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Introduction

Dye-sensitized solar cells (DSCs) provide an appealing alternative to the conventional solid-state cells.¹ This is mainly due to their ability to function indoors and under low light conditions, their potential transparency and flexibility, their invariant efficiency with the operating temperature, and their relatively low production cost.² A DSC device is comprised of two facing electrodes: the photoanode, which is transparent, consists of a thin nanoparticulate film of a mesoporous large band gap semiconductor deposited on conductive glass. A monolayer of sensitizer (dye) molecules is chemically grafted onto the semiconductor through anchoring functionalities such as carboxylic or phosphonic acids. An electrolyte containing a redox couple is placed between the photoelectrode and the cathode, typically comprised of platinum deposited onto conductive glass, to transfer the charges.

Novel Ru(μ) sensitizers bearing an unsymmetrical pyridine-quinoline hybrid ligand with extended π -conjugation: synthesis and application in dye-sensitized solar cells

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Heteroleptic ruthenium(II) sensitizers **DV42** and **DV51**, encompassing a novel unsymmetrical pyridinequinoline hybrid ligand with extended π -conjugation, were synthesized, characterized, and utilized in nanocrystalline dye-sensitized solar cells. Due to the extended conjugation of **DV42** and **DV51**, the absorption of the corresponding sensitized TiO₂ films extends into the red spectral range, shifted by 30–40 nm relative to the absorption of TiO₂ films sensitized with the standard **Z907** ruthenium(II) dye. Contact angle measurements of **DV42**- and **DV51**-sensitized TiO₂ films suggest that these films are hydrophilic with contact angle values commonly observed upon sensitization with the standard **N3** ruthenium(II) dye. Electrochemical studies of the novel ruthenium(II) dyes show that their first oxidation potentials lie well below the I⁻/I₃⁻ redox potential allowing easy regeneration. The excited-state oxidation potentials of both dyes lie above the TiO₂ conduction band, permitting efficient electron injection from the excited dye molecules into the semiconductor conduction band. Liquid electrolyte dyesensitized solar cells incorporating **DV42**- or **DV51**-sensitized TiO₂ photoelectrodes afford overall power conversion efficiencies of 3.24 or 4.36% respectively. These efficiencies are up to 56% of the power conversion efficiencies attained by TiO₂ photoelectrodes sensitized by the benchmark **Z907** ruthenium(II) dye under similar experimental conditions.

> The dye, which is the heart of the DSC device, undergoes transition from its ground to its excited state upon light absorption. One electron is then injected from the dye into the conduction band of the semiconductor, resulting in an oxidized dye molecule. Ideally, the photoinjected electrons percolate through the nanoparticulate network and get collected at the back contact. They subsequently flow through the external circuit performing useful work and eventually arrive at the counter electrode. The oxidized dye is regenerated to its ground state by taking an electron from the redox couple, which is in turn reduced at the counter electrode completing the circuit. The device maximum voltage (V_{max}) that can be generated equals the difference between the semiconductor Fermi level and the electron mediator species' redox potential. The result of this regenerative cycle is the conversion of photons to electrons, while no chemical species undergo permanent transformations.

> Charge generation, *i.e.*, the injection of an electron from the dye into the conduction band of the semiconductor, is one of the most important steps in the DSC photoelectrochemical cycle. The "ideal" dye has to fulfill a variety of photophysical,

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structural, and electrochemical requirements: (i) a broad, strong absorption extending from the visible to the near-infrared; (ii) chemical stability in its ground, excited, and oxidized states; (iii) its excited state should not be deactivated through the emission of heat or light; (iv) an irreversible adsorption onto the surface of the semiconductor; (v) a strong electronic coupling between its excited state and the semiconductor's conduction band to ensure efficient electron injection; (vi) an excited-state oxidation potential sufficiently higher (by about 150–200 mV)³ than the semiconductor conduction band edge in order to result in an effective electron injection; and (vii) a ground-state reduction potential sufficiently lower (by about 200–300 mV)³ than the redox potential of the electron mediator species, in order to be regenerated rapidly.

Although many different compounds have been utilized as sensitizers in DSC applications,² Ru(II) polypyridyl complexes comprise the most successful family of DSC dyes in terms of both photovoltaic performance and long-term stability. N3 and N719 (Fig. 1) were the first high performance Ru(II) sensitizers to be reported.⁴ N3 and N719, which differ only in their protonation state, afford a very high conversion of incident photons into electric current over a large spectral range, giving DSCs with overall power conversion efficiencies of 10.0% and 11.2% respectively. The higher power conversion efficiency of N719, when compared to the tetra-protonated parent dye N3, originates from the increased cell voltage. The structural finetuning of these early Ru(II) polypyridyl dyes has led to even more efficient sensitizers with amphiphilic properties and extended conjugation that achieve power conversion efficiencies up to 12.3%. Thus, CYC-B1 (Fig. 1), reported in 2006, bears a highly conjugated ligand substituted with alkyl bithiophene groups.5 The overall power conversion efficiency of CYC-B1 was reported to be 8.5%, 10% higher than that of N3 under the same cell fabrication and measuring conditions. Z991, the mono(tetrabutylammonium) salt of CYC-B1 (Fig. 1), holds the 12.3% DSC power conversion efficiency record. This was achieved with phosphinate amphiphile dineohexyl bis-(3,3-dimethyl-butyl)-phosphinic acid (DINHOP) as the coadsorbent.6

The structural and photoelectrochemical properties of a $Ru(\pi)$ polypyridyl dye and, therefore, its efficiency in a DSC are dictated by the coordinated ligands. As part of our ongoing work in the development of novel $Ru(\pi)$ photosensitizers for



Fig. 1 Molecular structures of Ru(11) polypyridyl dyes N3, N719, CYC-B1, and Z991.



Fig. 2 Ru(μ) dyes **DV42** and **DV51** bearing a novel bidentate pyridine-quino-line hybrid ligand with extended aromatic conjugation.

DSC applications,⁷ we herein report the synthesis, characterization, and sensitizing ability evaluation of two new Ru(π) dyes (**DV42** and **DV51**, Fig. 2). **DV42** and **DV51** bear a novel pyridine-quinoline hybrid ligand with extended aromatic conjugation. The unsymmetrical, bidentate pyridine-quinoline ligand in **DV42** and **DV51** was designed with a long aromatic moiety. This novel architecture should facilitate an increased extinction coefficient of the main metal-to-ligand charge transfer (MLCT) band of its Ru(π) complexes and an increased response to red light in the corresponding sensitized TiO₂ electrodes.^{5,8} Moreover, this ligand scaffold was constructed in order to enable the detailed study of the influence of exceedingly long aromatic moieties on the hydrophobicity and wettability of the corresponding Ru(π) polypyridyl dyes.

Experimental

Materials

Unless otherwise stated, all reagents were purchased from Aldrich. Solvents were purchased from Fluka or Panreac and used without further purification. A dichloro(p-cymene)ruthenium(II) dimer was purchased from Alfa Aesar. 2,2'-Bipyridine-4,4'-dicarboxylic acid (H2dcbpy) was obtained from Dyesol. Acetonitrile, used in the electrochemical studies, was degassed by a freeze-pump-thaw cycle and stirred overnight over P_2O_5 , at room temperature, under an argon atmosphere. It was then distilled under argon and degassed again via another freezepump-thaw cycle, before being stored over activated 4 Å molecular sieves. DMF, used in the electrochemical studies, was degassed by a freeze-pump-thaw cycle and stirred overnight over activated MgSO₄, at room temperature, under an argon atmosphere. A further quantity of activated MgSO4 was added and DMF was then distilled under reduced pressure, before being stored over activated 4 Å molecular sieves. All synthetic reactions were performed under an argon atmosphere in degassed (15 min of argon bubbling) solvents. cis-Diisothiocyanato-(2,2'bipyridyl-4,4'-dicarboxylic acid)-(4,4'-dinonyl-2,2'-bipyridine)ruthenium(π) dye (**Z907**, Fig. 3) was purchased from Dyesol.



Fig. 3 Ru(n) complex **Z907** was utilized as a benchmark dye in the present study.

Analytical measurements

¹H, ¹³C, HSOC, and COSY Nuclear Magnetic Resonance (NMR) spectra were obtained with a Bruker Avance 500 MHz spectrometer in (CD₃)₂SO or CDCl₃. Chemical shifts are reported in ppm downfield from Me₄Si, by using the residual solvent peak as an internal standard. Data for NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, and integration. Electronic spectra (UV-vis) in solution $[5 \times 10^{-5} \text{ M in ethanol}]$ (DV51 and Z907) or DMF (DV42)] were recorded with a Hitachi 3010 spectrophotometer in standard 1 cm path length cuvettes. Diffuse reflectance (R%) and transmittance (T%) UV-vis spectra of the dye-sensitized TiO₂ films (for this purpose one layer of a transparent Dyesol paste was doctor-bladed onto microscopy glass) were obtained on the same instrument using an integrating sphere with 60 mm diameter and were transformed in absorbance (A%) units (A% = 100 - R% - T%). Infrared spectra (FTIR) in the powder form were obtained using an FTIR Nicolet 6700 spectrometer. Data for FTIR spectra are reported as follows: frequency (cm⁻¹) and strength (s = strong; m = medium; w = weak). Despite our repeated attempts, we were unable to get reliable Elemental Analysis data for the newly synthesized complexes, possibly due to insufficient combustion. High Resolution Mass Spectra (HRMS) were recorded using a Bruker Daltonics APEXIV 4.7 Tesla Fourier Transform Ion Cyclotron Resonance Mass spectrometer. Micro-Raman spectra were measured in the backscattering configuration using a Renishaw inVia spectrometer with an excitation at 514.5 nm by an Ar⁺ ion laser. In all cases, very low laser power density (0.01 mW μ m⁻²) was applied in order to avoid dye degradation and thermal shifts of the modes. The advancing contact angle of water droplets on the films was measured with a Contact Angle Meter (CAM) 100, KSV Instruments, Ltd, equipped with a horizontal microscope and a protractor eyepiece. Cyclic voltammetry measurements were performed in 10⁻³ M solutions of the corresponding complexes in acetonitrile (DV42) or DMF (DV51) containing 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as a supporting electrolyte, at a sweep rate of 100 mV s⁻¹, using the Autolab PGSTAT-30 potentiostat (Ecochemie). A three-electrode, one-compartment electrochemical cell was used, with Metrohm dot (6.0302.000) and planar (6.0305.000) platinum working and counter electrodes, respectively, as well as a Metrohm Ag/AgCl 6.0726.100 reference electrode (LiCl saturated in EtOH). The experiments were performed in

deoxygenated solutions purified by N_2 gas (99.9%) for 30 min prior to use. During the experiments, N_2 was passed over the solution surface.

Electrodes preparation and devices assembly-characterization

Titania films were prepared using the doctor-blade technique by depositing one transparent layer (7-8 µm, measured with an AMBIOS XP-2 profilometer) of a commercial paste (DSL18NR-T, Dyesol) onto a pre-cleaned fluorine-doped tin oxide (FTO) conductive glass (Pilkington Solar, 3.2 mm thickness). The DSL18NR-T paste solely consists of anatase particles and elongated nanorods with an average size of 17 nm, while its pore size distribution is wide, presenting a maximum at 30 nm. The films were then dried at 125 °C for 6 minutes. A second layer (4.5-5.0 µm) was deposited on top by doctorblading a paste of large scattering particles (WER2-O, average size of cubic-like particles: 150-250 nm, Dyesol). Next, the films were gradually annealed at 125 °C (5 min), 325 °C (15 min) and then at 525 °C for 30 min. The double layered films were post-treated at 70 °C for 60 min with an aqueous solution of 0.04 M TiCl₄, then thoroughly cleaned with water and ethanol and re-annealed at 450 °C for 1 h. The thermallytreated titania films were sensitized by overnight immersion in 0.3 mM dye solutions. The solvents utilized were DMF for DV42, ethanol for DV51, and acetonitrile/tert-butanol for Z907. In the case of **Z907** the corresponding solution also contained an equimolar quantity of chenodeoxycholic acid as a coadsorbent.

In order to evaluate their photovoltaic performance, the dye-sensitized films were incorporated as the active photoelectrode (PE) in a lamellar solar cell configuration of the following structure: conductive glass/TiO₂ + dye/electrolyte/Pt/conductive glass. 1.1 mm thick TCO10-10 conductive glasses (Solaronix), platinized by sputtering (resulting in a thickness for the Pt layer of about 100 nm), were used as counter electrodes (CE). Non-sealed DSCs were fabricated by placing a drop of a liquid electrolyte (1.0 M 1,3-dimethylimidazolium iodide, 50 mM LiI, 15 mM I₂, 0.5 M *tert*-butylpyridine, and 0.1 M guanidinium thiocyanate dissolved in acetonitrile-valeronitrile (85:15)) onto the photoelectrode and sandwiching the CE on top of the PE.

Current-voltage (I-V) measurements were performed by illuminating the DSCs using solar-simulated light (1 sun AM 1.5 G, 1000 W m⁻²), from a 300 W Xe lamp. Illumination under 400 nm was excluded using a cut-off UV filter (Oriel). The active area of the DSCs was set at 0.15 cm², using a black metallic mask of very large area to exclude parasitic light in front of the cell (while the aperture area was larger, 0.36 cm²).⁹ I-V characteristics were obtained using linear sweep voltammetry (scan speed: 50 mV s⁻¹) on an Autolab PGSTAT-30 potentiostat.

Synthesis

Synthesis of 6-bromo-4-phenyl-2-pyridin-2-ylquinoline (1).¹⁰ In a round-bottomed flask equipped with a reflux condenser and a magnetic stirrer under an argon atmosphere

were added 2-amino-5-bromobenzophenone (5.5 g, 20.0 mmol), acetic acid (20 mL), and H_2SO_4 (98%, 0.1 mL), along with an excess of 2-acetylpyridine (4.5 mL, 40.0 mmol). This reaction mixture was heated at 110 °C under stirring for 48 h. Upon cooling to room temperature, a needle-like solid precipitated from the resulting reaction mixture. This was filtered and washed repeatedly with hot water and methanol. Subsequent drying under vacuum afforded **1** (6.5 g, 90%). ¹H NMR (CDCl₃, 500 MHz): δ 8.72 (d, 1H), 8.67 (d, 1H), 8.54 (s, 1H), 8.11 (d, 1H), 8.08 (d, 1H), 7.87 (t, 1H), 7.80 (dd, 1H), 7.49–7.56 (m, 5H), 7.36 (t, 1H).

Synthesis of 4-phenyl-2-pyridin-2-yl-6-(4-vinyl-phenyl)-quinoline (3). In a degassed three-necked flask equipped with a reflux condenser and a magnetic stirrer were added 1 (4.0 g, 11.0 mmol), (4-vinylphenyl)boronic acid (4.5 g, 22.0 mmol), and Pd(PPh₃)₄ (0.63 g, 0.55 mmol). To this flask were then added degassed toluene (200 mL) and a degassed 2 M aqueous solution of Na₂CO₃ (50 mL). The mixture was heated under reflux and vigorously stirred for 48 h. After cooling to room temperature, the resulting mixture was filtered and the organic layer was separated, washed with H_2O (3 × 50 mL), and evaporated under reduced pressure. The obtained solid was suspended in methanol and filtered to afford a pale white solid. Drying under vacuum resulted in the final product 3 (3.4 g, 80%). ¹H NMR (CDCl₃, 500 MHz): δ 8.71 (m, 2H), 8.59 (s, 1H), 8.29 (d, 1H), 8.14 (s, 1H), 8.01 (d, 1H), 7.88 (t, 1H), 7.46-7.64 (m, 9H), 7.35 (t, 1H), 6.75 (dd, 1H), 5.81 (d, 1H), 5.27 (d, 1H).

Synthesis of 6-{4-[(*E*)-2-(9-anthryl)vinyl]phenyl}-4-phenyl-2pyridin-2-ylquinoline (LP1). In a two-necked round-bottomed flask equipped with a reflux condenser and a magnetic stirrer, under an argon atmosphere, were added 3 (1.50 g, 3.90 mmol), an excess of 9-bromoanthracene (1.51 g, 5.87 mmol), Pd(OAc)₂ (18 mg, 71.3 µmol), and tris(3-methylphenyl)phosphine (72 mg, 235 µmol). DMF (45 mL) along with Et₃N (6 mL) were then added and the system was carefully degassed again. The reaction mixture was heated under reflux for 72 h and after cooling to room temperature was poured into a mixture of crushed ice and water (500 mL). A yellowish solid started to form immediately. This mixture was filtered and repeatedly washed with water to remove any excess of solvents. The solid crude product was vigorously stirred for 24 h in ethanol and filtered again. Crude LP1, obtained after drying under reduced pressure at 50 °C for 24 h, was redissolved in the minimum amount of DMF and precipitated with H₂O to afford ligand LP1 as a yellow powder (1.31 g, 60%). ¹H NMR (CDCl₃, 500 MHz): δ 8.88 (s, 1H), 8.80 (d, 1H), 8.65 (s, 1H), 8.50 (s, 1H), 8.41-8.39 (m, 2H), 8.27 (s, 1H), 8.15 (d, 1H), 8.08-8.04 (m, 2H), 8.00-7.98 (m, 2H), 7.81-7.76 (m, 5H), 7.73-7.71 (m, 2H), 7.64-7.58 (m, 3H), 7.54-7.50 (m, 4H), 7.46-7.44 (m, 1H), 7.03 (d, 1H). ${}^{13}C{}^{1}H$ NMR (CDCl₃, 125 MHz): δ 156.36, 155.65, 149.41, 149.22, 148.05, 140.14, 138.92, 138.38, 136.99, 136.71, 131.54, 130.81, 129.72, 128.88, 128.74, 128.64, 128.46, 127.84, 127.15, 126.59, 125.96, 125.56, 125.33, 125.22, 124.09, 123.48, 121.92, 119.78. FTIR ν_{max} (cm⁻¹) 1673.9 (w), 1587.1 (m), 1546.6 (w), 1488.8 (m), 1469.5 (m), 1440.6 (m), 1361.5 (m), 1257.4 (w), 1072.2 (w), 977.8 (w), 966.2 (w), 887.1 (m), 833.1 (m), 798.4

(m), 783.0 (m), 730.9 (s), 698.1 (s), 617.1 (m), 590.1 (m), 520.7 (m), 424.3 (w). Anal. Calcd for $C_{42}H_{28}N_2$: C, 89.97; H, 5.03; N, 5.00. Found: C, 89.98; H, 5.06; N, 4.96.

Synthesis of *cis*-[Ru(LP1)(H₂dcbpy)Cl₂] (DV42). A twonecked 50 mL round-bottomed flask, equipped with a stirring bar and a reflux condenser, was charged with [RuCl-(p-cymene)]₂ (76.5 mg, 0.125 mmol), LP1 (140.2 mg, 0.250 mmol), and degassed DMF (35 mL) at room temperature under argon. The reaction mixture was heated in the dark at 60 °C for 4 hours. H₂dcbpy (61.1 mg, 0.250 mmol) was then added and the reaction mixture was heated in the dark under argon at 140 °C for 4 hours. This solution was cooled to room temperature with a water bath, and DMF was removed on a rotary evaporator. The resulting black solid was taken up and washed on a G4 sintered glass crucible with Et_2O (3 × 10 mL), EtOH (6 \times 5 mL), and again Et₂O (3 \times 5 mL). The remaining black powder was dissolved in the minimum amount of DMF, precipitated with Et₂O and washed on a G4 sintered glass crucible with Et_2O (5 × 10 mL), to afford complex DV42 as a black powder that was dried overnight under high vacuum (178 mg, 73%). ¹H NMR (DMSO-d₆, 500 MHz, due to the existence of two diastereoisomeric pairs of enantiomers, each having twenty six diastereotopic protons in the aromatic region, proton signals cannot be fully assigned and integrations are not given): δ 10.42 (d), 10.21 (d), 10.11 (s), 10.10 (s), 10.05 (d), 9.89 (d), 9.47 (d), 9.25-9.11 (m), 9.08 (s), 8.98-8.93 (m), 8.90 (s), 8.72 (s), 8.67 (s), 8.61-8.59 (m), 8.38-8.13 (m), 8.00-7.51 (m), 7.24 (d), 7.19–7.17 (m), 7.08–6.94 (m), 6.78 (d). ${}^{13}C{}^{1}H{}$ NMR (DMSO-d₆, 125 MHz): δ 165.83, 165.71, 165.60, 165.34, 165.11, 162.33, 162.16, 161.50, 161.30, 160.61, -159.93, 159.27, 158.76, 158.06, 155.35, 154.56, 154.39, 153.84, 153.58, 153.09, 153.04, 152.10, 147.72, 146.89, 146.79, 137.02, 136.76, 136.22, 135.88, 135.52, 132.11, 132.06, 130.93, 130.34, 129.46, 129.16, 128.92, 128.21, 128.15, 127.96, 127.92, 126.91, 126.69, 126.62, 126.42, 126.13, 125.93, 125.65, 125.11, 124.84, 124.62, 123.74, 123.48, 122.61, 121.25, 120.38. FTIR ν_{max} (cm⁻¹) 1710.6 (m), 1598.7 (m), 1477.2 (m), 1403.9 (w), 1249.7 (s), 1211.1 (s), 1184.1 (s), 1137.8 (m), 1062.6 (w), 931.5 (m), 885.2 (s), 827.3 (s), 781.0 (s), 759.8 (s), 734.8 (s), 702.0 (m), 663.4 (m), 524.5 (w). HRMS (ESI⁻): calculated for $C_{54}H_{36}Cl_2N_4O_4Ru [M - H]^-$ 975.1088, observed 975.1068.

Synthesis of Na-*cis*-[Ru(LP1)(Hdcbpy)(NCS)₂] (DV51). A twonecked 50 mL round-bottomed flask, equipped with a stirring bar and a reflux condenser, was charged with [RuCl-(p-cymene)]₂ (76.5 mg, 0.125 mmol), LP1 (140.2 mg, 0.250 mmol), and degassed DMF (35 mL) at room temperature under argon. The reaction mixture was heated in the dark at 60 °C for 4 hours. H₂dcbpy (61.1 mg, 0.250 mmol) was then added and the reaction mixture was heated in the dark under argon at 140 °C for 4 hours. NH₄NCS (475.8 mg, 6.3 mmol) was added to the reaction mixture and heating at 140 °C continued for 4 more hours. This solution was cooled to room temperature with a water bath, and DMF was removed on a rotary evaporator. The resulting black solid was taken up and washed on a G4 sintered glass crucible with H₂O (5 × 10 mL), MeOH (10 × 1 mL), and Et₂O (5 × 5 mL). The remaining solid

was dissolved in the minimum amount of DMF, precipitated with Et₂O and washed on a G4 sintered glass crucible with Et_2O (5 × 5 mL), to afford complex DV44 as a black powder that was dried overnight under high vacuum (186 mg, 73%). Chromatographed DV51 was obtained from DV44 by the following procedure: 90 mg of DV44 were dissolved in a 0.02 M NaOH solution in MeOH (5 mL) and MeOH (2.5 mL). This solution was filtered, loaded on a Sephadex LH-20 column (equilibrated with MeOH), and purified with MeOH as an eluent. The collected main band (deep red) was concentrated on a rotary evaporator to about 7 mL and slowly titrated with a 0.02 M HNO₃ solution in MeOH to pH 5.2 (monitored by a pH meter). The solvent was then removed on a rotary evaporator and the remaining black solid was dissolved in DMF, precipitated with Et₂O, and washed on a G4 sintered glass crucible with Et₂O $(5 \times 5 \text{ mL})$, to afford purified **DV51**. Yield with three times column purification: 30 mg (33%). ¹H NMR (DMSO-d₆, 500 MHz, due to the existence of two diastereoisomeric pairs of enantiomers, each having twenty six diastereotopic protons in the aromatic region, proton signals cannot be fully assigned and integrations are not given): δ 9.64 (s), 9.51 (s), 9.41–9.38 (m), 9.30-9.17 (m), 9.08-8.99 (m), 8.81 (s), 8.75 (s), 8.57-8.55 (m), 8.44-8.11 (m), 8.02-7.54 (m), 7.34-7.31 (m), 7.02 (d), 6.94 (d). ${}^{13}C{}^{1}H$ NMR (DMSO-d₆, 125 MHz): δ 165.55, 165.18, 163.14, 161.54, 159.69, 159.34, 158.13, 157.58, 156.76, 154.98, 154.33, 154.17, 153.44, 152.82, 150.08, 150.01, 149.20, 148.85, 140.27, 139.92, 139.49, 139.04, 138.24, 137.48, 137.40, 137.08, 137.03, 136.97, 136.42, 136.19, 135.74, 135.63, 134.89, 134.63, 134.26, 132.24, 131.06, 130.68, 130.64, 130.07, 129.52, 129.33, 129.05, 128.40, 128.34, 128.24, 128.18, 128.02, 127.04, 126.91, 126.56, 126.29, 126.06, 125.81, 125.27, 125.02, 124.82, 123.50, 122.78, 122.37, 120.79, 120.52, 119.47, 119.18. FTIR v_{max} (cm⁻¹) 2098.2 (s), 1976.7 (m), 1714.4 (m), 1600.6 (m), 1538.9 (m), 1475.3 (m), 1403.9 (m), 1375.0 (s), 1255.4 (m), 1230.4 (s), 1124.3 (m), 1020.2 (m), 981.6 (m), 896.7 (m), 808.0 (m), 781.0 (s), 759.8 (s), 734.8 (s), 702.0 (s), 601.7 (m), 524.5 (m). HRMS (ESI⁻): calculated for $C_{56}H_{36}N_6O_4RuS_2$ (DV44) [M - H]⁻ 1021.1235, observed 1021.1255.

Results and discussion

Synthesis, NMR, and MS studies of ruthenium dyes

The synthetic approach followed for the preparation of the bidentate pyridine-quinoline hybrid ligand **LP1** is presented in Scheme 1. **LP1** was synthesized by a Suzuki coupling reaction of 6-bromo-4-phenyl-2-pyridin-2-ylquinoline (1) with (4-vinyl-phenyl)boronic acid (2), followed by a Heck coupling reaction of the resulting 4-phenyl-2-pyridin-2-yl-6-(4-vinyl-phenyl)-quinoline (3) with 9-bromoanthracene (4). **LP1** was obtained in 43% total isolated yield and characterized by ¹H, ¹³C, COSY, and HSQC NMR spectroscopy, as well as with FTIR and Elemental Analysis. Complexes **DV42** and **DV44**, both with *cis* geometry, were prepared by straightforward experimental procedures (Scheme 2), both in 73% isolated yields. These reactions were monitored by removing small aliquots, which were

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Scheme 1 Synthetic route followed for the preparation of the novel pyridinequinoline hybrid ligand LP1.



Scheme 2 Synthesis of Ru(II) photosensitizers DV42 and DV44

analyzed *via* UV-vis and ¹H NMR spectroscopy. Purified and half-deprotonated **DV51** (Fig. 2), free of S-coordinated NCS linkage isomers, was obtained from **DV44** in 33% isolated yield by Sephadex LH-20 column chromatography. **DV42** and **DV51** were characterized by ¹H, ¹³C, COSY, and HSQC NMR spectroscopy. Additional characterization was performed including UV-vis spectroscopy, FTIR spectroscopy, Raman spectroscopy, and HRMS.

Due to the unsymmetrical nature of LP1, there are two possible diastereoisomeric pairs of enantiomers for DV42 and DV51 (as well as for DV44). Indeed, the existence of two diastereoisomers for both DV42 and DV51 is clear in their respective NMR spectra. For example, two well-resolved doublets at δ 7.02 and 6.94 ppm, for the major and the minor

isomers respectively, were recorded in the ¹H NMR spectra of **DV51**. Integration of these two peaks, which correspond to the vinylic protons next to the phenyl ring of coordinated **LP1**, suggests a 62/38 ratio for the two diastereoisomeric pairs of **DV51**. Although the existence of two diastereoisomers for **DV42** and **DV51** results in fifty two diastereotopic aromatic protons for each, making the complete NMR peak assignment impossible, this does not impose any problem in their function as efficient photosensitizers in DSCs. Equally important, the molecular ions for **DV42** and **DV44** (the precursor of **DV51**) were detected by negative mode high resolution ESI at *m/z* 975.1068 and 1021.1255 respectively (requiring 975.1088 and 1021.1235) indisputably proving the structure of these novel Ru(π) complexes.

UV-visible studies

The UV-vis spectra of the dye solutions (Fig. 4a) show low frequency MLCT transitions (λ_{max}) at 588 nm for **DV42** and 552 nm for **DV51**; this shift is mainly due to the solvatochromic effect. Extinction coefficients (ε_m) equal to 9438 and 8896 M⁻¹ cm⁻¹ for **DV42** and **DV51**, respectively, were calculated. In comparison to the **Z907** dye (Fig. 3), with $\lambda_{max} = 518$ nm and $\varepsilon_m = 10\,180 \text{ M}^{-1} \text{ cm}^{-1}$, the absorption of the new dyes is slightly lower and shifts well to the red. The UV-vis spectra of the sensitized TiO₂ films show a maximum at about 550 nm for both **DV42** and **DV51**. These maxima are red-shifted by 30 nm in relation to the corresponding maximum of the films sensitized with the structurally related **Z907** dye (520 nm), which was used as a reference. Even though the thickness of the TiO₂ films cannot be precisely controlled, the films



Fig. 4 Absorption spectra of dyes **DV42** (DMF), **DV51** (EtOH), and **Z907** (EtOH) in solution (a), and the corresponding spectra of the same dyes chemisorbed onto transparent TiO_2 films (b).

sensitized by **DV51** present better absorbance than those sensitized by **DV42**, while both show slightly lower absorbance than **Z907**-sensitized films. The absorption edges of the sensitized films were found to be 715 and 725 nm, for **DV51** and **DV42** respectively, by the tangential method (Fig. 4b). Thus, the absorption of both **DV42**- and **DV51**-sensitized films extends well into the red spectral range, shifted by 30–40 nm relative to the absorption of the **Z907** dye,¹¹ in accordance with our anticipation for a red-shift for **DV42** and **DV51** due to their extended aromatic conjugation.

Vibrational (infrared, Raman, and resonance Raman) spectroscopy

The infrared spectra of **DV42** and **DV51** were recorded in the 4000–400 cm⁻¹ region. These spectra are very rich in the fingerprint region (1600–400 cm⁻¹) due to the various atomic vibrations of the two coordinated bidentate ligands **LP1** and H₂dcbpy. Noteworthily, the presence of a strong absorption band at 2098 cm⁻¹ [ν (C=N) stretching], along with the absence of such a band at about 2080 cm⁻¹, in the infrared spectra of **DV51**, confirms solely N-coordination for the ambidentate NCS ligands.^{7b,12}

Resonant Raman spectra of dyes **DV42** and **DV51** are shown in Fig. 5. The two strong bipyridine modes, ν (C=N) and ν (C=C), appear at 1475 cm⁻¹ and 1540 cm⁻¹, at the same frequencies observed for the **Z907** dye,¹³ although reversed in intensity. A new ν (C=C) mode is observed at 1603 cm⁻¹ and dominates over the 1613 ν (C=C) cm⁻¹ one, which is resolved as a satellite peak in the spectra, after the fitting analysis. This last mode is present in **Z907** spectra too. Furthermore, characteristic Raman peaks of the quinoline hybrid ligand C-C stretching modes¹⁴ at 1358 cm⁻¹ and several C-H modes above 2600 cm⁻¹ from the extended aromatic conjugation unit are observed.

Upon grafting the dyes onto TiO_2 , the corresponding resonant Raman spectra are enriched with the TiO_2 anatase modes at frequencies below 650 cm⁻¹. The strongest mode



Fig. 5 Resonant Raman spectra of dyes **DV42** and **DV51** in the powder form and resonant Raman spectra of dyes **DV42**, **DV51**, and **Z907** after sensitization of thick TiO₂ films. Raman modes discussed in the text are marked in the figure.

observed is the E_{1g} at 143 cm⁻¹. The weak Raman peak of the protonated carboxyl group at about 1720 cm⁻¹ is even more reduced in intensity, while in the case of **DV51** it vanishes, indicating chemisorption of the dye on the semiconducting surface.^{7*f*,*g*,13} Moreover, weak shifts and changes in the relative intensities of the C–H and C–C modes in the 1250–1320 cm⁻¹ region are observed after fitting analysis, in agreement with literature findings regarding related dyes.^{7*g*,13}

Contact angle studies

Contact angle measurements provide information on the chemical nature of the sensitized photoelectrode surface and, amongst others, can be used as a preliminary diagnostic method for determining the efficient and optimum duration of TiO_2 dye sensitization.^{11,15} The surface of the non-sensitized TiO₂ photoelectrodes is very hydrophilic and rough. As a result, the corresponding contact angle, measured for 10 µL water droplets on the various films, is very low with $\theta = 11^{\circ}$. Following sensitization, the films show higher contact angles (Table 1), 55° for the DV51 and 27° for the DV42 films, but remain hydrophilic with values that are commonly observed upon sensitization with the N3 dye.^{15,16} In this respect, DV51- and DV42-sensitized films differ significantly from the Z907sensitized TiO₂ films, which present strong hydrophobic character exhibiting a measured contact angle of θ = 125°; this contact angle is in agreement with that reported in the literature.¹¹ Therefore, the increased steric bulk of the novel pyridine-quinoline polyaromatic ligand does not result in a significantly enhanced hydrophobicity, as one would anticipate based on the ligand's extended aromatic system.

Electrochemical studies

The cyclic voltammograms of both **DV42** and **DV51** dyes present quasi-reversible waves with a large peak separation between the anodic (E_p^a) and cathodic (E_p^c) peak potentials $(\Delta E_p = E_p^a - E_p^c \sim 0.26-0.28 \text{ V})$, attributed to the oxidation of Ru(II) to Ru(III). The first oxidation potentials (E_{ox}) were estimated to be +1.04 and +1.14 V *vs.* NHE,^{17,18} lying well below the I⁻/I₃⁻ redox potential (+0.31 V *vs.* NHE)¹⁷ and allowing easy regeneration for both dyes. The 0.1 V difference in the oxidation potential of the two dyes (Table 2) may be attributed to the contribution of the NCS *vs.* the Cl ligands on the HOMO levels of the respective complexes, as proposed in the literature for several other ruthenium(II)-based dyes.¹⁹ Chloride ligands, having an increased electron-donating nature in comparison with thiocyanates,²⁰ promote the easier oxidation of the

Table 1 Measured contact angles for 10 μL water droplets on DV42-, DV51-, and Z907-sensitized TiO_2 films

Surface	$ heta\left(^{\circ} ight)$
TiO ₂	11 ± 2
TiO ₂ -DV42	27 ± 3
TiO ₂ -DV51	55 ± 3
TiO ₂ - Z907	125 ± 7

Table 2 First oxidation potentials, optical bandgap, and excited-state oxidation potentials of Ru(n) complexes DV42 and DV51

Sensitizer	$E_{\rm ox}^{a}$ (V vs. NHE)	$E_{\rm g}^{\ b} ({\rm eV})$	$E_{\rm ox}^{*c}$ (V vs. NHE)	
DV42	+1.04	+1.72	-0.68	
DV51	+1.14	+1.90	-0.76	

 a Electrochemical data. b Derived from the optical spectra of the dyes in solution (Fig. 4b). c Calculated.

corresponding ruthenium(II) ion. Both E_{ox} values are analogous to the previously measured E_{ox} values for the benchmark **Z907** dye (+1.01 V *vs.* NHE).²¹ Given that neither **DV42** nor **DV51** emit when photoexcited in the visible, their LUMO energy levels could not be estimated from the intersection of the corresponding superimposed UV-vis and emission spectra.^{7g} Alternatively, the dye excited-state oxidation potentials $(E_{ox}^*)^{22}$ were estimated at -0.68 and -0.76 V for **DV42** and **DV51**, respectively, by using the values of the absorption threshold (E_g) determined from the optical spectra. E_{ox}^* values of both dyes are more negative than the conduction band edge of TiO₂ (-0.5 V *vs.* NHE)²³ permitting efficient electron injection from the excited dye molecules into the semiconductor conduction band.

Photovoltaic studies

The photovoltaic performance of the sensitized TiO₂ photoelectrodes was examined following their incorporation into sandwich-type liquid DSCs. The *J*–*V* characteristics were obtained under 1 sun (AM 1.5 G) illumination (Fig. 6) and the corresponding derived electric parameters are summarized in Table 3. The overall power conversion efficiency (η) determined for the **DV42** dye-based cells was as high as 3.24%. **DV51**based cells showed 4.36% power conversion efficiency accompanied with a short-circuit current (J_{sc}) of 9.30 mA cm⁻²,



Fig. 6 *J–V* characteristics of DSCs using optimum TiO₂ electrodes (employing a scattering layer) sensitized by **DV42**, **DV51**, and **Z907** dyes under illumination of 1 sun (AM 1.5 G).

Table 3 Performance parameters of DSCs based on titania films sensitized by DV42, DV51, and Z907 dyes

Sensitizer	$J_{\rm sc} ({\rm mA}~{\rm cm}^{-2})$	$V_{\rm oc}$ (V)	FF	η (%)
DV42	7.85	0.63	0.66	3.24
DV51	9.30	0.68	0.69	4.36
Z907	14.15	0.81	0.68	7.82

an open-circuit potential (V_{oc}) of 0.68 V, and a filling factor (FF) of 0.69. Thus, all photovoltaic parameters are improved in **DV51**-sensitized cells in comparison with the **DV42**-sensitized cells.

In view of the fact that electron collection is similar for photoelectrodes consisting of the same TiO₂ type, the Jsc increase in the DV51-based cells can be attributed to improved light harvesting in comparison to the DV42sensitized cells. Consistent with this hypothesis, simple TiO₂ films (without any scattering layer) sensitized by the DV51 dye present a higher optical density (A = 0.88 at MLCT) when compared with those sensitized by DV42 (A = 0.83 at the respective MLCT, Fig. 4b). Besides improved light harvesting, the current increase could also be realized because DV51 either enhances electron injection (having an excited-state oxidation potential 80 mV higher than that of the DV42 dye)²² or is regenerated more efficiently by the redox electrolyte. An improved DV51 regeneration could originate from the highly efficient electron transfer from the iodine ions to the NCS ligands, which are known to be excellent electron acceptors,²⁴ despite the fact that the driving force for DV51 is 100 mV smaller than that of DV42 (see the first oxidation potentials in Table 2).

The 0.05 V V_{oc} increase in the DV51-sensitized cells can be attributed to a small shift of the TiO₂ conduction band. Given that DV42 leaves two protons on the TiO₂ surface upon adsorption, in comparison to one proton for DV51, the semiconductor may be charged more positively in the case of DV42. Suppressed recombination between electrons injected in the semiconductor and triiodides, in the case of DV51-sensitized cells, seems to be an even more possible reason for the improved Voc. This suppressed recombination may originate from the increased hydrophobicity of the DV51-sensitized cells, when compared with their DV42 counterparts. The use of hydrophobic dyes in order to increase $V_{\rm oc}$ is a well-known concept in DSCs literature;25 furthermore, Grätzel and coworkers have observed a 50 mV difference between two dyes that differ about 9° in the contact angles of the respective films.¹¹ In order to more accurately elucidate the observed differences and correlate the photovoltaic performance with the electron dynamics in DV42- vs. DV51-sensitized solar cells, comprehensive studies are currently underway and will be reported in due course.

Finally, comparative experiments performed on identical DSCs sensitized by the widely utilized standard **Z907** dye, which attains power conversion efficiencies over 10% in the literature,²⁶ show that the efficiency of the cells obtained from **DV51** is about 56% of that attained by **Z907** (Table 3). Again, the reduced J_{sc} and V_{oc} values of **DV42**- and **DV51**-sensitized



Fig. 7 IPCE spectra of DSCs based on DV42, DV51, and Z907 dyes.

cells in relation with those sensitized by the archetypal **Z907** dye (Fig. 6) can be ascribed to the more hydrophobic character of **Z907**, preventing electrons from recombining with triiodides at the TiO_2 surface.

To better understand the DSC performance of DV42 and DV51, the corresponding IPCE (incident photon-to-current efficiency) spectra were recorded (Fig. 7). Slight differences were observed concerning the shape of the action spectra profiles for the **Z907** and **DV51** dyes, presenting IPCE values over 85% and close to 60% at about 530 nm, respectively. This is in agreement with their J_{sc} values reported in Table 3. In contrast, DV42-sensitized cells presented a significant red shift of about 30 nm, attaining a maximum IPCE value of 47% at about 560 nm. This shift is not consonant with the absorbance characteristics of DV42 shown in Fig. 4a (note that the transmittance/reflectance of the films was recorded on transparent films); the shift can be attributed to the stronger interaction of the DV42 dye with the scattering TiO₂ layer employed in the IPCE measurement. By integrating the product of the incident photon flux density and the IPCE values over the 400 to 800 nm wavelength regime, the calculated short-circuit photocurrents closely match the experimental J_{sc} values for all cells (within a maximum deviation of 10%).

Conclusions

Two novel, heteroleptic ruthenium(π) sensitizers (**DV42** and **DV51**), bearing an unsymmetrical pyridine-quinoline hybrid ligand with extended π -conjugation, were synthesized, extensively characterized, and utilized in liquid electrolyte dye-sensitized solar cells. The absorption of both **DV42**- and **DV51**-sensitized TiO₂ films is red-shifted by 30–40 nm relative to the absorption of TiO₂ films sensitized with the benchmark **Z907** ruthenium(π) dye. This red shift is attributed to the extended aromatic conjugation of **DV42** and **DV51**. Contact angle measurements of **DV42**- and **DV51**-sensitized TiO₂ films

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suggest that these films are hydrophilic with contact angle values that are commonly observed upon sensitization with the standard N3 ruthenium(π) dye. The excited-state oxidation potentials of **DV42** and **DV51** lie well above the TiO₂ conduction band, permitting efficient electron injection from the excited dye molecules into the semiconductor conduction band. Moreover, both novel ruthenium(π) dyes have first oxidation potentials that lie below the I^-/I_3^- redox potential allowing easy regeneration. Dye-sensitized solar cells integrating **DV42**- or **DV51**-sensitized TiO₂ photoelectrodes afford power conversion efficiencies of 3.24 or 4.36% respectively. These power conversion efficiencies are up to 56% of the corresponding efficiencies attained by TiO₂ photoelectrodes sensitized by the standard **Z907** ruthenium(π) dye under similar experimental conditions.

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