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Highly efficient benzodifuran based ruthenium sensitizers for thin-film dye-sensitized solar cells

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ABSTRACT

The synthesis of 4,4′-dibenzodifuran-2,2′-bipyridine derivatives as ligands of organic ruthenium dyes for DSSC applications is described. Two new heteroleptic ruthenium complexes have been prepared and compared with commercially available **N719** and **Z907** dyes, using dip dyeing and flow dyeing methods in large area testing cells prepared for industrial purposes. The newly synthesized dyes revealed higher solar-to-electric energy conversion efficiency (η), measured at the AM1.5G conditions, up to 21% compared to **N719** and up to 46% compared to **Z907**, and external quantum efficiency of 53%. These results can be explained by enhanced light-harvesting of the benzodifuran moiety of the dyes that is related to photocurrent.

1. Introduction

Since 1991 when O'Regan and Grätzel [1] described the first dye-sensitized solar cell (DSSC) containing ruthenium dye as a photosensitizer, this technology have attracted tremendous interest due to its low manufacturing cost, a remarkable stability, and respectable high solar-to-electric energy conversion efficiency (η) up to 12% [2]. Although the perovskite type sensitizers derived from lead halides and applied by spin coating technique allowed to reach the efficiency of ~19.3% [3], there is still place for organic ruthenium dyes soluble in “green” organic solvents, such as ethanol, and easily applicable by “dip coating” or “flow dyeing” techniques, well suited for the preparation of large area solar panels.

The first commonly used homoleptic ruthenium complexes for DSSC applications (**N3** and **N719**) developed in Grätzel group [4,5] revealed η~11% for devices based on these dyes under one-sun illumination (Fig. 3) [6,7] The main drawback of the devices was their low stability. To improve their durability an amphiphilic ruthenium sensitizer **Z907** was developed by replacing one 4,4′-dicarboxylic-2,2′-bipyridine (dcbpy) ligand in the **N3** dye with an ancillary 4,4′-dinonyl-2,2′-bipyridine ligand [8–10]. Although stability of the device based on **Z907** improved significantly, the efficiency decreased, mainly due to lower light-harvesting, related to the molar extinction coefficient for two UV–Vis absorption bands – at 350–450 nm (ligand-centered charge transfer (LCCT) transitions (π - π^*)), as well as at 500–600 nm (metal-to-ligand charge transfer (MLCT) transitions (4d - π^*)). To improve the light-harvesting efficiency via an enhanced molar extinction coefficient, many heteroleptic ruthenium complexes derived from 2,2′-bipyridine substituted with aryl, heteroaryl and aryl-vinyl groups were developed [11–25]. Herein, the synthesis and photovoltaic characterization of benzodifuran (**BDF**) derived ruthenium dyes of high energy conversion efficiency is described.

2. Experimental

2.1. Materials and general methods

Experiments with air and moisture sensitive materials were carried under argon atmosphere. Glassware was oven dried for several hours, assembled hot, and cooled in a stream of argon. Silica gel 60, Merck 230–400 mesh, was used for preparative column flash chromatography. Analytical TLC was performed using Sigma–Aldrich silica gel on TLC Al foils with fluorescent indicator

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254 nm, 0.2 mm plates. 1-Octanol, iodine, morpholine, 4,4′-dibromo-2,2′-bipyridine, [1,1′-bis(diphenylphosphino)ferrocene] dichloropalladium(II), copper iodide, diisopropylamine, ethynyltrimethylsilane, 1M tetrabutylammonium fluoride solution in THF, dichloro(*p*-cymene)ruthenium(II) dimer, 2,2′-bipyridine-4,4′-dicarboxylic acid, ammonium thiocyanate, and tetrabutylammonium hydroxide were commercially available from Sigma–Aldrich, Merck or Fluorochem, and were used without further purification. [2,2′-Bipyridine]-4,4′-dicarbaldehyde was prepared according to the literature procedure [26]. Solvents were purchased from Avantor and Sigma–Aldrich. Toluene was distilled from sodium benzophenone ketyl prior to use, DMF was stirred overnight with calcium hydride, filtered, distilled at 20 mmHg, and stored over 4A molecular sieves. Chloroform, diethyl ether, methanol, anhydrous ethanol, THF, *n*-heptane, and ethyl acetate were used without further purification. Deuterated solvents for NMR spectroscopy were purchased from Sigma–Aldrich. Sephadex LH-20 was purchased from GE Healthcare. **N719** and **Z907** dyes were purchased from Dyesol. Melting points were determined with a Büchi SMP 32 and Barnstead-Thermolyne Mel-Temp II apparatus in open capillaries and are uncorrected. Elemental analyses were performed at Elementary Analysensysteme GmbH Vario MACRO CHN analyzer.

2.1.1. *Spectroscopic measurements*

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance III 400 MHz or Bruker Advance III 700 MHz instrument at ambient temperature. Chemical shifts are reported in parts per million (δ scale), coupling constants (J values) are listed in Hertz. Anhydrous ethanol (spectrometric grade from Sigma–Aldrich) was employed as solvent for absorption measurements. UV/Vis absorption spectra of dyes solutions and sensitized TiO_2 films were recorded by means of a Jasco V670 UV–Vis–NIR spectrophotometer equipped with liquid a cell holder (10 mm quartz cell, versus solvent blank) and thin film holder. IR spectra were recorded on a Perkin Elmer FT-IR Spectrum Two spectrometer equipped in diamant ATR.

2.2. *Synthesis of the compounds*

2.2.1. *Ethyl 5-hydroxy-2-methylbenzofuran-3-carboxylate (**1**)*

A solution of *p*-benzoquinone (54.045 g, 0.5 mol) and ethyl acetoacetate (200 mL, 1.583 mol) in dry acetone (200 mL) was added dropwise during 9 h to a mechanically stirred solution of anhydrous zinc chloride (70 g, 0.513 mol) in acetone (100 mL) and acetic acid (5 mL) at 75 °C. The mixture was stirred for additional 10 min, transferred into a large crystallizer and left opened in fume cupboard overnight. The crystallizer was transferred into freezer and left for 24 h. Precipitate was filtered off, washed with cold MeOH (2 × 50 mL) and dried on air. Crude product was crystallized from toluene to give 47.50 g (43%) of white solid, mp = 143–144 °C. Lit [27]. 143.5–144 °C. ^{1}H NMR (700 MHz, $CDCl_3$); δ ppm: 1.41 (t, $J = 7$ Hz, 3H, CH_3), 2.71 (s, 3H, CH_3), 4.38 (q, $J = 7$ Hz, 2H, CH), 6.79–6.80 (dd, $J = 9.1$ Hz, $J = 2.8$ Hz, 2H, CH_2), 5.88 (s, 1H, CH), 7.24 (d, $J = 4.2$ Hz, 1H, CH), 7.26 (s, 1H, CH), 7.48 (d, $J = 2.8$, 1H, CH). ^{13}C NMR ($CDCl_3$, 175 MHz); δ ppm: 15.38 (CH_3), 15.75 (CH_3), 61.53 (CH_2), 107.84 (CH), 109.86 (C), 112.25 (CH), 113.72 (CH), 128.26 (C), 149.52 (C), 153.67 (C), 165.52 (C), 165.86 (C). IR (ATR) ν_{max} cm^{-1}: 3323, 1668, 1623, 1607, 1580, 1475, 1464, 1417, 1382, 1348, 1300, 1259, 1217, 1168, 1111, 1087, 1027, 954, 866, 853, 838, 809, 784, 736, 682, 652, 617, 573. Anal. Calcd. for $C_{12}H_{12}O_4$: C, 65.45; H, 5.49. Found: C, 65.61; H, 5.44.

2.2.2. *Octyl 5-hydroxy-2-methylbenzofuran-3-carboxylate (**2**)*

To a dispersion of ethyl 5-hydroxy-2-methylbenzofuran-3-carboxylate (29.54 g, 134 mmol) in 1-octanol (300 mL), concentrated sulfuric acid (1 mL) was added and the mixture was heated to 150 °C in opened flask and stirred at this temperature for 18 h. It was poured into concentrated solution of sodium bicarbonate (200 mL) and brine (100 mL), stirred for several minutes and extracted with ethyl acetate (3 × 100 mL). Combined organic layers were dried with anhydrous magnesium sulfate. The ethyl acetate was removed using rotary evaporator and the remaining 1-octanol was distilled off under reduced pressure. To a slurry *n*-heptane (500 mL) was added, the mixture was heated to reflux and filtered through a warm Büchner funnel. The filtrate was cooled overnight and the flaky precipitate was filtered off and dried to obtain 32.87 g (80%) of pure solid, mp 93–94 °C. ^{1}H NMR ($CDCl_3$, 400 MHz); δ ppm: 0.90 (t, $J = 6.8$ Hz, 3H, CH_3), 1.28–1.42 (m, 8H, $4CH_2$), 1.45–1.52 (m, 2H, CH_2), 1.78–1.86 (m, 2H, CH_2), 2.76 (s, 3H, CH_3), 4.36 (t, $J = 6.8$ Hz, 2H, CH_2), 5.23 (s, 1H, OH), 6.82 (dd, $J = 8.8$ Hz, $J = 2.6$ Hz, 1H, CH_{Ar}), 7.30 (d, $J = 8.8$ Hz, 1H, CH_{Ar}), 7.46 (m, 1H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz); δ ppm: 14.07 (CH_3), 14.81 (CH_3), 22.63 (CH_2), 26.10 (CH_2), 28.73 (CH_2), 29.19 (CH_2), 29.22 (CH_2), 31.78 (CH_2), 64.82 (CH_2), 106.81 (CH), 108.90 (C), 111.25 (CH), 112.79 (CH), 127.31 (C), 148.50 (C), 152.85 (C), 164.38 (C), 165.07 (C). IR (ATR) ν_{max} cm^{-1}: 3348, 2948, 2923, 2854, 1670, 1622, 1605, 1577, 1463, 1415, 1394, 1382, 1359, 1298, 1268, 1258, 1212, 1173, 1111, 1094, 1020, 962, 944, 863, 837, 806, 789, 783, 735, 724, 648, 619, 611, 581. Anal. Calcd. for $C_{18}H_{24}O_4$: C, 71.03; H, 7.95. Found: C, 71.21; H, 7.97.

2.2.3. *Ethyl 5-hydroxy-6-iodo-2-methylbenzofuran-3-carboxylate (**3**)*

Ethyl 5-hydroxy-2-methylbenzofuran-3-carboxylate (**1**) (26.43 g, 120 mmol) and iodine (48.72 g, 192 mmol, 1.6 equiv.) were dispersed in anhydrous methanol (100 mL) and stirred for 5 min under argon. The mixture was cooled to 0 °C, and morpholine (30.32 g, 348 mmol, 2.9 equiv.) was added dropwise at a rate to keep the temperature below 30 °C, slowly heated to 35 °C, and stirred at this temperature for 120 h. Water (20 mL) was added and the mixture was left at −20 °C overnight. Precipitate was filtered off, washed with cold methanol of (−25 °C, 3 × 60 mL), and dried to obtain 46.91 g of beige solid. It was extracted with diethyl ether (450 mL) using a Soxhlet extractor for 48 h. The crude product was finally crystallized from methanol to obtain 13.97 g (34%) of pure white solid, mp = 196–197 °C. Lit [27]. 194–194.5 °C. ^{1}H NMR ($CDCl_3$, 700 MHz); δ ppm: 1.44 (t, $J = 7.2$ Hz, 3H, CH_3), 2.73 (s, 3H, CH_3), 4.40 (q, $J = 7.2$ Hz, 2H, CH_2), 5.28 (s, 1H, OH), 7.56 (s, 1H, CH_{Ar}), 7.73 (s, 1H, CH_{Ar}). ^{13}C NMR ($CDCl_3$, 100 MHz); δ ppm: 14.42 (CH_3), 14.56 (CH_3), 60.47 (CH_2), 80.68 (C), 106.25 (CH), 108.98 (C), 119.63 (CH), 128.38 (C), 148.73 (C), 151.25 (C), 164.11 (C), 165.11 (C). IR (ATR) ν_{max} cm^{-1}: 3255, 1672, 1614, 1582, 1447, 1405, 1380, 1345, 1279, 1268, 1183, 1166, 1150, 1115, 1093, 1033, 964, 909, 862, 841, 800, 786, 722, 657, 590. Anal. Calcd. for $C_{12}H_{11}IO_4$: C, 41.64; H, 3.20. Found: C, 41.48; H, 3.21.

2.2.4. *Octyl 5-hydroxy-6-iodo-2-methylbenzofuran-3-carboxylate (**4**)*

Octyl 5-hydroxy-2-methylbenzofuran-3-carboxylate (**2**) (12.16 g, 40 mmol) and iodine (24.38 g, 96 mmol, 2.4 equiv.) were dispersed in anhydrous methanol (60 mL) and stirred for 10 min under argon. The mixture was cooled to 0 °C and morpholine (15.20 mL, 175 mmol, 4.35 equiv.) was added dropwise at a rate to keep the temperature below 30 °C, slowly heated to 35 °C, and stirred at this temperature for 48 h. Water (12 mL) was added and the mixture was left at −20 °C overnight. Precipitate was filtered off, washed with cold methanol (−25 °C, 5 × 25 mL) and dried to obtain 17.10 g of beige solid. It was dispersed in chloroform (300 mL) and stirred for 5 min. Insoluble precipitate of morpholine hydroiodide was filtered off and the filtrate was concentrated to obtain 10.02 g of crude brown product. Crystallization from methanol/water (200 mL/25 mL) gave 8.89 g (52%) of light yellow