surface. Furthermore, our data showed slight reduction in the values of V_{oc} for **PRT1** and **PRT2** with respect to **PRT3** and PRT4. These results reveal the effect upon incorporation of a hydrophobic long alkyl chain or tert-butyl group into the ancillary pypz ligand, which consequently reduces the unwanted back electron transfer from the TiO₂ conduction band to oxidized charge carriers in the liquid electrolyte. Overall,



Fig. 2 (A) The photocurrent action spectra of DSSCs sensitized with various **PRT** dyes. (B) The respective photocurrent–voltage characteristics of DSSCs.

PRT4 represents the best sensitizer among this series of dyes, which gives $J_{sc} = 21.6 \text{ mA cm}^{-2}$, $V_{oc} = 714 \text{ mV}$, and FF = 0.652, corresponding to an overall $\eta = 10.05\%$. This efficiency value is 10.8% greater than that of the reference solar cell fabricated employing the well-known black dye.

One of the superiorities of these PRT dyes may lie in their photostability due to their panchromatic chelating configuration. To test this, the evolution of the photovoltaic parameters of **PRT4** was measured under irradiance of AM 1.5 G sunlight during visible-light soaking at 60 $^{\circ}$ C (see ESI†). The resulting data shown in Fig. 3 reveal excellent stability. The device efficiency changed from 4.46% to 4.06% after 1000 h illumination.

In conclusion, a new series of neutral, panchromatic Ru(II) terpyridine sensitizers **PRT1–PRT4** were strategically designed and synthesized. In comparison to the black-dye standard, these heteroleptic sensitizers exhibit much higher molar extinction coefficients at 400–550 nm. This enhancement, together with the extension of the absorption onset to the longer wavelength region >800 nm and excellent photostability, leads to superior light-harvesting cross-sections and hence better DSSC performance. Upon optimization, **PRT4** has attained $\geq 10\%$ efficiency reproducibly along with an acetonitrile based



Fig. 3 Evolution of photovoltaic parameters of **PRT4** measured under the irradiance of AM 1.5 G sunlight during soaking at 60 °C. A 405 nm cut-off long pass filter was put on the cell surface during illumination. Electrolyte: DMII/EMII/EMITCB/I₂/NBB/GNCS (molar ratio: 12/12/16/1.67/3.33/0.67). See ESI for definitions.†

electrolyte. Despite numerous attempts at the derivation of N3 (or N719) dyes, the improvement of solar-cell performance based on the black-dye framework, especially on its ancillary chelate ligands, making neutral panchromatic coordination, to increase absorptivity and stability, is scant. The exploration reported here paves another avenue to greatly expand the development of solar energy harvesting.

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