5-(Methylidene)barbituric acid as a new anchor unit for dye-sensitized solar cells (DSSC)

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This paper is dedicated to Professor Oleg N. Chupakhin on the occasion of his 80th birthday

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Abstract

Novel dyes bearing a 5-(methylidene)barbituric acid moiety as a new acceptor/anchor fragment were obtained and exhibited remarkable photophysical properties, according to a preliminary assessment of their sensitization activity as elements for dye-sensitized solar cells.

Keywords: Barbituric acid, carbazole, pyrimidine, anchor group, push-pull structure, dye-sensitized solar cells

Introduction

Dye-Sensitized Solar Cells (DSSCs) 1-4 based on organic dyes adsorbed on nanocrystalline semiconductor (e.g. TiO₂, SnO₂, ZnO) electrodes are considered to be promising electronic devices having a number of advantages, such as a high efficiency of solar light-to-electricity conversion, light weight, low cost and nontoxic manufacturing. The photochemical properties of a variety of organic sensitizers have been extensively investigated. 2,4 However, the design of new dye-sensitizers with a visible light absorption coupled to long-lived excited states is still very important for improving of DSSCs. Typically, the metal-free organic dyes consist of donor (D) and acceptor/anchor (A) moieties connected with a π-bridge system, forming a so-called push–pull structure. Due to this structure of dye molecules, intramolecular electron-charge transfer takes place on absorption of light (Figure 1).
Figure 1. The diagramatic structure of a push-pull organic dye-sensitizer.

It should be noted that the acceptor moiety of a dye-sensitizer has a significant influence for electron-transfer processes and optical absorption of the dye. Besides that, it serves for anchoring of dye molecules onto the semiconductor surface. In contrast to a diversity of electron-donating groups and π-bridges for effective sensitizers, a limited number of acceptors have been reported in the literature. One of the commonly used acceptor/anchor moieties is 2-cyanoacrylic acid.\textsuperscript{5-7} In this connection the development of novel acceptors/anchors for dye-sensitizers is a very crucial task to enhance performance of DSSCs.

Results and Discussion

In this paper we report the synthesis of two novel dyes bearing a 5-(methylidene)barbituric acid fragment, as a new acceptor/anchor group, and a carbazole unit, as a donor, which has recently been used successfully for the design of efficient dye-sensitizers.\textsuperscript{8-10} Moreover, two novel related sensitizers with 2-cyanoacrylic acid, as a classical acceptor/anchor group, were prepared for comparison of their properties. Thus, the carbazol-3-ylboronic acid 4 was obtained from 3-bromocarbazole 3 according to a slightly modified literature procedure.\textsuperscript{11} The brominated compound 3 was prepared by using successive bromination with N-bromosuccinimide (NBS) and standard N-alkylation procedures from carbazole 1 (Scheme 1).\textsuperscript{12}
Scheme 1. Preparation of carbazol-3-ylboronic acid 4.

The aromatic aldehydes 5,6 bearing the carbazole unit were obtained in high yields using the Suzuki reaction between boronic acid 4 and 5-bromothiophene-2-carbaldehyde or 4-bromo-benzaldehyde, respectively. These cross-coupling reactions were carried out at ambient temperature in air for 24 hours, with 2 mol% trans-bis(dicyclohexylamine)palladium(II) acetate (DAPCy)\textsuperscript{13} as the catalyst (Scheme 2).

Scheme 2. Preparation of aldehydes 5,6.

The aldehydes 5 and 6 were used for the synthesis of push-pull dyes, as building-blocks containing the carbazole unit. Novel dyes 7,8 were obtained easily in excellent yields (compound 7, 96%; compound 8, 91%) by using the Knoevenagel condensation of aldehydes 5,6 with barbituric acid in glacial acetic acid under catalysis with piperidine at reflux for 5 hours. In a
similar way, dyes 9,10 were prepared in good yields under the same reaction conditions, starting from appropriate aldehydes and 2-cyanoacetic acid (compound 9, 81%; compound 10, 74%) (Scheme 3). It should be noted that incorporation of the fragments of 5-(methylidene)barbituric and 2-cyanoacrylic acids into the structure of dyes, as acceptor/anchor groups proceeded very smoothly.


The UV-visible absorption spectra of dyes 7-10 in ethanol solution (2×10^{-5} mol/L) and adsorbed on TiO₂ nanoparticles were recorded at ambient temperature (Figure 2 and 3). Adsorption of these dyes on a TiO₂ surface was carried out from their THF solutions (2×10^{-5} mol/L) at ambient temperature for 24 hours. Samples of TiO₂ coated with the dyes were washed with ethanol and dried at 120 °C under vacuum.

Figure 2. UV-vis spectra of dyes 7,9 and 8,10 in EtOH solution (2×10^{-5} mol/L).
The UV-spectra of dyes demonstrate maximum absorption wavelengths ($\lambda_{max}$) at 493 nm for 7, 489 nm for 8, 411 nm for 9, and 362 nm for 10 (Figure 2). These peaks are ascribed to the intramolecular charge transfer from the electron-donating parts in these molecules to their acceptor fragments. The corresponding maximum molar extinction coefficients ($\varepsilon$) for dyes 7-10 are 2.92×10$^4$, 1.89×10$^4$, 1.25×10$^4$, and 0.84×10$^4$ Lmol$^{-1}$cm$^{-1}$, respectively. The red-shifts of the absorption band for 5-(methylidene)barbituric dyes 7,8 are approximately 90–120 nm in comparison to 2-cyanoacrylic dyes 9,10, respectively. This trend continued after the dyes were anchoring on a TiO$_2$ surface, and $\lambda_{max}$ for dyes 7-10 were 531, 495, 426 and 418 nm, respectively (Figure 3). Compared to the spectrum in ethanol solution, a slight red-shift and broadening of the absorption peak was observed for all dyes on a TiO$_2$ surface, which can be attributed to the formation of J-type aggregates. These results show that 5-(methylidene)barbituric acid unit exhibits a stronger acceptor ability in the dye, thus increasing intramolecular charge transfer, and leading to the red-shift of absorption maximum with enhancement of molar extinction. It should be noted that the maximal visible light absorption is one of the most important characteristics of a dye-sensitizer for DSSC.

Figure 3. UV-vis spectra of dyes 7,9 and 8,10 anchoring on TiO$_2$.

Conclusions

We have obtained two novel dyes bearing a 5-(methylidene)barbituric acid fragment, as acceptor/anchor group, which have better characteristics for absorption visible light in comparison with those of the related dyes containing a 2-cyanoacrylic acid fragment (according to the maximum absorption wavelengths and corresponding molar extinction coefficients ($\varepsilon$) in their UV-spectra). In this respect, the 5-(methylidene)barbituric acid fragment is a new, promising acceptor/anchor unit for the design and further studies of novel dye-sensitizers for solar cell applications.
Experimental Section

General. $^1$H and $^{13}$C NMR spectra were obtained on Bruker DRX-400 and AVANCE-500 spectrometers with TMS as the internal standard. Elemental analysis was carried on a Eurovector EA 3000 automated analyzer. Melting points were determined on Boetius combined heating stages and are not corrected. IR spectra of samples (solid powders) were recorded on a Spectrum One Fourier transform IR spectrometer (Perkin Elmer) equipped with a diffuse reflectance attachment (DRA). Spectrum processing and band intensity determination were carried out using the special software supplied with the spectrometer. UV-visible spectra were recorded for a $2 \times 10^{-5}$ M EtOH solution with Shimadzu UV-2401PC spectrophotometer (Diffuse Reflection with Shimadzu integrating sphere for solid samples).

General procedure for the preparation of aldehydes 5,6. K$_3$PO$_4$ (890 mg, 4.2 mmol) was added to a solution of 5-bromothiophene-2-carbaldehyde (270 mg, 1.4 mmol) or 4-bromobenzaldehyde (260 mg, 1.4 mmol), (9-ethylcarbazol-3-yl)boronic acid 4 (360 mg, 1.5 mmol) and trans-bis(dicyclohexylamine)palladium(II) acetate (16 mg, 0.028 mmol, 2 mol%) in MeOH (15 mL). The resulting suspension was stirred at ambient temperature for 24 h. MeOH was evaporated under vacuum and the residue was suspended in CH$_2$Cl$_2$ (20 mL), filtered from inorganic salts and concentrated under vacuum. The resulting residue was purified by flash chromatography of silica gel with CHCl$_3$/n-hexane (1:1) to remove by-products and then with EtOAc to give the appropriate aldehyde, 5 or 6.

5-(9-Ethyl-9H-carbazol-3-yl)thiophene-2-carbaldehyde (5). Orange needles, yield 365 mg (85%), mp 145-6 °C (EtOAc); $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 9.88 (s, 1H, CHO), 8.40 (d, $J$ 1.7 Hz, 1H), 8.14 (d, $J$ 7.7 Hz, 1H), 7.78 (dd, $J$ 8.5, 1.9 Hz, 1H), 7.75 (d, $J$ 3.9 Hz, 1H), 7.54 – 7.47 (m, 1H), 7.46 – 7.41 (m, 3H), 7.30 – 7.26 (m, 1H), 4.38 (q, $J$ 7.3 Hz, 2H, CH$_2$), 1.46 (t, $J$ 7.3 Hz, 3H, CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 182.6, 156.3, 141.2, 140.5, 137.8, 126.4, 124.4, 124.1, 122.9, 122.7, 120.7, 119.6, 118.6, 118.9, 110.9, 108.3, 37.8, 13.8; IR(DRA): 416, 504, 551, 583, 625, 663, 725, 742, 789, 867, 917, 1066, 1054, 1155, 1126, 1231, 1271, 1345, 1382, 1431, 1474, 1523, 1597, 1628, 1657, 1733, 1869, 2797, 2969, 3059 cm$^{-1}$; Anal. Calcd for C$_{19}$H$_{15}$NOS: C, 74.73; H, 4.95; N, 4.59. Found: C, 74.34; H, 4.92; N, 4.94.

4-(9-Ethyl-9H-carbazol-3-yl)benzaldehyde (6). Colourless crystals, yield 375 (89%), mp 152-3 °C (EtOAc); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 10.06 (s, 1H, CHO), 8.38 (d, $J$ 1.4 Hz, 1H), 8.16 (d, $J$ 7.8 Hz, 1H), 7.97 (d, $J$ 8.4 Hz, 2H), 7.88 (d, $J$ 8.3 Hz, 2H), 7.76 (dd, $J$ 8.5, 1.8 Hz, 1H), 7.59 – 7.38 (m, 3H), 7.30 – 7.25 (m, 1H), 4.40 (q, $J$ 7.2 Hz, 2H, CH$_2$), 1.47 (t, $J$ 7.2 Hz, 3H, CH$_3$); $^{13}$C NMR (126 MHz, CDCl$_3$) $\delta$ 192.0, 148.27, 140.5, 140.1, 134.5, 130.6, 130.4, 127.6, 126.2, 125.2, 123.7, 123.0, 120.6, 119.4, 119.3, 109.0, 108.8, 37.7, 13.9; IR(DRA): 521, 689, 737, 757, 802, 836, 905, 942, 1024, 1084, 1126, 1168, 1213, 1235, 1282, 1306, 1333, 1379, 1449, 1475, 1594,
1688, 2743, 2838, 2978, 3054 cm\(^{-1}\); Anal. Calcd for C\(_{21}\)H\(_{17}\)NO\(_{0.05}\)CH\(_3\)CO\(_2\)C\(_2\)H\(_5\): C, 83.82; H, 5.77; N, 4.61. Found: C, 83.74; H, 5.62; N, 4.76.

**General procedure for the preparation of dyes 7-10.** The appropriate aldehyde 5 (153 mg, 0.5 mmol) or 6 (150 mg, 0.5 mmol) and barbituric acid (128 mg, 1 mmol) or 2-cyanoacetic acid (85 mg, 1 mmol) were added to glacial acetic acid (10 mL) and the suspension was warmed to obtain a clear solution. Piperidine (170 mg, 0.2 mL, 2 mmol) was added and the reaction mixture was stirred at 120 °C for 5 h. The precipitate of product was filtered off and washed with MeOH (5×5 mL) and then dried at 100 °C to give a pure appropriate dye, 7-10.

5-\{5-(9-Ethyl-9\(H\)-carbazol-3-yl)thiophen-2-yl\}methylene|pyrimidine-2,4,6(1\(H\),3\(H\),5\(H\))-trione (7). Dark-red powder, yield 200 mg (97%), mp 242-1 °C (AcOH); \(^1\)H NMR (500 MHz, DMSO-\(d_6\) ) \(\delta\) 11.26 (s, 1H, NH), 11.24 (s, 1H, NH), 8.70 (d, J 1.6 Hz, 1H), 8.51 (s, 1H), 8.33 (d, J 7.7 Hz, 1H), 8.22 (d, J 4.2 Hz, 1H), 7.96 (dd, J 8.6, 1.7 Hz, 1H), 7.86 (d, J 4.1 Hz, 1H), 7.74 (d, J 8.6 Hz, 1H), 7.66 (d, J 8.3 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.27 (t, J 7.4 Hz, 1H), 4.49 (q, J 7.0 Hz, 2H, CH\(_2\) ), 1.34 (t, J 7.1 Hz, 3H, CH\(_3\) ); \(^{13}\)C NMR (126 MHz, DMSO-\(d_6\) ) \(\delta\) 163.6, 163.2, 160.6, 150.3, 147.9, 145.7, 140.4, 140.1, 134.4, 126.5, 124.4, 124.1, 123.8, 122.9, 122.1, 120.9, 119.5, 118.6, 110.0, 109.5, 109.4, 37.2, 13.7; IR(DRA): 463, 525, 509, 552, 622, 750, 729, 797, 855, 967, 1086, 1124, 1155, 1191, 1235, 1297, 1258, 1347, 1393, 1448, 1471, 1506, 1544, 1595, 1657, 1692, 1734, 1942, 2171, 2830, 2974, 3058, 3188, 3180 cm\(^{-1}\); Anal. Calcd for C\(_{23}\)H\(_{17}\)N\(_3\)O\(_3\)S\(_{0.5}\)H\(_2\)O: C, 65.08; H, 4.27; N, 9.90. Found: C, 65.15; H, 4.02; N, 9.87.

5-[4-(9-Ethyl-9\(H\)-carbazol-3-yl)benzylidene|pyrimidine-2,4,6(1\(H\),3\(H\),5\(H\))-trione (8). Red powder, yield 185 mg (91%), mp 211-2 °C (AcOH); \(^1\)H NMR (500 MHz, DMSO-\(d_6\) ) \(\delta\) 11.39 (s, 1H, NH), 11.26 (s, 1H, NH), 8.69 (d, J 1.5 Hz, 1H), 8.37 – 8.32 (m, 3H), 8.29 (d, J 7.7 Hz, 1H), 7.97 (d, J 8.6 Hz, 2H), 7.94 (dd, J 8.6, 1.7 Hz, 1H), 7.73 (d, J 8.6 Hz, 1H), 7.25 (t, J 7.4 Hz, 1H), 4.49 (q, J 7.1 Hz, 2H, CH\(_2\) ), 1.35 (t, J 7.1 Hz, 3H, CH\(_3\) ); \(^{13}\)C NMR (126 MHz, DMSO-\(d_6\) ) \(\delta\) 163.6, 163.2, 160.6, 150.3, 147.9, 145.7, 140.4, 140.1, 134.4, 126.5, 124.4, 124.1, 123.8, 122.9, 122.1, 120.9, 119.5, 118.6, 110.0, 109.5, 109.4, 37.2, 13.7; IR(DRA): 463, 525, 509, 552, 622, 750, 729, 797, 855, 967, 1086, 1124, 1155, 1191, 1235, 1297, 1258, 1347, 1393, 1448, 1471, 1506, 1544, 1595, 1657, 1692, 1734, 1942, 2171, 2830, 2974, 3058, 3188, 3410 cm\(^{-1}\); Anal. Calcd for C\(_{25}\)H\(_{19}\)N\(_3\)O\(_3\)\(_{0.2}\)H\(_2\)O: C, 72.70; H, 4.73; N, 10.17. Found: C, 72.68; H, 4.49; N, 10.24.

2-Cyano-3-[5-(9-ethyl-9\(H\)-carbazol-3-yl)thiophen-2-yl]acrylic acid (9). Red powder, yield 150 mg (81%), mp 195-6 °C (AcOH); \(^1\)H NMR (500 MHz, DMSO-\(d_6\) ) \(\delta\) 13.66 (br.s, 1H, CO\(_2\)H), 8.65 (d, J 1.7 Hz, 1H), 8.50 (s, 1H), 8.31 (d, J 7.7 Hz, 1H), 8.05 (d, J 4.1 Hz, 1H), 7.88 (dd, J 8.6, 1.8 Hz, 1H), 7.81 (d, J 4.0 Hz, 1H), 7.72 (d, J 8.6 Hz, 1H), 7.66 (d, J 8.2 Hz, 1H), 7.55 – 7.48 (m, 1H), 7.26 (t, J 7.4 Hz, 1H), 4.48 (q, J 7.1 Hz, 2H, CH\(_2\) ), 1.34 (t, J 7.1 Hz, 3H, CH\(_3\) ); \(^{13}\)C NMR (126 MHz, DMSO-\(d_6\) ) \(\delta\) 163.84, 155.28, 146.69, 141.86, 140.23, 140.15, 133.23, 126.47, 124.34, 123.84, 123.29, 122.86, 122.05, 120.93, 119.43, 118.48, 116.67, 110.00, 109.53, 96.78, 37.16, 13.69; IR(DRA): 460, 513, 533, 550, 573, 589, 629, 654, 722, 729, 752, 797, 818, 894, 930, 972, 1065, 1023, 1125, 1089, 1157, 1272, 1293, 1350, 1390, 1433, 1471, 1492, 1506, 1577,
1627, 1663, 1687, 2219, 2508, 2597, 2815, 2965, 3062, 3088 cm⁻¹; Anal. Calcd for C₂₂H₁₆N₂O₂S: C, 70.95; H, 4.33; N, 7.52. Found: C, 70.82; H, 4.35; N, 7.65.

2-Cyano-3-[4-(9-ethyl-9H-carbazol-3-yl)phenyl]acrylic acid (10). Orange powder, yield 135 mg (74%), mp 190-1 °C (AcOH); ¹H NMR (400 MHz, DMSO-d₆) δ 13.93 (s, 1H, CO₂H), 8.68 (s, 1H), 8.28 (d, J 7.7 Hz, 1H), 8.18 (d, J 8.4 Hz, 2H), 7.93 (d, J 8.6 Hz, 1H), 7.74 (d, J 8.6 Hz, 1H), 7.65 (d, J 8.2 Hz, 1H), 7.50 (t, J 7.5 Hz, 1H), 7.25 (t, J 7.5 Hz, 1H), 4.49 (q, J 7.1 Hz, 2H, CH₂), 1.34 (t, J 7.1 Hz, 3H, CH₃); ¹³C NMR (126 MHz, DMSO-d₆) δ 163.48, 153.88, 145.57, 140.05, 139.77, 131.49, 129.39, 129.15, 126.94, 126.10, 124.78, 122.93, 122.35, 120.67, 119.09, 119.06, 116.41, 109.67, 109.34, 102.16, 37.07, 13.67; IR(DRA): 459, 517, 552, 580, 615, 626, 671, 726, 748, 766, 786, 798, 846, 894, 946, 1022, 1064, 1085, 1123, 1123, 1155, 1190, 1234, 1294, 1348, 1428, 1476, 1492, 1515, 1546, 1569, 1629, 1697, 2223, 2548, 2618, 2676, 2816, 2971, 3054 cm⁻¹; Anal. Calcd for C₂₄H₁₈N₂O₂: C, 78.67; H, 4.95; N, 7.65. Found: C, 78.32; H, 4.92; N, 7.49.

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