



The influence of anchoring group position in ruthenium dye molecule on performance of dye-sensitized solar cells



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ABSTRACT

The effect of anchoring group position and, in consequence, the orientation of the ruthenium dye molecule on titania surface on the performance of dye-sensitized solar cells has been studied intensively. Three model ruthenium sensitizing dyes bearing carboxylic anchoring group in *ortho*, *meta* or *para* position were synthesized and well characterized by spectroscopic, electrochemical, photophysical and photochemical measurements. The results were confronted with the quantum-mechanical calculations and discussed. The *para* derivative has been found as the most effective sensitizer with the cells efficiency twice higher than the *meta* and four times higher than the *ortho* derivatives.

1. Introduction

Dye-sensitized solar cells (DSSCs) seem to be promising devices efficiently converting sunlight to electricity, because of their relatively high efficiency, simple fabrication methods and low cost of production [1–4]. Typical DSSC is composed of dye-sensitized nanocrystalline semiconducting oxide, liquid or solid electrolyte and a counter electrode, but the dye is one of the most important component and is often called “the heart of the system” which indicates its key role in determination of the device photovoltaic performance. The initial types of DSSCs based on a combination of mesoporous titania sensitized with ruthenium complex cooperating with iodine-based electrolytes permitted the efficiencies up to 11.9%, but the devices of this kind, up to now, have never surpassed the efficiency level of about 12% and the recent record is 12.3% [5,6]. Further application of the new type of organic donor- π -acceptor dyes based on porphyrin with cobalt-based redox mediators permitted obtaining efficiencies over 13% and still has much potential of development [7–10].

Ruthenium sensitizers development is focused on structural modification of the ancillary ligands to improve electron injection

efficiency, light harvesting and, in consequence, the performance of DSSCs. Modification of anchoring ligands is performed very seldom and only a few papers have been published in this area. Funaki et al. have synthesized the “black dye” analogues with π -expanded terpyridine ligand having phenylene-ethynylene chains and the anchoring carboxyl group shifted to the end of expanding chain [11]. They found that the longer the phenylene-ethynylene chain the lower the efficiency of the cell and explained this phenomenon by the aggregation of the dye molecules on the electrode surface. The improvement in the cells efficiencies sensitized by a “black dye” with the anchoring chain modified by cyanoacetic acid-2-thienyl moiety, have been reported by Vincent Joseph et al. [12].

In our previous work we investigated the dinuclear ruthenium bipyridine complex B1 with dendritic anchoring ligand [13,14]. The B1 dye was less active in the cell conditions than its commercially available mononuclear analogue. One of possible reasons for relatively poor performance of B1 dye, proposed by us, was the *meta* position of the carboxylic anchoring group in relation to the ruthenium bipyridine complex moieties that may lead to poor electronic communication with the TiO₂ orbitals. Previously published papers clearly indicate that the

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meta position of the anchoring group in the ruthenium dye molecule results in lower efficiency of the sensitized cells [15–17]. However, the hitherto literature on the subject has been focused on the dyes with at least two anchors in one molecule and the *meta* location triggers competing reactions and steric problems during the dye adsorption process. Moreover, Hart et al. have investigated the effect of anchoring group position in the porphyrin sensitizers with only one anchoring group and they found that the *meta* position is the most effective in electron injection process and, in consequence, gives more effective cells [18], but further investigations of other groups have strongly refute these findings [19,20].

In this work, we do not aim at reaching the next DSSC efficiency record but we try to find the answer to the fundamental question on the effect of the position of a single anchoring group on the overall photon-to-current efficiency of the cell. Therefore, in order to better understand the electron transfer process between the dye molecule and the titania electrode three model-dyes, each of them with only one anchoring group, already known *para* [21] and two new *meta* and *ortho* moieties, have been synthesized and examined by electrochemical, photophysical and photochemical techniques as well as density functional theory (DFT) calculations. Solar cells with the *para* derivative as a sensitizer exhibit the highest performance with the photoconversion efficiency twice higher than the *meta* derivatives and four times higher than the *ortho* ones.

2. Experimental

2.1. Synthesis

The compound 4-bromo-2,2'-bipyridine and 4-ethynyl-2,2'-bipyridine was obtained by published methods [14,22], other compounds were commercial products (Sigma-Aldrich, USA).

2.1.1. Ethyl ethynylbenzoates (2)

A solution of corresponding ethyl bromobenzoate (5.00 g; 22 mmol) and trimethylsilylacetylene (15 mL; 108 mmol) in triethylamine (80 mL) was deoxygenated and 200 mg of Pd₂(dba)₃, 300 mg of triphenylphosphine and 50 mg of cooper(I) iodide were added. The mixture obtained was stirred under argon at 353 K, over 24 h, then the solvent was evaporated, the residue was mixed with 5% HCl (200 mL) and the product was extracted with diethyl ether (2 × 100 mL). The organic layer was washed with water, dried over Na₂SO₄ and evaporated. The crude trimethylsilyl derivative **1** was dissolved in freshly distilled THF (100 mL), then 1.25 mL of glacial acetic (22 mmol) acid and solution of 7.15 g (23 mmol) of tetrabutylammonium fluoride trihydrate in 20 mL of THF was added. The mixture was allowed to react over 0.5 h, the solvent was evaporated and the product was purified by column chromatography (SiO₂; hexane/dichloromethane, 2:1 v/v).

m-2: Yellowish brown crystals; m.p. ~293 K. Yield: 90% (3.45 g). ¹H NMR (CDCl₃): δ 8.17 (d, 1H; 1.4 Hz), 8.02 (dt, 1H; 7.7 & 1.4 Hz), 7.66 (dt, 1H; 7.7 & 1.4 Hz), 7.41 (t, 1H; 7.7 Hz), 4.39 (q, 2H; 7.3 Hz), 3.12 (s, 1H), 1.41 (t, 3H; 7.3 Hz). HRMS: 174.0680 (calc. for C₁₁H₁₀O₂: 174.0681). ¹³C NMR (CDCl₃): δ 165.5, 136.9, 132.7, 131.7, 130.9, 129.8, 128.7, 82.3, 81.1, 61.2, 14.1.

p-2: Yellowish brown crystals; m.p. ~293 K. Yield: 94% (3.60 g). ¹H NMR (CDCl₃): δ 8.00 (*pseudod*, 2H), 7.55 (*pseudod*, 2H), 4.38 (q, 2H; 7.3 Hz), 3.22 (s, 1H), 1.40 (t, 3H; 7.3 Hz). HRMS: 174.0677 (calc. for C₁₁H₁₀O₂: 174.0681). ¹³C NMR (CDCl₃): δ 165.9, 132.0, 130.4, 129.4, 126.6, 82.8, 79.9, 61.1, 14.2.

2.1.2. Ethyl (2-(2,2'-bipyridin-4-yl)ethynyl)benzoates (3)

1.00 g of corresponding ethyl ethynylbenzoate (5.7 mmol) and 1.40 g of 4-bromo-2,2'-bipyridine (6.4 mmol) was dissolved in 60 mL of deoxygenated triethylamine and 100 mg of Pd₂(dba)₃, 150 mg of triphenylphosphine and 30 mg of cooper(I) iodide were added. The mixture obtained was heated under argon over 24 h. After that the solvent

was evaporated, the product was extracted with chloroform and recrystallized from methanol.

m-3: Dirty yellow flocks; m.p. 438–441 K. Yield: 85% (1.59 g). ¹H NMR (CDCl₃): δ 8.71 (bs, 2H), 8.57 (bs, 1H), 8.43 (bs, 1H), 8.24 (t, 1H; 1.6 Hz), 8.06 (dt, 1H; 7.8 & 1.4 Hz), 7.84 (t, 1H; 7.5 Hz), 7.73 (dt, 1H; 7.8 & 1.4 Hz), 7.47 (t, 1H; 7.8 Hz), 7.42 (bs, 1H), 7.35 (bs, 1H), 4.41 (q, 2H; 7.2 Hz), 1.43 (t, 3H; 7.2 Hz). ¹³C NMR (CDCl₃): δ 165.7, 156.1, 155.3, 149.1, 137.0, 135.8, 133.0, 132.1, 131.0, 130.0, 128.6, 125.3, 124.1, 123.3, 122.6, 121.2, 92.8, 87.8, 61.3, 14.3. HRMS: 328.1205 (calc. for C₂₁H₁₆N₂O₂: 328.1212).

p-3: Dirty yellow flocks; m.p. 453–455 K. Yield: 87% (1.63 g). ¹H NMR (CDCl₃): δ 8.71 (bs, 1H), 8.68 (bs, 1H), 8.56 (bs, 1H), 8.42 (d, 1H; 8.0 Hz), 8.06 (*pseudod*, 2H), 7.83 (td, 1H; 7.7 & 1.6 Hz), 7.62 (*pseudod*, 2H), 7.40 (d, 1H; 4.6 Hz), 7.34 (dd, 1H; 6.8 & 5.0 Hz), 4.40 (q, 2H; 7.1 Hz), 1.41 (t, 3H; 7.1 Hz). ¹³C NMR (CDCl₃): δ 165.8, 156.2, 155.3, 149.2, 137.0, 131.8, 131.7, 130.6, 129.5, 126.6, 125.2, 124.1, 123.2, 121.2, 92.8, 89.5, 61.2, 14.3. HRMS: 328.1217 (calc. for C₂₁H₁₆N₂O₂: 328.1212).

2.1.3. (2-(2,2'-Bipyridin-4-yl)ethynyl)benzoic acids (m-4, p-4; Lm, Lp)

1.00 g of **3** (3 mmol) was dissolved in 150 mL of THF and 100 mL of methanol. To the solution obtained 0.5 g of lithium hydroxide (21 mmol) in 25 mL of water was added. The mixture was stirred overnight at room temperature, the solvent was evaporated and the solid residue was suspended in water (50 mL). The solution was neutralized with 10% HCl and the precipitated product was filtered off, washed with water and dried.

m-4 (Lm): Yellowish powder; m.p. 496 K. Yield: 95% (0.86 g). ¹H NMR (DMSO-d₆): δ 11.3 (bs, 1H), 8.73 (dd, 1H; 4.9 & 0.8 Hz), 8.71 (dd, 1H; 4.7, 1.9 & 1.0 Hz), 8.45 (dd, 1H; 1.7 & 1.0 Hz), 8.38 (dd, 1H; 7.9 & 1.0 Hz), 8.10 (td, 1H; 1.7 & 0.8 Hz), 7.98 (td, 1H; 7.7 & 1.7), 7.95 (dt, 1H; 7.6 & 1.3 Hz), 7.60 (m, 2H), 7.50 (ddd, 1H; 7.5, 4.8 & 1.0 Hz), 7.40 (t, 1H; 7.6 Hz). ¹³C NMR (DMSO-d₆): δ 168.3, 155.6, 154.3, 149.8, 149.4, 140.8, 137.5, 132.5, 132.0, 131.5, 130.4, 127.9, 125.4, 124.6, 121.9, 120.6, 120.0, 94.4, 86.2. HRMS: 300.0891 (calc. for C₁₉H₁₂N₂O₂: 300.0899).

p-4 (Lp): Yellowish powder; m.p. 518–524 K. Yield: 97% (0.87 g). ¹H NMR (DMSO-d₆): δ 11.0 (bs, 1H), 8.73 (dd, 1H; 4.9 & 0.8 Hz), 8.71 (ddd, 1H; 4.7, 1.8 & 0.9 Hz), 8.45 (dd, 1H; 1.6 & 0.8 Hz), 8.39 (dt, 1H; 7.9 & 1.1 Hz), 7.98 (ddd, 1H; 7.9, 7.7 & 1.6 Hz), 7.92 (*pseudod*, 2H), 7.59 (dd, 1H; 5.0 & 1.8 Hz), 7.57 (*pseudod*, 2H), 7.50 (ddd, 1H; 7.4, 4.7 & 1.2 Hz). ¹³C NMR (DMSO-d₆): δ 168.6, 155.6, 154.3, 149.8, 149.4, 141.5, 137.5, 131.5, 130.9, 129.3, 125.4, 124.7, 121.9, 121.2, 120.6, 94.3, 87.2. HRMS: 300.0888 (calc. for C₁₉H₁₂N₂O₂: 300.0899).

2.1.4. 2-Bromobenzoic acid trimethylsilyl ester (5)

2-Bromobenzoic acid (5.00 g; 25 mmol) was dissolved in dry dichloromethane (100 mL) and 26 mg of sodium saccharinate (0.125 mmol) was added. The mixture was heated under reflux in inert atmosphere and the hexamethyldisilazane (3.23 g, 20 mmol) was added dropwise over 5 min. After 2 h the mixture was filtered and the solvent and excess of silanizing agent were evaporated in vacuum. The crude product was obtained as colorless liquid (6.63 g; yield: 98%), readily hydrolyzing on air. ¹H NMR (CDCl₃): δ 7.87 (dd, 1H; 7.7 & 1.8 Hz), 7.65 (d, 1H; 7.7 Hz), 7.35 (t, 1H; 7.7 Hz), 7.31 (td, 1H; 7.7 & 1.8 Hz). HRMS: 271.9860 (calc. for C₁₀H₁₃BrO₂Si: 271.9868).

2.1.5. 2-(2-(2,2'-Bipyridin-4-ylethynyl)benzoic) acid (o-4; Lo)

1.50 g (5.5 mol) of protected 2-bromobenzoic acid (**5**) was dissolved in mixture of 50 mL of anhydrous triethylamine with 30 mL anhydrous toluene and 1 g (2.2 mmol) of 4-ethynyl-2,2'-bipyridine was added. After adding of the catalysts (150 mg of Pd₂(dba)₃, 300 mg of PPh₃ and 75 mg of CuI) the mixture was heated at 353 K over 24 h. After that the solvent was evaporated and the mixture was stirred with water over 1 h. The product was filtered off and purified by column chromatography (SiO₂; CH₂Cl₂/Et₂O, 1:1 v/v) to obtain 0.49 g (75%) of yellowish

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