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New ruthenium sensitizers containing styryl and antenna fragments

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Abstract

Amphiphilic ligands 4'-((4-(5-pyridin-4-yloxy)pentyloxy)styryl)-4-methyl-2,2'-bipyridine (L1), 4,4'-bis((*E*)-4-(5-(pyridin-4-yloxy)pentyloxy)styryl)-2,2'-bipyridine (L2), 4'-(4-(5-(4'-cyano-4-biphenoxy)pentyloxy)styryl)-4-methyl-2,2'-bipyridine (L3), and 4'-(4-(5-(zinc tetrakis-5,10,15-tritolyl-20-(4-hydroxyphenyl)porphyrin)pentyloxy)styryl)-4-methyl-2,2'-bipyridine (L4) and their heteroleptic ruthenium(II) complexes of the types [Ru(L1)(L)(NCS)₂] (D20), [Ru(L2)(L)(NCS)₂] (D21), [Ru(L3)(L)(NCS)₂] (D22), and [Ru(L4)(L) (NCS)₂] (D23) (where L = 4,4'-bis(carboxylic acid)-2,2'-bipyridine) have been synthesized, as photosensitizers for nanocrystalline dye-sensitized solar cells. All complexes D20–D23 exhibit a broad MLCT band around 520–530 nm in DMF and an emission band around 740–790 nm in DMF. We have studied photovoltaic performances based on the newly synthesized dyes. Under standard AM 1.5 sunlight, the dye D20 gave a short-circuit photocurrent density of 13.31 mA/cm², an open-circuit voltage of 0.64 V, and a fill factor of 0.68, corresponding to an overall conversion efficiency of 5.81%.

Keywords: Ru; Dye-sensitized; Alkoxy-pyridine unit; Porphyrin; Solar cell; Amphiphilic

1. Introduction

Dye-sensitized solar cells are attracting widespread interest for the conversion of sunlight into electricity because of their low cost and high efficiency [1]. In these cells, the dye is one of the key elements for high-power conversion efficiencies. Several Ru(II) complexes such as $([Ru(dcbpyH_2)_2(NCS)_2])$ (N3) and $((Bu_4N)_2[Ru(dcb$ pyH)₂(NCS)₂]) (N719) have been used in DSSCs as efficient sensitizers [2]. Considerable attention has been focussed on understanding the factors that control cell performance to improve the conversion efficiency and stability of DSSCs. Thus the quest for new dyes that efficiently harvest solar light and meet the stability criteria continues to be an important goal. The enhanced absorption is expected by extending the conjugated system of the hydrophobic spectator ligand [3] or by substituting the sensitizer molecule with a sensitizer-antenna molecular unit [4]. A success-

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ful synthetic method has been to replace one of the 2,2'bipyridyl-4,4'-dicarboxylate groups in the N3 dye by a styryl-substituted bipyridine [5] or by an antenna fragment. This not only increases the extinction coefficient of the sensitizer but also its hydrophobicity, stabilizing device performance under long-term light soaking.

A recent work by Grätzel's group [6] has revealed that the use of K-19 as amphiphilic bipyridyl ruthenium complex is promising. The dye has an alkoxy styryl group in its ligand and this ligand was reported to enhance the harvesting of solar light as well as to retain the stability. Recently, we [7] reported the oligophenylenevinylene-functionalized Ru(II)-bipyridine sensitizers for efficient dyesensitized nanocrystalline TiO₂ solar cells relative to that of a cell using N3 dye. Polynuclear complexes exhibiting an antenna effect were also investigated as sensitizers for DSSCs, in which only one metal complex is directly attached to TiO_2 film through its anchoring ligand [8]. Kim and co-workers [9] reported that the linking of N3 with another TiO₂-attached N3 through trans-1,2-bis(4pyridyl)ethylene rendered an enhanced short-circuit photocurrent and thereby conversion efficiency for the pertinent

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DSSC due to an antenna effect. Sugihara [10] also reported that addition of heterocycles such as pyridine and quinoline in electrolyte for the pertinent DSSC rendered an enhanced conversion efficiency with increasing open-circuit voltage due to an intermolecular charge interaction with iodine electrolyte.

We envisioned that the introduction of pyridyl, cyanobiphenyl [11] or porphyrin [12] unit in the peripheral position of bipyridyl ruthenium complex shows an enhanced conversion efficiency because the antenna unit has the role of absorbing the incident light and transferring the electronic energy to the sensitizer fragment. In line with the continuation of the efforts in this direction for improving the solar energy conversion efficiency, we synthesized new type of ruthenium sensitizers, consisting of both styryl and antenna fragment as light harvester. These extended conjugation dyes were successfully employed in DSSCs.

2. Results and discussion

2.1. Synthesis of dyes

The novel ruthenium dyes D20–D23 were synthesized by the stepwise synthetic protocol illustrated in Scheme 1. Ligands L1–L4 were synthesized in two steps using *O*-alkylation and Wittig coupling reaction. The reaction of $[Ru(p-cymene)Cl_2]_2$ complex with L1–L4 in DMF under nitrogen resulted in a mononuclear complex. The heteroleptic dichloro complexes were synthesized by reaction of the mononuclear complex with 4,4'-dicarboxyl-2,2'-bipyridine. The chloro complexes were reacted with a large excess of ammonium thiocyanate ligand to afford the ruthenium dyes D20–D23 (Scheme 1). The complexes D20–D23 were spectroscopically characterized, and all data are consistent with the formulated structures (Fig. 1).

2.2. Optical and electrochemical properties of dyes

Fig. 2a shows the UV/Vis spectra of the dyes D21 and D22 measured in DMF solution and the data are collected in Table 1. The strong absorption band of D20–D22 around 300 nm is due to π - π * transition. Two absorption maxima at 360–370 nm and 522–532 nm, which are due to the metal-to-ligand charge-transfer (MLCT) bands in DMF, are observed in the spectra of D20–D22. The rela-





D22

D23

tionship of the MLCT band among D20–D22 is similar to that of *cis*-[Ru(H₂dcbpy)₂X₂] (X = Cl or SCN) [13]. The molar extinction coefficient of the lowest energy MLCT band in D22 is slightly higher than those of two dyes D20 and D21 due to the introduction of cyanobiphenyl as light harvester. However, the molar extinction coefficient of the MLCT band in D22 is lower about 15% compared to that of *cis*-dithio-cyanato(4,4'-dicarboxylic acid-2,2'-bipyridine)ruthenium(II) complex [14].



Scheme 1. Synthetic protocol for the preparation of D20–D23.



Fig. 2. (a) Absorption and emission spectra of dyes D21 (\longrightarrow) and D22 (----). (b) Absorption spectra of D23 in DMF (\longrightarrow) and adsorbed on TiO₂ film (----). The inset shows the expanded absorption spectra.

The UV/Vis spectrum of the dye D23 exhibits an intense soret or B-band around 425 nm, assigned to a π - π ^{*} transition to the second electronic excited state, and two Q-bands at 562 and 604 nm, corresponding to π - π ^{*} transition to the first electronic excited state [15]. In addition to that, the dye D23 shows a broad visible band at 518 nm due to MLCT transition. When the dye D23 was absorbed to TiO₂ electrode, a slight red shift from 518 to 521 nm was found due to the interaction of the anchoring group with the surface titanium anions [16]. The absorption intensity of D23 on the TiO_2 film is lower than those of D20–D22, indicating that D23 is less efficiently absorbed on the TiO_2 surface than D20–D22.

The emission maxima of D20–D22, which were obtained at room temperature by excitation within their MLCT bands at 530 nm in an air-equilibrated DMF solution, are summarized in Table 1. Fig. 2a shows representative emission spectra of D21 and D22. They exhibit strong luminescence maxima at 789 and 746 nm, respectively, steeply rising at 650 nm. From the intersection of the lowest energy absorption and its emission band, one derives for the E_{0-0} transition energy of D21–D22 a value of 2.02 and 2.03 eV [17].

To thermodynamically evaluate the possibility of electron transfer from the excited state of the dye to the conduction band of TiO₂ electrode, cyclic voltammogram was carried out to determine the redox potential (Table 1). The redox potentials of four ruthenium dyes D20-D23 on TiO₂ films were measured in CH₃CN with 0.1 M tetrabutylammonium hexafluorophosphate $(n-C_4H_9)_4$ -NPF₆. The oxidation potential of D20 shows a quasireversible behavior at 0.31 V (versus Fc/Fc^+) with a peak separation of 0.09 V, which is attributed to the Ru^{III/II} redox couple and is in good agreement with the reported value of 0.38-0.40 V (versus Fc/Fc⁺) for a similar type of complex and N3 [18]. The separation between the cathodic and the anodic wave at a scan rate of 50 mV s⁻¹ is 250 mV. Dyes D21, D22, and D23 show a quasi-reversible couple at 0.32, 0.41, and 0.23 V, respectively, assigned to the metal-centered oxidation process. The Ru^{III/II} oxidation potential of dye D22 is more positive than those of dyes D20, D21, and D22. This implies the increased electron donating properties of ligands L1, L2, and L4, compared to that of L3. The reduction potentials of D20-D23 calculated from the oxidation potential and the E_{0-0} determined from the intersection of absorption and emission spectra are listed in Table 1. The excited state oxidation potential (E_{ox}^*) of the dyes (D20: -1.96 V versus Fc/Fc⁺, -1.29 V versus NHE; D21: -1.70 V versus Fc/Fc⁺, -1.03 V versus NHE; D22: -1.62 V versus Fc/Fc⁺, -0.95 V versus NHE; D23: -1.67 V versus Fc/Fc⁺, -1.02 V versus NHE) is much negative than the conduction band level of TiO₂ at

 Table 1

 Optical, redox and DSSC performance parameters of dyes

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Dye	$\lambda_{abs}^{a}/nm \ (\epsilon/dm^{3} \ M^{-1} \ cm^{-1})$	$E_{\rm ox}^{\ \ b}(\Delta E_{\rm p})$ (V)	$E_{0-0}^{c}(V)$	$E_{\text{LUMO}}^{d}(V)$	E_{LUMO} (V) vs. NHE	$J_{\rm sc}~({\rm mA~cm^{-2}})$	$V_{\rm oc}\left({ m V} ight)$	ff	η ^e (%)
D20	522 (10400)	0.31 (0.25)	2.27	-1.96	-1.29	13.31	0.64	0.68	5.81
D21	532 (9820)	0.32 (0.14)	2.02	-1.70	-1.03	9.32	0.65	0.73	4.40
D22	527 (11400)	0.41 (0.14)	2.03	-1.62	-0.95	8.79	0.67	0.69	4.09
D23	518 (5840)	0.23 (0.19)	1.92	-1.69	-1.02	6.45	0.63	0.73	2.98
N3	530 (14100)	0.38 (0.05)	2.03	-1.65	-0.98	13.13	0.73	0.66	6.32

^a Absorption spectra were measured in DMF solution.

^b Redox potential of dyes on TiO₂ was measured in CH₃CN with 0.1 M (*n*-C₄H₉)₄N-PF₆ with a scan rate of 50 mV s⁻¹ (vs. Fc/Fc⁺).

^c E_{0-0} was determined from intersection of absorption and emission spectra in DMF.

^d E_{LUMO} was calculated by $E_{\text{ox}} - E_{0-0}$.

^e Performances of DSSCs were measured with 0.18 cm² working area.

approximately -0.5 V versus NHE [18]. Therefore, the LUMO levels of these dyes D20–D23 are sufficiently negative to inject electrons into the conduction band of TiO₂.

2.3. Photovoltaic performance

Fig. 3 shows the typical photocurrent–voltage (J-V) curves of five DSSCs fabricated with TiO₂ films, which are anchored with N3, and D20–D23. The photovoltaic performances of the devices are listed in Table 1. Under standard global AM 1.5 solar condition, an overall conversion efficiency (η) of 5.81% was attained from the D20 sensitized cell with J_{sc} of 13.31 mA/cm², V_{oc} at 0.64 V, and ff of 0.68. Under the same conditions, we obtained η of 6.32% for the Ru(dcbpy)₂(NCS)₂/TiO₂ solar cell (short-circuit photocurrent density, $J_{sc} = 13.13 \text{ mA/cm}^2$; open-circuit photovoltage, $V_{oc} = 0.73 \text{ V}$; fill factor, ff = 0.66), indicating that η for the D20/TiO₂ solar cell is about0.5% inferior to that of the N3/TiO₂ solar cell.

By contrast, the D23 sensitized cell gave an overall efficiency (η) of 2.98% with low J_{sc} of 6.45 mA/cm². The low performance of the D23/TiO2 solar cell is due at least to the inefficient absorption of the dye. The J_{sc} enhancement of D20 relative to D23 can be correlated with the increased amount of dye molecules on TiO2. The amount of adsorbed dyes D20-D23 was determined by desorbing the dyes from the TiO₂ surfaces from the KOH $(3.5 \times 10^{-5} \text{ M})$ in ethanol. With use of molar absorptivities in Table 1, the moles of D20–D23 absorbed to their TiO_2 films of $0.5 \text{ cm} \times 0.5 \text{ cm} \times 10 \mu\text{m}$ are found to be 2.3×10^{-8} , 1.7×10^{-8} , 1.6×10^{-8} , and 1.1×10^{-8} mol, respectively. The low absorption of D23 can be interpreted to be due to the presence of a bulky porphyrin group. The bulky sensitizers require more space on the TiO₂ surface and penetrate less easily in the small cavities of the nanocrystalline TiO₂ than the sterically less hindered complexes. Contrary to a big chance of J_{sc} in the dyes D20–D23, the invariance of $V_{\rm oc}$ of the cells with the four sensitizers



Fig. 3. Photocurrent–voltage characteristics of representative TiO_2 electrodes sensitized with dyes: N3 (—), D20 (----), D21 (-----), D22 (-----), D23 (-----).

D20-D23 is ineffective for inducing self-organization near the surfaces of their TiO₂ nanoparticles, in a fashion facilitating the V_{oc} increase. It was well documented that the open-circuit photovoltage (Voc) of solar cells sensitized with ruthenium dyes increased when 4-tert-butylpyridine was added into an electrolyte because TBP is regarded as a blocking agent of reverse electron transfer and shifts the E_{cb} value more negatively [19]. We anticipated that the presence of pyridine moiety in D20-D21 increased the open-circuit voltage due to the suppression of the dark current at the semiconductor electrolyte injection. However, the open-circuit voltages of the dyes D20-D21 relative to those of D22-D23 were not increased. It demonstrates that the long alkyl chains with pyridine moiety in D20-D21 could not form hydrophobic layers around their corresponding TiO₂ particles. The formation of such a layer can reduce the back electron transfer from the conduction band of TiO₂ to the I_3^- ions in the electrolyte solution and thereby increase the $V_{\rm oc}$ [18d,20].

The incident monochromatic photon-to-current conversion efficiencies (IPCEs) for the DSSCs based on the five dyes are presented in Fig. 4. The IPCE data of D20 sensitizer plotted as a function of excitation wavelength exhibit a high plateau at 58%. The decline of the IPCE above 600 nm toward the red is caused by the decrease in the extinction coefficient of D20. In contrast, the DSSC based on D22 shows a relatively low IPCE with the maximum of 46% at 535 nm. The IPCE spectrum of D20 is red shifted by about 20 nm compared to the D22 as a result of increased amount of dye molecules on TiO₂. Therefore, the increased absorption coefficient of D22 relative to D20 does not necessarily lead to an enhanced light absorption on the TiO₂ electrode because of the reduced surface concentration of the bulkier dye on the nanoporous TiO₂.

In summary, we have synthesized new efficient dyes D20–D23 containing the chromophores such as cyanobiphenyl or porphyrin unit. The photovoltaic performance



Fig. 4. Typical action spectra of incident photon-to-current conversion efficiencies (IPCE) obtained for nanocrystalline TiO_2 solar cells sensitized by N3 (-----), D20 (-----), D21 (-----), D22 (-----).

of the solar cells sensitized with D20–D23 was compared with that of the N3-sensitized cell. A solar-to-electricity conversion efficiency of 5.81% in D20 is comparable to η of 6.32% for the N3/TiO₂ solar cell. However, the D23 sensitized cell gave an overall efficiency (η) of 2.98%. The low efficiency of D23 is correlated with lower absorption coefficient of this dye due to the decreased amount of dye molecules on TiO₂. Analysis of the absorption spectra of the dye-coated TiO₂ films and the desorbed dyes in an aqueous KOH solution indicates that D23 sensitizer was less absorbed to its TiO₂ films due to the presence of a bulky porphyrin group. By modulating the substituted group, we can design more efficient dyes for photovoltaic performance.

3. Experimental section

All reactions were carried out under an argon atmosphere. Solvents were distilled from appropriate reagents. 2,2'-Bipyridyl-4,4'-dicarboxylic acid was purchased from Strem. 4'-Hydroxy-4-biphenylcarbonitrile and 4-hydroxypyridine were purchased form Sigma-Aldrich. 4-(5-Bromopentyloxy)benzaldehyde [21], 4-(diethylphosphonomethyl)-4'-methyl-2,2'-bipyridine [22], 4,4'-bis(diethylphosphnomethyl)-2,2'-bipyridine [22] and zinc tetrakis-5, 10,15-tritolyl-20-(4-hydroxyphenyl)porphyrin [23] were synthesized using a modified procedure of previous references. ¹H and ¹³C NMR spectra were recorded on a Varian Mercury 300 spectrometer. The absorption and photoluminescence spectra were recorded on a Perkin-Elmer Lambda 2S UV-Vis spectrometer and a Perkin LS fluorescence spectrometer, respectively.

3.1. 4'-(4-(5-(Pyridin-4-yloxy)pentyloxy)styryl)-4-methyl-2,2'-bipyridine (L1)

A mixture of 4-(5-(pyridin-4-yloxy)pentyloxy)benzaldehyde (0.3 g, 1.1 mmol), 4-(diethylphosphonomethyl)-4'methyl-2,2'-bipyridine (0.3 g, 1.0 mmol), and potassium tert-butoxide (0.24 g, 2.1 mmol) was vacuum-dried and added to THF (40 mL). The solution was refluxed for 12 h. After cooling the solution, H₂O (50 mL) and methylene chloride (50 mL) were added. The organic layer was separated and dried with MgSO₄. The organic layer was removed in vacuo. The pure product L1 was obtained by silica gel chromatography (eluent; EA, $R_{\rm f} = 0.1$) to afford L1 (0.13 g) in 32% yield. Mp: 169 °C. ¹H NMR (CDCl₃): δ 8.61 (d, 1H, J = 5.4 Hz), 8.57 (d, 1H, J = 5.4 Hz), 8.49 (s, 1H), 8.42 (d, 2H, J = 6.6 Hz), 8.27 (s, 1H), 7.50 (d, 2H, J = 8.4 Hz), 7.41 (d, 1H, J = 16.2 Hz) 7.35 (d, 1H, J = 4.8 Hz), 7.16 (d, 1H, J = 4.8 Hz), 6.99 (d, 2H, J = 16.2 Hz) 6.92 (d, 2H, J = 8.4 Hz), 6.80 (d, 2H, J = 6.6 Hz), 4.04 (m, 4H), 2.45 (s, 3H), 1.89 (m, 4H), 1.67 (m, 2H). ${}^{13}C{}^{1}H{}$ NMR (CDCl₃): δ 165.1, 159.6, 156.7, 156.1, 151.2, 149.6, 149.1, 148.3, 146.2, 132.9, 129.1, 128.6, 124.9, 124.0, 122.1, 120.9, 118.1, 114.9, 110.4, 67.8, 67.7, 29.0, 28.8, 22.8, 21.3. MS: m/z 451

 $[M^+]$. *Anal.* Calc. for $C_{29}H_{29}N_3O_2$: C, 77.13; H, 6.47. Found: C, 76.86; H, 6.35%.

3.2. 4,4'-Bis((E)-4-(5-(pyridin-4-yloxy)pentyloxy)styryl)-2,2'-bipyridine (L2)

A mixture of 4-(5-(pyridin-4-yloxy)pentyloxy)benzaldehyde (0.48 g, 2.2 mmol), 4,4'-bis(diethylphosphonomethyl)-2,2'-bipyridine (0.45 g, 1.0 mmol), and potassium tert-butoxide (0.48 g, 4.2 mmol) was vacuum-dried and added to THF (60 mL). The solution was refluxed for 12 h. After cooling the solution, H₂O (50 mL) and methylene chloride (50 mL) were added. The organic layer was separated and dried with MgSO₄. The organic layer was removed in vacuo. The pure product L2 was obtained by silica gel chromatography (eluent; acetone, $R_{\rm f} = 0.1$) to afford L2 (0.21 g) in 30% yield. Mp: 174 °C. ¹H NMR $(CDCl_3)$: δ 8.64 (d, 2H, J = 5.4 Hz), 8.52 (s, 2H), 8.42 (d, 4H, J = 4.8 Hz), 7.50 (d, 4H, J = 7.8 Hz), 7.41 (d, 2H, J = 16.2 Hz) 7.36 (d, 2H, J = 5.4 Hz), 6.99 (d, 2H, J = 16.2 Hz), 6.91 (d, 4H, J = 7.8 Hz), 6.79 (d, 4H, J = 4.8 Hz), 4.04 (m, 8H), 1.88 (m, 8H), 1.67 (m, 4H). ¹³C{¹H} NMR (CDCl₃): δ 165.1, 159.7, 156.6, 151.1, 149.6, 146.2, 133.0, 129.1, 128.5, 124.0, 121.0, 118.1, 114.9, 110.4, 67.8, 67.7, 29.0, 28.8, 22.8. MS: m/z 718 $[M^+]$. Anal. Calc. for C₄₆H₄₆N₄O₄: C, 76.85; H, 6.45. Found: C, 76.59; H, 6.32%.

3.3. 4'-(4-(5-(4'-Cyano-4-biphenoxy)pentyloxy)styryl)-4methyl-2, 2'-bipyridine (L3)

Potassium tert-butoxide (0.20 g, 1.8 mmol) was added to a solution of 4-(5-(4'-cyano-4-biphenoxy)pentyloxy)benzaldehyde (0.5 g, 1.29 mmol) and 4-(diethylphosphonomethyl)-4'-methyl-2,2'-bipyridine (0.41 g, 1.29 mmol) in THF (30 mL). The reaction mixture was stirred for 10 h at room temperature. After addition of water (10 mL), THF was removed under reduced pressure, and the aqueous residue was extracted with CH₂Cl₂ (50 mL). The collected organic layer was washed with water (50 mL), dried over magnesium sulfate, and filtered. The solvent was removed in vacuo. The pure product L3 was obtained by chromatographic work-up (eluent; EA, $R_{\rm f} = 0.3$) as a yellow solid in 70% yield. Mp: 117 °C. ¹H NMR (CDCl₃): δ 8.60 (d, J = 5.1 Hz, 1H), 8.56 (d, J = 5.1 Hz, 1H), 8.48 (s, 1H), 8.26 (s, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.61 (d, J =8.1 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 16.2 Hz, 1H), 7.32 (d, J = 4.8 Hz, 1H), 7.14 (d, J = 4.8 Hz, 1H), 6.98 (d, J = 8.1 Hz, 2H), 6.96 (d, J = 16.2 Hz, 1H), 6.91 (d, J = 8.7 Hz, 2H), 4.03 (m, 4H), 2.43 (s, 3H), 1.89 (m, 2H), 1.70 (m, 2H), 1.24 (m, 2H). ¹³C{¹H} NMR (CDCl₃): δ 191.0, 164.2, 159.8, 157.0, 156.3, 149.5, 148.7, 146.5, 145.3, 132.7, 132.1, 131.5, 128.6, 128.4, 127.1, 125.0, 123.7, 122.5, 121.6, 121.1, 119.2, 116.2, 114.8, 110.1, 68.2, 67.9, 29.0, 27.2, 24.9, 22.8. MS: m/z 551 [M⁺]. Anal. Calc. for C₃₇H₃₃N₃O₂: C, 80.55; H, 6.03. Found: C, 80.12; H, 5.98%.

3.4. 4'-(4-(5-(Zinc tetrakis-5,10,15-tritolyl-20-(4hydroxyphenyl)porphyrin) pentyloxy)styryl)-4-methyl-2,2'bipyridine (L4)

A mixture of 4-(5-(zinc tetrakis-5.10.15-tritolyl-20-(4hydroxyphenyl)porphyrin)pentyloxy)benzaldehyde (0.26 g, 0.28 mmol), 4-(diethylphosphonomethyl)-4'-methyl-2,2'bipyridine (0.1 g, 0.31 mmol), and potassium tert--butoxide (0.04 g, 0.31 mmol) was vacuum-dried and added to THF (30 mL). The solution was refluxed for 12 h. After cooling the solution, $H_2O(50 \text{ mL})$ and methylene chloride (50 mL) were added. The organic layer was separated and dried with MgSO₄. The organic layer was removed in vacuo. The pure product L4 was obtained by silica gel chromatography (eluent; EA, $R_f = 0.1$) to afford L4 (0.1 g) in 33% yield. Mp: 193 °C. ¹H NMR (CDCl₃): δ 8.99 (s, 8H), 8.53 (d, 1H, J = 4.80 Hz), 8.48 (d, 1H, J = 4.80 Hz), 8.39 (s, 1H), 8.19 (s, 1H), 8.11 (d, 8H, J = 7.80 Hz), 7.55 (d, 6H, J = 7.80 Hz), 7. 48 (d, 2H, J = 8.70 Hz), 7.37 (d, 1H, J = 16.2 Hz) 7.27 (d, 1H, J = 4.80 Hz), 7. 25 (d, 2H, J = 7.80 Hz), 7.11 (d, 1H, J = 4.80 Hz), 6.93 (d, 1H, J =16.2 Hz), 6.92 (d, 2H, J = 8.70 Hz), 4.25 (t, 2H), 4.07 (t, 2H), 2.71 (s, 9H), 2.43 (s, 3H), 2.00 (m, 4H), 1.82 (m, 2H). ¹³C{¹H} NMR (CDCl₃): δ 159.77, 158.77, 156.62, 155.89, 150.61, 150.41, 149.54, 148.97, 148.03, 146.05, 140.10, 137.17, 135.57, 135.36, 134.52, 133.14, 132.02, 129.05, 128.57, 127.41, 124.82, 123.88, 122.17, 121.19, 120.92, 118.10, 115.01, 112.70, 68.11, 68.06, 29.36, 29.19, 23.03, 21.68, 21.34. MS: m/z 1090 [M⁺]. Anal. Calc. for C₇₁H₅₈N₆O₂Zn: C, 78.05; H, 5.35. Found: C, 77.87; H, 5.26%.

3.5. Synthesis of $[Ru(L1)(L)(NCS)_2]$ (D20)

A mixture of $[{RuCl_2(p-cymene)}_2](0.095 \text{ g}, 0.16 \text{ mmol})$ and L1 (0.14 g, 0.31 mmol) was vacuum-dried and added to DMF (30 mL). The reaction mixture was heated at 80 °C under nitrogen for 4 h and then, 2,2'-bipyridyl-4,4'dicarboxylic acid (L) (0.075 g, 0.31 mmol) was added to the solution. The reaction mixture was refluxed at 160 °C for another 4 h under dark condition to avoid light induced cis to trans isomerisation. Then an excess of NH₄NCS (1.86 mmol) was added to the reaction mixture and heated at 130 °C for further 5 h. The solvent was removed using a rotary-evaporator under vacuum. Water was added to the resulting semisolid to remove excess NH₄NCS. The waterinsoluble product was collected on a sintered glass crucible by suction filtration and washed with distilled water, followed by diethyl ether and dried. The crude complex was dissolved in a solution of tetrabutyl ammonium hydroxide (0.4 g) in methanol (4 mL). The concentrated solution was charged onto a Sephadex LH-20 $(2 \times 30 \text{ cm})$ column and eluted with methanol. The main red band was collected and concentrated to 3 mL. The pure complex was isolated upon addition of a few drops of 0.01 M HNO₃. Yield = 0.073 g (52%). ¹H NMR (DMSO): δ 9.43 (d, 1H), 9.16 (d, 1H), 8.99 (s, 1H), 8.91 (d, 1H), 8.85 (s, 1H), δ 8.69 (d, 1H, J = 5.4 Hz), 8.60 (d, 1H, J = 5.4 Hz), 8.54 (s, 1H), 8.43 (d, 2H, J = 6.6 Hz), 8.36 (d, 2H), 8.27 (s, 1H), 7.58 (d, 2H, J = 8.4 Hz), 7.40 (d, 1H, J = 16.2 Hz) 7.36 (dd, 1H), 7.13 (dd, 1H), 7.06 (d, 2H, J = 16.2 Hz) 6.99 (d, 2H, J = 8.4 Hz), 6.90 (d, 2H, J = 6.6 Hz), 4.07 (m, 4H), 2.49 (s, 3H), 1.80 (m, 4H), 1.57 (m, 2H). MS: m/z 913 [M⁺]. *Anal.* Calc. for C₄₃H₃₇N₇O₆RuS₂: C, 56.57; H, 4.08; N, 10.74. Found: C, 56.39; H, 4.01; N, 10.50%.

3.6. Synthesis of $[Ru(L2)(L)(NCS)_2]$ (D21)

Complex D21 was synthesized by a procedure similar to D20 except that L2 (0.3 g, 0.417 mmol) was used in place of L1. Yield = 0.106 g, 43%. ¹H NMR (DMSO): δ 9.43 (d, 1H), 9.14 (d, 1H), 8.98 (s, 1H), 8.92 (s, 1H), 8.85 (d, 1H), 8.64 (d, 2H, J = 5.4 Hz), 8.56 (s, 2H), 8.47 (d, 4H, J = 4.8 Hz), 7.59 (d, 4H, J = 7.8 Hz), 7.50 (d, 2H, J = 16.2 Hz) 7.40 (d, 2H, J = 5.4 Hz), 7.01 (d, 2H, J = 16.2 Hz), 6.90 (d, 4H, J = 7.8 Hz), 6.77 (d, 4H, J = 4.8 Hz), 4.08 (m, 8H), 1.78 (m, 8H), 1.54 (m, 4H). MS: m/z 1180 [M⁺]. Anal. Calc. for C₆₀H₅₄N₈O₈RuS₂: C, 61.05; H, 4.01; N, 9.49. Found: C, 60.98; H, 3.96; N, 9.28%.

3.7. Synthesis of $[Ru(L3)(L)(NCS)_2]$ (D22)

Complex D22 was synthesized by a procedure similar to D20 except that L3 (0.15 g, 0.27 mmol) was used in place of L1. Yield = 0.071 g, 54%. ¹H NMR (DMSO): δ 9.28 (d, 1H), 9.20 (d, 1H), 8.81 (s, 1H), 8.72 (s, 1H), 8.67 (d, J = 5.1 Hz, 1H), 8.60 (d, J = 5.1 Hz, 1H), 8.52 (s, 1H), 8.34 (s, 1H), 8.24 (d, 1H), 8.13 (d, 1H), 7.78 (d, J = 4.2 Hz, 1H), 7.69 (d, J = 4.8 Hz, 1H), 7.66 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.7 Hz, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 16.2 Hz, 1H), 6.98 (d, J = 8.1 Hz, 2H), 4.06 (m, 4H), 2.41 (s, 3H), 1.83 (m, 2H), 1.65 (m, 2H), 1.24 (m, 2H). MS: m/z 1013 [M⁺]. Anal. Calc. for C₅₁H₄₁N₇O₆RuS₂: C, 60.46; H, 4.08; N, 9.68. Found: C, 60.12; H, 4.00; N, 9.47%.

3.8. Synthesis of $[Ru(L4)(L)(NCS)_2]$ (D23)

Complex D23 was synthesized by a procedure similar to D20 except that L4 (0.18 g, 0.165 mmol) was used in place of L1. Yield = 0.072 g, 56%. ¹H NMR (DMSO): δ 9.42 (d, 1H), 9.12 (d, 1H), 8.96 (s, 1H), 8.83 (s, 1H), 8.82 (d, 1H), 8.76 (s, 8H), 8.60 (d, 1H, J = 4.8 Hz), 8.53 (d, 1H, J = 4.8 Hz), 8.38 (d, 1H), 8.36 (s, 1H), 8.21 (s, 1H), 8.05 (d, 8H, J = 7.8 Hz), 7.75 (d, 1H), 7.59 (d, 6H, J = 7.8 Hz), 7.50 (d, 2H, J = 8.7 Hz), 7.34 (d, 1H, J = 16.2 Hz) 7.26 (d, 1H, J = 4.8 Hz), 6.91 (d, 1H, J = 16.2 Hz), 6.85 (d, 2H, J = 8.7 Hz), 4.28 (t, 2H), 4.04 (t, 2H), 2.66 (s, 9H), 2.40 (s, 3H), 1.74 (m, 2H), 1.57 (m, 2H). MS: m/z 1552 [M⁺]. Anal. Calc. for C₈₅H₆₆N₁₀O₆Ru S₂Zn: C, 65.69; H, 4.28; N, 9.01. Found: C, 65.39; H, 4.19; N, 8.83%.

3.9. Fabrication of sandwich type cells

For the preparation of DSSC, the washed FTO (Pilkington, 8 Ω sq⁻¹, 2.3 mm thickness) glass plate was immersed in 40 mM TiCl₄ aqueous solution at 60 °C for 30 min and washed with water and ethanol as reported by the Grätzel group [14]. A transparent nanocrystalline layer on the FTO glass plate was prepared by screen printing TiO₂ paste (Solaronix, 13 nm anatase) and was sintered at 450 °C for 30 min. And then, a paste for the scattering layer (Solaronix, 300 nm, anatase) was coated on the transparent layer and was again sintered at 450 °C for 30 min. The resulted laver was composed of 15 µm thickness of transparent layer and 5 µm thickness of scattering layer. The TiO₂ electrode was immersed into the dye solution (0.3 mM dye in ethanol containing 10 mM) and kept at room temperature for 18 h. Counter electrode was prepared by coating with a drop of H₂PtCl₆ solution (2 mg Pt in 1 mL ethanol) on a FTO plate and heated at 400 °C for 15 min. The dye adsorbed TiO₂ electrode and Pt-counter electrode were assembled into a sealed sandwich type cell by heating with a Surlyn film (25 µm thickness, Du-Pont) as a spacer between the electrode. The electrolyte was then introduced into the cell, which was composed of 0.6 M 3-hexyl-1,2dimethyl imidazolium iodide, 0.04 M iodine, 0.025 M LiI, 0.05 M guanidium thiocyanate and 0.28 M tert-butylpyridine in acetonitrile. The DSSCs were characterized for their photoelectrochemical characteristics using a Keithley 2400 source measure unit. A 300 W solar simulator (Model: 69920, Newport-Oriel Instruments, Stratford, CT, USA) was used as a light source. The light intensity was adjusted using a Si solar cell. IPCE values were measured using a system by PV Measurement, Inc.

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