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Spectroscopic, electrochemical, thermal properties and electroluminescence ability of new symmetric azomethines with thiophene core

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ABSTRACT

Six novel azomethines with substituted thiophene central core were synthesized and their properties are reported. They were obtained by the condensation reaction between 2,5-diamino-thiophene-3,4-dicarboxylic acid diethyl ester and various aldehydes. The imines were characterized by NMR and FTIR spectroscopies and by elemental analysis. DSC measurements revealed that the prepared compounds are molecular glasses (except for one) with high T_g varying from 94 and 183 °C. Their redox properties were investigated in solution by cyclic voltammetry and differential pulse voltammetry. It was found that all imines were electrochemically active and showed low values of energy band gap ranging from 1.61 to 1.78 eV. Photoluminescence measurements indicated that they emitted light in solution with quantum yield (Φ_{PL}) in the range of 1.2–14.3% and in solid state as film and blend with poly(methyl methacrylate) and binary blend with poly(9-vinylcarbazole) (PVK) and (2-(4-tert-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole) (PDB) with Φ_{PL} form 0.24–1.77% and from 0.52% to 1.66%, respectively. The density functional theory (DFT) was applied for calculating their geometries and frontier molecular orbitals. Their electroluminescence ability was examined in guest-host diode with structure ITO/PEDOT:PSS/PVK:PBD:imine/Al and emission of light with maximum of emission band from 626 to 674 nm was observed. This work demonstrates, to the best of our knowledge, the first example of light emitting devices based on thiophene azomethines as active layer component.

1. Introduction

During the last decades appreciable amount of research has been focused on organic semiconductors for electronic applications including photovoltaics (OPV), light emitting diodes (OLED) and field effect transistors (FET). Although devices based on organic compound are commercially available, the development of new highly efficient and long-term stable optical and electrical processable organic semiconductors is still a challenge. The most important factors that determine the device performance include but are not limited to the type of materials and applied deposition processes and device design, with the crucial role played by used compounds [1]. Among the rich chemistry of various semiconductors, the conjugated compounds with chain nitrogen-containing, electron poor moieties, such as CH = N Schiff base linker, seem to be attractive for optoelectronics. The main representatives of this family, are azomethines, also named Schiff bases or imines [2–4]. Azomethines possess the ability to form liquid crystals and coordinating complexes with metals, are characterized with high thermal stability; being isoelectronic to their vinylene analogues and exhibit therapeutic activity, therefore they are widely used in different fields such as analytical chemistry, organic synthesis, medicine, biology, as well as in organic electronics as electrochromic material and photovoltaic (OPV) cell components [4–8]. They are interesting alternatives to conventional semiconductors due to both the possibility of tuning their properties by the proper choice of the precursors, that is, (di)amine and (di)aldehyde and the synthesis advantages. The strategy of preparation of conjugated compounds generally based on Suzuki-, Stille, Grignard-, Witting- and Kumada-coupling [9]. Compounds synthesized via listed methods need extensive purification to remove the catalysts and undesired byproducts. While azomethines are obtained in

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mild reaction conditions without metal catalyst, water is the only byproduct, thus purification is rather minimal. It was found that azomethines showed also good conductivity, comparable to a vinyl analogue, which can be useful for electronic applications [10]. It was demonstrated that azomethines bearing various 5-membered aryl heterocycles, especially thiophene derivatives, are perspective materials for optoelectronic applications [3–5,11–13]. Thiophene derivatives are considered to be promising building blocks for most organic functional materials studied for plastic electronics including electrochromic devices (ECD), OLED, OPV cells, and OFET [14]. Considering the enhanced properties of thiophene azometines relative to their homaryl counterparts reported by the Skene research group [4], we have undertaken a synthesis and characterization of new azomethines containing as a core thiophene derivative coupled with various homoaryl units. Their thermal (DSC, TGA), optical (UV–vis, PL), and electrochemical (CV) properties together with their ability to emit light under applied voltage were examined. Additionally, their electronic structure and photophysical properties were calculated by density functional theory (DFT). Recently, we have described the structure-property relationship for the series of symmetrical azomethines with 1,4-phenyl central core end-capped with anthracene, phenanthrene and pyrene units [15]. In connection with this, the properties of two imines reported herein, that is, prepared from 9-anthracenecarboxaldehyde and 1-pyrenecarboxaldehyde, are also discussed in relation to the analogous azomethines that differ in the central core structure reported in our previous article [15]. This comparison underlines the effect of thiophene ring substituted with carboxylic acid ethyl ester groups on thermal, optical and electrochemical characteristics.

2. Experimental section

2.1. Materials

9-Anthracenecarboxaldehyde, 1-pyrenecarboxaldehyde, 3-phenoxybenzaldehyde, 9-ethyl-3-carbazolecarboxaldehyde, 4-[(trimethylsilyl) ethynyl]benzaldehyde,N,N-dimethylacetamide (DMA), dimethylformamide (DMF), N-methyl-pyrrolidone (NMP), methanol, sulfur, ethyl cyanoacetate and triethylamine were purchased from Sigma-Aldrich. 4-(2-Phenyleth-1-ynyl)benzaldehyde was purchased from Chempur GmbH. 2,5-Diamino-thiophene-3,4-dicarboxylic acid diethyl ester (DAT) was synthesized according to publication [16].

2.2. Azomethines synthesis

The azomethines from 9-anthracenecarboxaldehyde and 1-pyrenecarboxaldehyde were synthesized using melt condensation. An aldehyde (0.5 mmol) was melted under argon atmosphere (9-anthracenecarboxaldehyde at 130 °C and 1-pyrenecarboxaldehyde at 180 °C), then DAT (0.25 mmol) was added and reaction mixture was stirred for 24 h. The product was dissolved in DMA and precipitated in methanol. The imines were purified by washing with hot methanol and dried at 80 °C in a vacuum oven for 4 h.

In the case of imine prepared from 3-phenoxybenzaldehyde, DAT (0.5 mmol) was dissolved in aldehyde (5.7 mmol) and reaction was carried out at 80 °C for 24 h. The product was purified by the Soxhlet extraction with hexane and dried at 80 °C in a vacuum oven for 4 h.

The other azomethines were synthesized from DAT (0.25 mmol) in DMA solution (1 mL) for 24 h at temperature 170, 150 and 130 °C using 9-anthracenecarboxaldehyde, 4-[(trimethylsilyl)ethynyl]benzaldehyde and 9-ethyl-3-carbazolecarboxaldehyde (0.5 mmol), respectively. Then the product was washed several times with methanol and dried at 80 °C in a vacuum oven for 4 h.

ThAz-1: Yield = 15%, ^{1}H NMR (600 MHz, CDCl$_3$, δ, ppm): 9.85 (s, 2H, HC=N), 9.13 (d, J = 8.7 Hz, 4H,CH), 8.60 (s, 2H,CH), 8.05 (d, J = 8.4 Hz, 4H,CH), 7.69 (ddd, J = 8.9, 6.5, 1.2 Hz, 4H,CH), 7.58–7.50 (m, 4H,CH), 4.47 (q, J = 7.2 Hz, 4H, O-CH$_2$-), 1.44 (t, J = 7.2 Hz, 6H, -CH$_3$). **^{13}C NMR** (151 MHz, CDCl$_3$, δ, ppm): 163.54, 159.94, 158.00, 151.24, 135.22, 133.26, 131.8 130.30, 129.34, 129.25, 129.09, 128.23, 127.27, 125.64, 125.51, 125.31, 124.90, 123.49, 60.27, 14.25. **FT-IR** (KBr, ν, cm^{-1}): 3047 (C-H aromatic), 2978, 2932 (C-H aliphatic), 1728 (C=O), 1622 (CH=N stretch), 1210 (C-N stretch). **Anal. Calcd** for $C_{40}H_{30}N_2O_4S$ (634.74): C,75.70; H,4.76; N,4.41; Found: C,75.20; H,4.09; N,4.31. **DSC**: I run: T$_m$ = 186 °C; II run: T$_g$ = 94 °C.

ThAz-2: Yield = 27%, ^{1}H NMR (600 MHz,CDCl$_3$, δ, ppm): 9.11 (s, 2H, HC=N), 9.09 (d, J = 9.2 Hz, 2H,CH), 8.47 (d, J = 7.9 Hz, 2H,CH), 8.15 (d, J = 7.4 Hz, 4H,CH), 8.12 (d, J = 8.5 Hz, 2H,CH), 8.06 (dd, J = 15.2, 7.1 Hz, 4H,CH), 8.02 (d, J = 12.7 Hz, 2H), 7.95 (t, J = 8.4 Hz, 2H), 4.55 (q, J = 7.1 Hz, 4H, O-CH$_2$-), 1.52 (t, J = 7.1 Hz, 6H, -CH$_3$). **^{13}C NMR** (151 MHz, CDCl$_3$, δ, ppm): 158.10, 134.07, 131.07, 130.88, 130.44, 129.53, 128.55, 127.34, 126.47, 126.26, 124.96, 122.94, 61.51, 14.39. **FT-IR** (KBr, ν, cm^{-1}): 3041 (-CH aromatic), 2979, 2931 (C-H aliphatic), 1728 (C=O), 1692 (CH=N stretch), 1232 (C-N stretch). **Anal. Calcd** for $C_{44}H_{30}N_2O_4S$ (682.78): C,77.40; H,4.43; N,4.10; Found: C,76.69; H,4.37; N,3.81. **DSC**: I run: T$_m$ = 221 °C; II run: T$_g$ = 128 °C.

ThAz-3: Yield = 21%, ^{1}H NMR (600 MHz,CDCl$_3$, δ, ppm): 8.60 (s, 2H, HC=N), 8.58 (s, 2H), 8.15 (d, J = 7.6 Hz, 2H), 8.08 (d, J = 7.4 Hz, 2H), 7.54–7.48 (m, 2H), 7.47–7.43 (m, 4H), 7.32–7.29 (m, 2H), 4.78–4.35 (m, 8H, -CH$_2$-), 1.52–1.42 (m, 12H, -CH$_3$). **^{13}C NMR** (151 MHz, CDCl$_3$, δ, ppm): 164.57, 154.37, 140.71, 140.46, 128.58, 126.73, 126.19, 123.20, 123.10, 120.82, 120.32, 109.14, 108.70, 96.16, 61.41, 60.18, 37.95, 14.45. **FT-IR** (KBr, ν, cm^{-1}): 3058 (C-H aromatic), 2974, 2935 (C-H aliphatic), 1718 (C=O), 1686 (CH=N stretch), 1233 (C-N stretch). **Anal. Calcd** for $C_{40}H_{36}N_4O_4S$ (668.80): C,71.84; H,5.43; N,8.38; Found: C,71.43; H,5.77; N,8.58. **DSC**: I run: T$_g$ = 144 °C; II run: T$_g$ = 183 °C.

ThAz-4: Yield = 12%, ^{1}H NMR (400 MHz, DMSO-d_6, δ, ppm) 8.63 (s, 2H, HC=N), 7.69 (d, J = 7.8 Hz, 2H,CH), 7.57 (t, J = 7.9 Hz, 2H,CH), 7.52 (s, 2H, CH), 7.48–7.38 (m, 4H, CH), 7.27 (dd, J = 7.7, 2.1 Hz, 2H, CH), 7.21 (t, J = 7.4 Hz, 2H, CH), 7.13–7.05 (m, 4H, CH), 4.17 (q, J = 7.1 Hz, 4H, O-CH$_2$-), 1.17 (t, J = 7.1 Hz, 6H, -CH$_3$). **^{13}C NMR** (101 MHz, DMSO-d_6, δ, ppm): 162.81, 160.88, 157.99, 156.44, 149.56, 137.32, 131.28, 130.69, 127.28, 125.42, 124.56, 123.13, 119.68, 117.49, 61.43, 14.46. **FT-IR** (KBr, ν, cm^{-1}): 3054 (C-H aromatic), 2987, 2936 (C-H aliphatic), 1730 (C=O), 1716 (CH=N stretch), 1254 (C-N stretch), 1152 (C-O-C). **Anal. Calcd** for $C_{36}H_{30}N_2O_6S$ (618.69): C, 72.32; H,5.00; N,4.53; Found: C,72.07; H,4.34; N,4.02. **DSC**: I run: T$_m$ = 127 °C.

ThAz-5: Yield = 17%, ^{1}H NMR (600 MHz,CDCl$_3$, δ, ppm): 8.39 (s, 2H, HC=N), 7.82 (d, J = 8.3 Hz, 4H, CH), 7.54 (d, J = 8.3 Hz, 4H, CH), 4.39 (q, J = 7.1 Hz, 4H, O-CH$_2$-), 1.38 (t, J = 7.1 Hz, 6H, -CH$_3$), 0.27 (s, 18H, Si-CH$_3$). **^{13}C NMR** (151 MHz, CDCl$_3$, δ, ppm): 163.12, 158.67, 149.66, 134.94, 132.40, 129.12, 127.70, 126.99, 104.47, 98.07, 61.44, 14.24. **FT-IR** (KBr, ν, cm^{-1}): 3071 (C-H aromatic), 2959 (C-H aliphatic), 2151 (C≡C), 1737 (C=O), 1698 (CH=N stretch), 1235 (C-N stretch), 874 (-Si-C). **Anal. Calcd** for $C_{34}H_{38}N_2O_4SSi_2$ (626.91): C,68.67; H,5.76; N,4.71; Found: C,68.07; H,6.09; N,4.19. **DSC**: I run: T$_m$ = 248 °C; II run: T$_g$ = 99 °C, T$_c$ = 141 °C, T$_m$ = 235 °C.

ThAz-6: Yield = 20%, ^{1}H NMR (600 MHz,CDCl$_3$, δ, ppm): 8.42 (s, 2H, HC=N), 7.87 (d, J = 8.2 Hz, 4H, CH), 7.61 (d, J = 8.3 Hz, 4H, CH), 7.57–7.56 (m, 5H, CH), 7.37 (d, J = 2.4 Hz, 5H, CH), 4.41 (q, J = 7.1 Hz, 4H, O-CH$_2$-), 1.41 (t, J = 7.1 Hz, 6H, -CH$_3$). **^{13}C NMR** (151 MHz, CDCl$_3$, δ, ppm): 151.67, 135.35, 132.05, 131.78, 131.74, 131.62, 129.54, 128.92, 128.43, 128.35, 128.22, 91.63, 89.26, 60.28, 14.24. **FT-IR** (KBr, ν, cm^{-1}): 3059 (C-H aromatic), 2979, 2933 (C-H aliphatic), 2214 (C≡C), 1726 (C=O), 1701 (CH=N stretch), 1207 (C-N stretch). **Anal. Calcd** for $C_{40}H_{30}N_2O_4S$ (634.74): C,75.69; H,4.76; N,4.41; Found: C,74.36; H,4.80; N,3.96. **DSC**: I run: T$_m$ = 193 °C; II run: T$_g$ = 124 °C.