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Unsymmetrical and symmetrical azines toward application in organic photovoltaic

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ABSTRACT

The unsymmetrical and symmetrical azines prepared by condensation of benzophenone hydrazone with (di)aldehydes with thiophene rings were reported in this study The structures of obtained compounds were characterized by FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopy as well as elemental analysis. Optical, electrochemical, and thermal properties of azines were investigated. The unsymmetrical azine with bithiophene unit exhibited liquid crystalline properties as was detected by DSC and POM experiments. All compounds are electrochemically active, however, only azines with bithiophene structure undergo reversible reduction process as was found in cyclic and differential pulse voltammetry (CV and DPV) studies. Additionally, the electronic properties, that is, orbital energies and resulting energy gap were calculated theoretically by density functional theory (DFT). The photovoltaic properties of two azines as active layer in organic solar cells at the configuration ITO/PEDOT:PSS/active layer/Al under an illumination of 1.3 mW/cm^2 were studied. Active cell layers blends of poly 3-hekxylthiophene (P3HT) or poly 3-butylthiophene (P3OT) with azines were applied. The device comprising P3HT with symmetrical azine containing bithiophene unit showed the highest value of power conversion efficiency (0.82%). To the best of our knowledge, the azines are very seldom considered as potential compounds in active layer in bulk heterojunction (BHJ) solar cells.

1. Introduction

Azines, that is, N—N linked diimines (R—CH═N—N═CH—R) are a class of very interesting organic compounds and have attracted plenty of research interest, due to their unique properties [1,2]. They are used for production of various type of pigments, dyes [3], and synthetic intermediates for preparation of heterocyclic compounds such as pyrazoles, purines and pyrimidines [4]. They exhibit antimicrobial [5], anticancer [6] and herbicidal [6a] properties. Due to the presence of imine groups with N—N bridge in their structure, they are used as ligands for the organometallic systems [7]. Azines show also interesting optical [8] and conductive [9] properties, which seem to be promising for organic (opto)electronics [10]. Compounds containing the diazabutadiene (—C═N—N═C—) linkers have been investigated as highly luminescent, covalent organic frameworks [11]. It is also important to note that azines are the subjects of intensive study as highly polar materials, they have been investigated as potential, novel linear and nonlinear optical materials [12]. They have been also studied as photosensitizers in solar cells [13] or as liquid crystals [14]. Considering various π-spaces, that is, vinylene, azine, arylimine and ethynylene it was found that vinylene and azine have the more favorable effect on the absorption spectrum and redox properties [15]. The research described in this work is the continuation of our efforts in the search of organic materials both polymers and low molecular weight compounds and for applications in organic (opto)electronics [10a,16].

This study concerns azines as potential compounds for organic optoelectronics and focuses on azines derived from benzophenone hydrazone and (di)aldehydes containing thiophene rings considering bulk-heterojunction (BHJ) solar cells applications. Organic solar cells based on π-conjugated compounds have attracted considerable attention over the past decades and efforts have focused on

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improving the device performances through developments of new materials and functional layers with providing a promising power conversion efficiency (PCE) [17]. A widely investigated the organic solar cell is BHJ device, which consists of a blend of an electron acceptor and a light absorbing polymer, which is hole transporter [18].

The compounds structurally similar to the ones reported in this paper have already been described in literature [19–23]. However, their electrochemical and photovoltaic properties have not been investigated and described. The synthesis of azine in our work denoted as BBA (obtained from benzophenone hydrazone and benzaldehyde) was first described by Curtius in 1891 [20] and its absorption properties in ethanol solution was reported in 1946 [21]. The new solvent-free reaction of benzophenone hydrazone with benzophenone using sulfated titania as catalytic system was also recently described by the Swaminathan group [4a]. Isomer of azine in our work denoted as BTD (synthesized from 2-thiophenealdehyde) have been prepared using benzophenone hydrazone and 3-bromothiophene-2-carboxaldehyde [22]. Moreover, a new, selective and mild synthesis of unsymmetrical azines from aromatic aldehydes and hydrazine sulfate in triethylamine has been reported recently [23]. This paper presents a comprehensive study of obtained azines; their physical properties such as thermal (DSC), optical (UV–Vis), and electrochemical (CV and DPV) were investigated and discussed in relation to their chemical structure. Additionally, HOMO, LUMO levels and E_g were calculated theoretically using density functional theory (DFT). Moreover, the photovoltaic activity of two azines as active layer in organic solar cells at the configuration ITO/PEDOT:PSS/active layer/Al under an illumination of 1.3 mW/cm^2 were studied. It should be stressed that, to the best of our knowledge, the azines are seldom studied in the context of being potential compounds in active layers in BHJ device [33].

2. Experimental

2.1. Materials

Benzophenone hydrazone, 2-thiophenealdehyde, 2,5-thiophenedialdehyde (99%), 2,2′-bithiophene-5-aldehyde (97%), trifluoroacetic acid, N,N-dimethylacetamide (DMA), trifluoroacetic acid were used from Aldrich. Ethanol anhydrous and benzaldehyde were purchased from POCH. 2,2′-bithiophene-5,5′-dialdehyde was prepared according to procedure described previously [24]. Indium tin oxide deposited on a glass (ITO), PEDOT:PSS (poly(3,4-ethylenedioxythiophene)poly(styrenesulfonate)) and P3HT (poly 3-hekxylthiophene) and P3OT (poly 3-butyllthiophene) were provided by Sigma–Aldrich.

2.2. Synthesis of obtained azines

2.2.1. Synthesis of benzaldehyde-benzophenone azine (BBA)

1 mmol (0.106 g) of benzaldehyde and 1 mmol (0.196 g) of benzophenone hydrazone were dissolved in 3 ml ethanol and then 2 drops of trifluoroacetic acid were added. This solution was heated at 70 °C under argon atmosphere. After 2 min orange product started to precipitated. The reaction mixture was stirred for 3 h. The precipitate was filtered, washed several times with ethanol and dried at 60 °C in vacuum.

Yield: 30%, m.p. = 223. ^{1}H NMR (CDCl$_3$), (ppm), δ: 8.67 (s, —CH═N, 1H), 7.86–7.82 (m, 4H,), 7.48–7.43 (m, 6H), 7.45–7.36 (m, 3H), 7.29–7.25 (m, 2H). ^{13}C NMR (CDCl$_3$, δ, ppm): 162.11 (—CH═N). FTIR (cm^{-1}): 3048, 2942 (CH aromatic), 1627 (CH═N stretching), 1566 (C═C stretching deformations in phenyl ring). Elem. anal.: found(calcd)% C 84.80(84.48), H 5.50(5.67), N 9.47(9.85).

2.2.2. Synthesis of benzophenone-(thiophene-2-aldehyde) azine (BTA)

0.75 mmol (0.084 g) of 2-thiophenealdehyde and 0.5 mmol (0.098 g) of benzophenone hydrazone were dissolved in 1 ml DMA. This solution was heated at 160 °C under argon atmosphere for 7 h and at 170 °C for 13 h. The product was precipitated in ethanol. The precipitate was filtered, washed several times with ethanol and dried at 60 °C in vacuum.

Yield: 29%, m.p. = 166 °C. ^{1}H NMR (CDCl$_3$, δ, ppm): 8.73 (s, —CH═N, 1H), 7.85–7.82 (m, 2H), 7.72–7.69 (m, 2H), 7.63–7.61 (m, 1H), 7.46–7.38 (m, 5H), 7.25–7.23 (m, 1H), 7.12 (dd, J = 5.0, 3.6 Hz, 1H), 7.08 (dd, J = 5.0, 3.6 Hz, 1H). ^{13}C NMR (CDCl$_3$, δ, ppm): 155.77 (—CH═N). FTIR (cm^{-1}): 3102, 3008 (CH aromatic), 1600 (CH═N stretching), 1573 (C═C stretching deformations in phenyl ring). Elem. anal.: found(calcd.)% C 75.19(74.45), H 4.87(4.85), N 9.37(9.40).

2.2.3. Synthesis of bis-benzophenone-(thiophene-2,5-dialdehyde) diazine (BTD)

0.5 mmol (0.07 g) of 2,5-thiophenedialdehyde and 1 mmol (0.1963 g) of benzophenone hydrazone were dissolved in 2 ml ethanol and then 1 drop of trifluoroacetic acid was added. This solution was heated to 65 °C under argon atmosphere. At 40 °C yellow product started to precipitate. After 1 h yellow product transformed into orange product. The reaction mixture was stirred for 3 h. The precipitate was filtered, washed several times with ethanol and dried at 60 °C in vacuum.

Yield: 92%, m.p. = 197 °C. ^{1}H NMR (CDCl$_3$), (ppm), δ: 8.63 (s, —CH═N, 2H), 7.69–7.68(m, 4H,), 7.43–7.38 (m, 12H), 7.32–7.29,(m, 5H) 7.30 (s, 1H). ^{13}C NMR (CDCl$_3$, δ, ppm): 166.86 (—CH═N). FTIR (cm^{-1}): 3051, 2981 (CH aromatic), 1664 (CH═N stretching), 1593 (C═C stretching deformations in phenyl ring). Elem. anal.: found(calcd)% C 76.44 (77.39), H 4.64(4.87), N 11.06(11.28).

2.2.4. Synthesis of benzophenone-(2,2′-bithiophene-5-aldehyde) azine (BBTA)

0.5 mmol (0.1 g) of 2,2′-bithiophene-5-aldehyde and 0.5 mmol (0.098 g) of benzophenone hydrazone dissolved in 2 ml ethanol and then 2 drops of trifluoroacetic acid were added. This solution was heated to 65 °C under argon atmosphere. After 1 h orange product started to precipitated. The reaction mixture was stirred for 6 h. The precipitate was filtered, washed several times with ethanol and dried at 60 °C in vacuum.

Yield: 63%, m.p. = 190 °C (LC formation). ^{1}H NMR (CDCl$_3$), (ppm), δ: 8.71 (s, —CH═N, 1H), 7.49–7.46 (m, 2H), 7.42–7.37 (m, 3H), 7.34–7.31 (m, 4H), 7.30–7.28 (m, 4H), 7.18 (d, J = 3.8 Hz, 1H), 7.06 (dd, J = 4.9, 3.7 Hz, 1H). ^{13}C NMR (CDCl$_3$, δ, ppm): 158.90 (—CH═N). FTIR (cm^{-1}): 3062, 2922 (CH aromatic), 1611 (CH═N stretching), 1500 (C═C stretching deformations in phenyl ring). Elem. anal.: found (calcd)% C 71.40 (70.93), H 4.39(4.33), N 7.92(7.52).

2.2.5. Synthesis of bis-benzophenone-(2,2′-bithiophene-5,5′-dialdehyde) diazine (BBTD)

0.25 mmol (0.055 g) of 2,2′-bithiophene-5,5′-dialdehyde and 0.5 mmol (0.098 g) of benzophenone hydrazone were dissolved in 3 ml ethanol. This solution was heated at 70 °C under argon atmosphere. After 20 min orange product started to precipitated. The reaction mixture was stirred for 3 h. The precipitate was filtered, washed several times with ethanol and dried at 60 °C in vacuum.

Yield: 43%, m.p. = 221 °C. ^{1}H NMR (CDCl$_3$), (ppm), δ: 8.65 (s, —CH═N, 2H), 7.85–7.83 (m, 4H,), 7.70–7.69 (m, 2H), 7.45–7.29 (m, 16H), 7.18–7.17 (m, 2H). ^{13}C NMR (CDCl$_3$, δ, ppm): 166.63