



Optical and electrochemical properties of novel thermally stable Schiff bases bearing naphthalene unit



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ABSTRACT

A series of novel Schiff bases via condensation reaction of 2-naphthylamine with benzaldehyde, terephthalaldehyde, 9-anthracenecarboxaldehyde, 9-phenantrenecarboxaldehyde, 2-naphthaldehyde and biphenyl-4-carboxaldehyde was synthesized and examined. In the most cases the prepared compounds exhibited the temperature of 5% weight loss about 270 °C. Resulting imines exhibited similar photoluminescence properties and emitted blue light in its blends with PMMA with quantum yield efficiency in the range of 1.98–9.69%.

The highest luminescence intensity exhibited Schiff bases consisting of two naphthalene units. Electrochemical measurements (CV and DPC) revealed, in the most cases, two reversible reduction and irreversible oxidation processes. They showed a low value of electrochemically calculated energy gap (E_g) about 1.6 eV. Additionally, the electronic properties, that is, orbital energies and resulting energy gap were calculated theoretically by density functional theory (DFT). Considering the obtained results it seems that the prepared imines can be interesting for optoelectronic applications. The reversible reduction and low E_g suggest that they can be treated as acceptors. Thus, the activity of selected compound was tested in photovoltaic solar cell with the following architecture ITO/PEDOT:PSS/P3HT or P3OT:imine/Al under illumination 1.3 mW/cm². The highest conversion efficiency was 0.32%, which confirmed its electron acceptor character.

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1. Introduction

Search for new organic materials with improved properties suitable for construction of optoelectrical devices is still challenge despite of the fact that many such materials have been commercialized till now. Improved properties can be achieved by architecture of the polymers or low molecular weight compounds that means by using for their synthesis substrates with proper chemical structure and linking them units. Schiff's base is the interesting stimuli-responsive linker also for compounds toward optoelectronics [1–3]. Schiff bases named after Hugo Schiff who discovered reaction gives products contain CH=N double bonds are also

known as azomethines and imines. Particular attention has been devoted to imines due to the possibility of applying them in biological systems, in catalysis, dyeing and nonlinear optics [4–5]. On the other hand, Schiff base family being isoelectronic to the vinyl bond is a π -conjugated organic semiconductor materials and constitutes a type of hole-transporting materials [6]. Moreover, free electron pair of nitrogen in imine group causes its ability to complex different metal ions and creates a wide range of applications in selective removal of metal ions from waste water and sea water [7] or as spectroscopic sensor for various ions [8–10]. It should be mentioned that nitrogen free electron pair in azomethine group can be protonated with organic and inorganic acids and it is a tool to tune optical and electrooptical properties of the azomethine compounds [11]. Azomethines offer significant advantages over their carbon analogues as they can be synthesized in much milder conditions and without expensive catalysts, in reaction of compounds

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bearing aldehyde and amine groups. The increasing interest in research of small molecules with imine units is observed [12]. Small molecules have the advantage over polymers because they exhibit well-defined molecular structure, molecular weight without any distribution and can be easily purified. Schiff bases demonstrated the potential application as optically driven molecular switches [13–14], luminescent and pH indicators [15], electrochromic and photochromic materials [16–18]. Moreover, molecules bearing imine linkages are tested as component of active layers in photovoltaic (PV) cells [6,19–21].

In our research group we have synthesized several new azomethines derivatives consisting also of phthalic and naphthalene diimides units and also thiophene, bithiophene, and pyridine rings [22–25]. The most of these compounds exhibited a low electrochemical energy band gap being suitable for a variety of applications. Following our research for low molecular organic materials for optoelectronics we have synthesized a series of new unsymmetrical Schiff bases being condensation products of 2-naphthylamine and various aldehydes. The selected physical properties such as absorption in UV–Vis range and photoluminescence (PL) and electrochemical (CV, DPV) were investigated. Additionally, HOMO, LUMO levels and E_g were calculated using density functional theory (DFT). Moreover, the photovoltaic activity of selected azomethine in bulk heterojunction (BHJ) photovoltaic (PV) cell at the configuration ITO/PEDOT:PSS/active layer/Al under an illumination 17 mW/cm² was preliminarily tested.

2. Experimental part

2.1. Materials

2-Naphthylamine, benzaldehyde, terephthalaldehyde, methanol and acetic acid (99.5%) were supplied from POCH. *N,N*-dimethylacetamide (DMA), 9-anthracenecarboxaldehyde, 9-phenantrenecarboxaldehyde, 2-naphthaldehyde, biphenyl-4-carboxaldehyde, indium tin oxide (ITO) with surface resistance about 15–20 Ω/cm², poly(3,4-(ethylenedioxy)thiophene):poly(styrenesulfonate) (PEDOT:PSS), poly(3-hexylthiophene-2,5-diyl) (P3HT) and 3-butylthiophene (P3OT) were purchased from Aldrich Chemical Co.

2.2. Synthesis of Schiff bases

2.2.1. Synthesis of *N*-(naphthalen-2-yl)-1-phenylmethanimine (**Az-1**)

1 mmol (0.143 g) of 2-naphthylamine and 1.2 mmol (0.127 g) of benzaldehyde were dissolved in 2 ml DMA and heated at 150 °C under argon atmosphere. After 13 h the mixture was cooled to room temperature and 2 ml methanol was added. The product was precipitated in water. The precipitate was filtered, washed several times with water and dried at 100 °C in vacuum.

Az-1: Brown powder. Yield: 20%. ¹H NMR (CDCl₃, δ, ppm): 8.59 (s, —CH=N, 1H), 7.96–7.94 (m, 2H), 7.87–7.83 (m, 3H), 7.60 (d, 1H), 7.50–7.44 (m, 6H). ¹³C NMR (CDCl₃, δ, ppm): 160.53 (CH=N). FTIR (cm⁻¹): 3055 (CH aromatic), 1633 (CH=N stretching), 1580 (C=C stretching deformations in phenyl ring). Elem. anal. calcd (%) for (C₁₇H₁₂N) (230.28): C 88.66, H 5.25, N 6.08; found C 87.80, H 5.86, N 6.18. T_m = 97 °C (DSC).

2.2.2. Synthesis of benzene-1,4-diylbis[*N*-(naphthalen-2-yl)methanimine] (**Az-2**)

1 mmol (0.1335 g) of terephthalaldehyde and 2 mmol (0.2866 g) of 2-naphthylamine were dissolved in 2 ml DMA and heated at 120 °C under argon atmosphere for 12 h. The product was precipitated in methanol. The precipitate was filtered, washed several times with methanol and dried at 60 °C in vacuum.

Az-2: Yellow powder. Yield: 87%. ¹H NMR (CDCl₃, δ, ppm): 8.68 (s, —CH=N, 2H), 8.09 (s, 4H), 7.90–7.87 (m, 6H), 7.66 (d, 2H), 7.50–7.49 (m, 6H). ¹³C NMR (CDCl₃, δ, ppm): 159.54 (CH=N). FTIR (cm⁻¹): 3048 (CH aromatic), 1620 (CH=N stretching), 1580 (C=C stretching deformations in phenyl ring). Elem. anal. calcd (%) for (C₂₈H₂₀N₂) (384.47): C 87.47, H 5.24, N 7.29; found C 87.50, H 5.38, N 7.38. T_m = 236 °C (DSC).

2.2.3. Synthesis of 1-(1,4-dihydroanthracen-9-yl)-*N*-(naphthalen-2-yl)methanimine (**Az-3**)

1 mmol (0.143 g) of 2-naphthylamine and 1 mmol (0.213 g) of 9-anthracenecarboxaldehyde were dissolved in 2 ml DMA and heated at 120 °C under argon atmosphere. After 13 h the mixture was cooled to room temperature. The product was precipitated in water. The precipitate was filtered, washed several times with water and dried at 100 °C in vacuum.

Az-3: Yellow powder. Yield: 80%. ¹H NMR (CDCl₃, δ, ppm): 9.82 (s, —CH=N), 8.82 (d, 2H), 8.58 (s, 1H), 8.07 (d, 2H), 8.05–7.89 (m, 3H), 8.79 (s, 1H), 7.66–7.64 (m, 1H), 7.61–7.58 (m, 2H), 7.55–7.49 (m, 4H). ¹³C NMR (CDCl₃, δ, ppm): 159.97 (CH=N). FTIR (cm⁻¹): 3050 (CH aromatic), 1623 (CH=N stretching), 1585 (C=C stretching deformations in phenyl ring). Elem. anal. calcd (%) for (C₂₅H₁₇N) (331.41): C 90.60, H 5.17, N 4.22; found C 90.10, H 5.21, N 4.01. T_m = 145 °C (DSC).

2.2.4. Synthesis of *N*-(naphthalen-2-yl)-1-(1,4,5,8-tetrahydrophenanthren-9-yl)methanimine (**Az-4**)

Synthesis of **Az-4** was carried out according to procedure described for **Az-3** using 9-phenantrenecarboxaldehyde instead of 9-anthracenecarboxaldehyde.

Az-4: Yellow powder. Yield: 75%. ¹H NMR (CDCl₃, δ, ppm): 9.28–9.26 (m, 1H), 9.22 (s, —CH=N), 8.77–8.69 (m, 2H), 8.38 (s, 1H), 8.01 (d, 1H), 7.93–7.87 (m, 3H), 7.74–7.70 (m, 4H), 7.64–7.46 (m, 4H). ¹³C NMR (CDCl₃, δ, ppm): 160.80 (CH=N). FTIR (cm⁻¹): 3050 (CH aromatic), 1624 (CH=N stretching), 1578 (C=C stretching deformations in phenyl ring). Elem. anal. calcd (%) for (C₂₅H₁₇N) (331.41): C 90.34, H 5.17, N 4.23; found C 90.70, H 5.27, N 4.53. T_m = 159 °C (DSC).

2.2.5. Synthesis of *N*,1-di(naphthalen-2-yl)methanimine (**Az-5**)

Synthesis of **Az-5** was carried out according to procedure described for **Az-3** using 2-naphthaldehyde instead of 9-anthracenecarboxaldehyde. After 13 h the mixture was cooled to room temperature and the product precipitated. The precipitate was filtered, washed several times with methanol and dried at 60 °C in vacuum.

Az-5: Yellow powder. Yield: 66%. ¹H NMR (CDCl₃, δ, ppm): 8.93 (s, —CH=N, 1H), 8.44 (s, 1H), 8.20 (d, 1H), 8.07–8.03 (m, 2H), 8.00–7.92 (m, 4H), 7.79 (d, 1H), 7.64–7.60 (m, 3H), 7.59–7.54 (m, 2H). ¹³C NMR (CDCl₃, δ, ppm): 160.52 (CH=N). FTIR (cm⁻¹): 3050 (CH aromatic), 1623 (CH=N stretching), 1585 (C=C stretching deformations in phenyl ring). Elem. anal. Calcd. (%) for (C₂₁H₁₅N) (281.34): C 89.65, H 5.37, N 4.98; found C 89.05, H 5.47, N 4.84. T_m = 176 °C (DSC).

2.2.6. Synthesis of 1-(biphenyl-4-yl)-*N*-(naphthalen-2-yl)methanimine (**Az-6**)

Synthesis of **Az-6** was carried out according to procedure described for **Az-3** using biphenyl-4-carboxaldehyde instead of 9-anthracenecarboxaldehyde. After 13 h the mixture was cooled to room temperature and the product precipitated. The precipitate was filtered, washed several times with methanol and dried at 60 °C in vacuum.

Az-6: Pale yellow powder. Yield: 83%. ¹H NMR (CDCl₃, δ, ppm): 8.64 (s, —CH=N, 1H), 8.03 (d, 2H), 7.89–7.84 (m, 3H), 7.74 (d, 2H), 7.67 (d, 2H), 7.62 (d, 1H), 7.50–7.38 (m, 6H). ¹³C NMR (CDCl₃, δ,

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