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Synthesis and characterization of two new dyes

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Abstract: Two novel aromatic carbazole-based structure dyes (AT and BT) were constructed facilely. Tree different reaction schemes were applied for synthesis. These reactions contain carbazole alkylation, formylation by Vilsmeier-Mayer reaction and ultimately Knoevenagel condensation. The structure of synthesized dye was study by IR, ^{1}HNMR, ^{13}CNMR analysis. The absorption properties of these novel carbazole base dyes were investigated by UV-Vis spectroscopy.

Keywords: Thiazolidine-2,4-dione, Carbazole, Knoevenagel condensation, Vilsmeier-Mayer reaction.

Introduction

One of the most important challenges ahead of human is to find replace for the fossil fuel. Therefore renewable energy sources are highly answering the demand of energy. The Sun is an obvious source of clean and cheap energy, already used by Nature. Therefore harnessing the power of the Sun with photovoltaic technologies appears to be the only reasonable large scale answer to the energy challenge. New generation of photovoltaic technologies are based on inorganic and organic dyes [1, 2]. Application of photovoltaic based on inorganic has some drawback such as: high costs and highly energy consuming preparation methods, several of those materials, like CdTe, are toxic and have low natural abundance. Application of organic dye in photovoltaic can avoids those problems. The efficiencies of organic-based photovoltaic cells are still behind those obtained with purely inorganic based photovoltaic technologies [3, 4].

In order to applying a dye in photovoltaic it is important to adsorb the dye molecule uniformly within the whole negative electrode material, Such as titanium dioxide (TiO_2) thin films [5]. The optimal adsorption is extremely dependent on the structure of dye. Conventional organic photovoltaic devices use donor-π-conjugation-bridge-acceptor (D-π-A) structure. Many kinds of organic dyes by D–π–A structure have been developed in recent year, such as dyes based on: carbazole [6,7], fluorene [8–10], coumarin [11,12], merocyanine [13], hemicyanine [14,15], indoline [16,17], polyene [18], triphenylamine (TPA) [19–29], tetrahydroquinoline [30,31] and Phenoxazine [32].

In organic dyes, the electron acceptor parts have significant influences on the photovoltaic properties due to the excited electrons from the dye molecules are injected to the semiconductor film through the acceptor parts. In this study, we have designed and synthesized a novel class of dyes carrying thiazolidine-2,4-dione as the new acceptor group, structures of the dyes that possess a donor–acceptor unit are shown in Scheme **1**. The structure of novel dyes was well characterized.

Results and discussion

Design and synthesis of sensitizers:

AT and BT were synthesized by a three-step reactions sequence which is depicted in Scheme **2**. In

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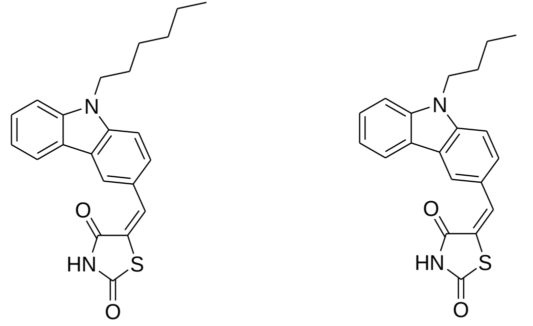
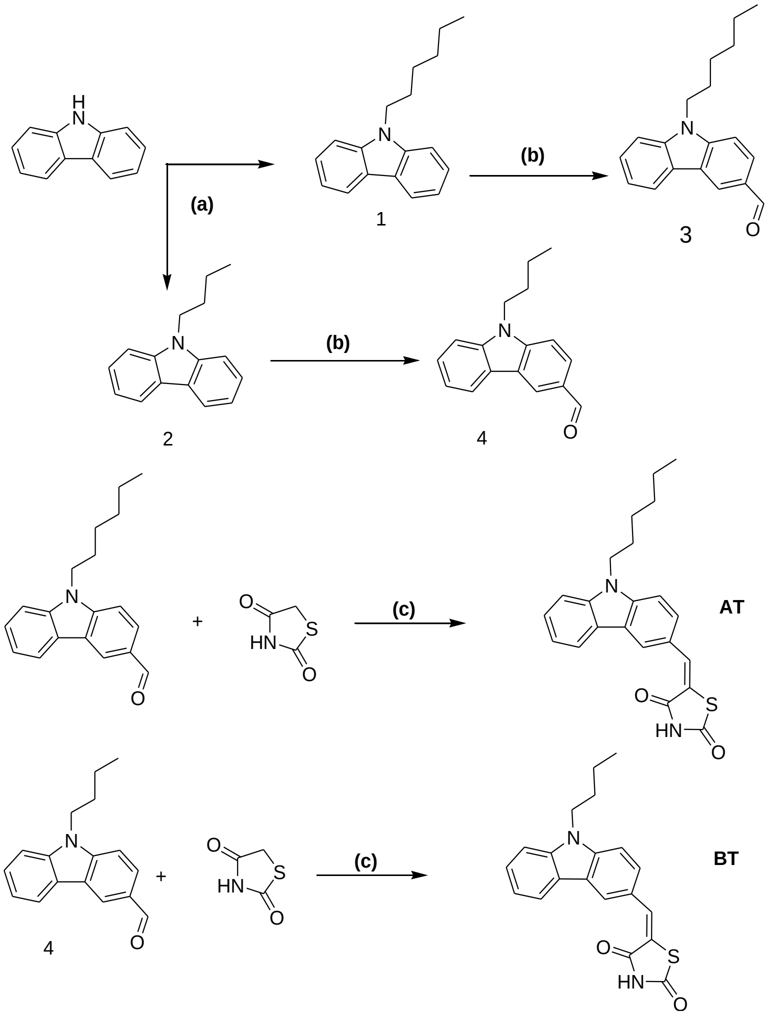
*Corresponding author. Tel: (+98) 741 2223048, Fax: (+98) 741 3342172, E-mail: salimibeni@mail.yu.ac.ir the first step 9-Hexyl-9H-carbazole and 9-Butyl-9H-carbazole were synthesized by application of carbazole, hexylbromide and butylbromide in the presence of NaOH in DMSO as solvent. The yield of this reaction was good and about 85%.



AT **BT**

Scheme 1: Chemical structure of designed dyes AT and BT.

Application of the alkyl group in dye structure cause less aggregation of dyes in the TiO_2 surface in solar cell. In the next step 9-alkyll-9H-carbazole formylated by Vilsmeier-Mayer reaction, for this purpose 9-Hexyl-9H-carbazole and 9-Butyl-9H-carbazole react by $POCl_3$ in the presence of DMF as reagent and solvent. Terminate step was include the reaction of 9-alkyl-9H-carbazole-3-carbaldehyde by thiazolidine-2,4-dione as acceptor units. This active methylene compound has been reacted by 9-alkyl-9H-carbazole-3-carbaldehyde via Knoevenagel condensation. In order to synthesis of AT and BT, formilated product has been reacted by ammonium acetate in acetic acid media. The overall yield for synthesis of AT and BT was 50 and 54%.



Scheme 2: Synthetic routes of AT and BT (a) 1-Bromoalkyl, NaOH, DMSO, 110℃, overnight (b) $POCl_3$, DMF, 95℃, overnight (c) Acetic acid, Ammonium acetate, 90℃, 10 h.

UV–Vis absorption spectra:

Dye is an essential and unique component in the preparation of dye-sensitized solar cells. This component plays a significant role for the DSSCs achieving high conversion efficiency. Actually its function is light harvesting. Therefore, in order to investigation the dyes capabilities; we measure the absorption spectra of the dyes.

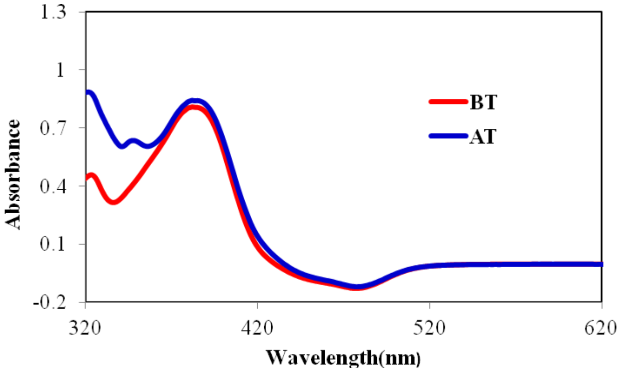


Figure 1: Absorption spectra of dyes AT and BT in THF.

Figure **1** shows the absorption spectra of AT and BT observed in THF. The UV-vis spectra of 1 and 2 in THF exhibit two intense absorption bands appearing in the region of 320-335 nm and 350-450 nm. Their maximum values (λmax) are observed at 314, 380 nm for AT and 323, 380 nm for BT, respectively. A relative intense absorption was observed at longer wavelength in our cases. The biggest pick for both dyes is the same. AT shows three picks in 310-450 nm but BT shows two picks, it may attribute the higher alkyl length in AT.

Conclusion

In this study, we have designed and synthesized two novel carbazole-based D–π–A dyes (AT and BT), by applying thiazolidine-2,4-dione as acceptor. Two alkyl include hexyl and butyl was used as donor group. These synthesized dyes were confirmed by FT-IR, ^{1}H and ^{13}C NMR. In order to investigate dyes absorption, UV-Vis was applied.

Experimental

Materials and characterization:

All solvents and other chemicals were reagent grade and used without further purification all chemical were purchased from Merck and Sigma Aldrich. Melting points were measured on an elecrtothermal KSB1N apparatus. TLC was performed on TLC-Grade silica gel-G/UV 254 nm plates (*n*-hexane and ethyl acetate). ^{1}H, ^{13}C NMR spectra were recorded on a FT-NMR Bruker Advance ultra-shield spectrometer (frequency line; 400. MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR ; solvents, $CDCl_3$ and DMSO-d_6) . FT-IR spectra were recorded in the matrix of KBr with JASCO FT-IR-680 plus spectrometer. Absorption spectra were measured with Perkin Elmer (Lambda 25) UV–VIS spectrophotometer.

Synthesis of dyes:

Synthesis of 9-Hexyl-9H-carbazole (1):

To a stirred solution of carbazole (0.20 g, 1.1 mmol) in DMSO (3 mL), NaOH (0.40 g) was added. Then the corresponding hexylbromide (0.33g, 1.01 mmol) was added drop wise. After complete addition, the reaction mixture was heated under reflux overnight. The organic layer was separated, washed with water, dried over $MgSO_4$ and concentrated. Pure product was obtained after silica gel column chromatography (normal hexane) as a white solid.

White powder, yield 85%, m.p = 75-77 ℃ ^{1}HNMR (400 MHz, $CDCl_3$) δ (ppm): 0.87 (t, *J*=7.043 Hz, 3H), 1.26–1.43 (m, 6H), 1.87 (m, 2H), 4.30 (t, *J*=7.043 Hz, 2H), 7.22 (t, *J*=7.825 Hz, 2H), 7.40–7.48 (m, 4H), 8.09 (d, *J*=7.825 Hz, 2H), ^{13}CNMR (100 MHz, $CDCl_3$) δ (ppm): 14.6, 23.1, 27.5, 29.4, 32.1, 43.4, 109.2, 119.2, 120.9, 123.3, 126.1and 140.9 IR (cm^{-1}): 3051, 2955, 2923, 2869, 2856, 1628, 1594, 1487, 1453, 1376, 1327, 1241, 1217, 1192, 1153 and 1128

Synthesis of 9-Butyl-9H-carbazole (2):

To a stirred solution of carbazole (0.2 g, 1.1 mmol) in DMSO (3 mL), NaOH (0.4 g) was added and then the corresponding n-butylbromide (0.137g, 1.01 mmol) was added drop wise. After complete addition, the reaction mixture was heated at 90 ℃ overnight. The organic layer was separated, washed with water, dried over Na_2SO_4 and concentrated. Pure product was obtained after silica gel column chromatography (normal hexane) as a white solid.

White powder, Yield: 83%, mp: 54-55 ℃, ^{1}HNMR (300 MHz, $CDCl_3$): 8.22 (m, 2H), 7.55 (m, 4H), 7.35 (m, 2H), 4.42 (t, *J*= 6.3 Hz, 2H), 1.98 (m, 2H), 1.52 (m, 2H), 1.06 (t, *J*= 7.2 Hz, 3H) ppm. FT-IR (cm^{-1}): 3043, 2953, 2928, 1918, 1625, 1591, 1482, 1463, 1348, 1325.

9-Hexyl-9H-carbazole-3-carbaldehyde (3):

Phosphorylchloride (1.55 mL, 1.25eq) was added drop wise to DMF (0.88mL, 1.15 eq) for 1 h at 0 ℃.

The mixture was stirred and then N-(hexyl) carbazole (0.25 g, 1 mmol) added over 1 h at room temperature. After standing for 5 hr. at 90 ℃, the mixture was poured into ice–water (30 mL), stirred 5h, and neutralized with sodium hydroxide. The solution was extracted three times with ethyl acetate and dried with $MgSO_4$. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/ n-hexane =1:9).

Cream powder, Yield: 55%, mp: 70-74 ℃, ^{1}HNMR (DMSO-d_6, 400 MHz) δ (ppm): 10.06 (s, 1H), 8.77 (s, 1H), 8.30 (d, *J* =8 Hz, 1H), 7.79 (d, *J* = 8Hz, 1H), 7.70 (m, 1H), 7.55 (m, 1H), 7.31 (t, 8Hz, 1H), 4.46 (t, *J*= 8 Hz, 2H), 1.77 (m, 2H), 1.25 (m, 6H) and 0.87 (t, *J*= 8 Hz, 3H), ^{13}CNMR (DMSO-d_6, 100 MHz) δ (ppm): 13.7, 22, 26, 28.4, 30.9, 42.5, 109.7, 110.2, 120, 120.7, 122.11, 122.2, 124, 126.6, 126.7, 128.2, 140.4, 142.6 and 192. IR (cm^{-1}): 3052, 2955, 2929, 2857, 2727, 1893, 1686, 1593, 1469, 1383, 1352, 1339, 1329, 1240, 1177, 1135, 807, 765, 748 and 730.

9-Butyl-9H-carbazole-3-carbaldehyde (4):

Phosphorylchloride (1.55 mL, 1.25eq) was added drop wise to N, N-dimethylformamide (DMF, 0.88mL, 1.15 eq) for 1 h at 0 ℃. The mixture was stirred and then N-(butyl) carbazole (0.25 g, 1 mmol) added over 1 h at room temperature. After standing for 5 hr. at 90℃, the mixture was poured into ice–water (30 mL), stirred 5h, and neutralized with sodium hydroxide. The solution was extracted three times with ethyl acetate and dried with Na_2SO_4. The solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/ n-hexane =1:9).

Cream powder, Yield: 55%, mp: 62-64 ℃, ^{1}HNMR (DMSO-d_6, 400 MHz) δ (ppm): 10.06 (s, 1H), 8.76 (s, 1H), 8.30 (d, *J*=8 Hz, 1H), 7.99 (m, 1H), 7.79 (d, *J*=8 Hz, 1H), 7.70 (d, *J*=8 Hz, 1H), 7.54 (m, 1H), 7.31 (t, *J*=7.6 Hz, 1H), 4.46 (t, *J*=8 Hz, 2H),1.76 (m, 2H),1.29 (m, 2H) and 0.87 (t, *J*=8 Hz, 3H) ^{13}CNMR (DMSO-d_6, 100 MHz) δ (ppm): 191.8, 143.4, 140.8, 128.2, 126.4, 124, 122.1, 120.8, 120.40, 110, 109.8, 42.2, 30.6, 19.8 and 13.8. FT-IR (cm^{-1}): 2985, 1691, 1625, 1594, 1473, 1352, 1133 and 808.

Synthesis of 5-(9-Hexyl-9H-carbazol-3-ylmethylene)-thiazolidine-2,4-dione (AT):

9-Hexyl-9H-carbazole-3-carbaldehyde (0.28 g, 1 mmol) and thiazolidine-2,4-dione (0.12 g, 1 mmol) and ammonium acetate(0.08g, 1mmol) were dissolved in acetic acid (1 mL). The reaction mixture was refluxed for 5h. The orange crystals thus obtained were filtered, washed with excess water three times. The dye AT obtained was purified by crystallization from EtOAc/n-hexane.

Yellow powder, Yield: 54%, ^{1}H NMR (400 MHz, DMSO-d_6, 20℃) δ (ppm): 11.36 (s, 2H), 11.27 (s,2H), 9.35 (s, 2H), 8.50 (s, 2H), 8.46 (d, j=16 Hz ,2H), 7.77 (d, j= 8 Hz, 2H), 4.48 (t, j=16 Hz, 2H), 1.78 (m, 2H), 1.22 (m, , 6H).0.77(t, j= 8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 20℃) δ (ppm): 141.4, 141.1, 133.8, 128.7, 128.1, 127.1, 124.4, 124.2, 123.7, 123.1, 122.3, 121.1, 120.2, 119.8, 110.7, 110.4, 42.7, 31.4, 20.2 and 14.1. FT-IR (KBr/cm^{-1}): 3432, 1685, 1583, 1335, 1098, 790and 470

Synthesis of 5-(9-Butyl-9H-carbazol-3-ylmethylene)-thiazolidine-2,4-dione (BT):

9-Butyl-9H-carbazole-3-carbaldehyde and thiazolidine-2,4-dione (0.12 g, 1 mmol) and ammonium acetate(0.08g, 1mmol) were dissolved in acetic acid (1 mL). The reaction mixture was refluxed for 5h. The orange crystals thus obtained were filtered, washed with excess water three times. The dye BT obtained was purified by crystallization from EtOAc/n-hexane.

Yellow powder, Yield: 50%, ^{1}H NMR (400 MHz, DMSO-$d_{6,}$ 20 ℃) δ (ppm): 12.48 (s, 1H), 8.4 (s, 1H), 8.20 (d, j=8, 1H), 7,95 (s, 1H), 7.70 (d, j=8 Hz, 1H), 7.63 (m, 2H), 7.50 (d, j=8, 1H),7.26 (t, j=8, 1H), 4.37 (t, j=8 2H), 1.73 (m , 2H), 1.19 (m, 6H), 0.77 (t, j=4, 3H). ^{13}C NMR (100 MHz, DMSO-d_6, 20℃) δ (ppm): 168.7, 168.1, 141.4, 141.1, 133.8, 128.1, 127.1, 124.2, 123.7, 123.1, 122.3, 121.1, 120.2, 119.7, 110.7, 110.3, 42.9, 31.4, 28.9, 26.5, 22.4 and 14.3. FT-IR (KBr/cm^{-1}): 3439, 2924, 2854, 1731, 1682, 1577, 1492, 1318, 1146 and 1021.

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