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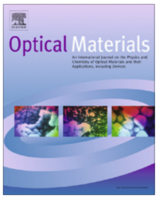

Spectral, electrochemical and thermal characteristics of glass forming hydrazine derivatives

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ABSTRACT

The azines being condensation products of benzophenone hydrazone with triphenylamine substituted with different numbers of aldehyde groups and also with terephthaldicarboxaldehyde were prepared. Their spectral, thermal and electronic properties that is, orbital energies and resulting energy gap calculated theoretically by density functional theory (DFT) and estimated by electrochemical measurements were explored. The prepared hydrazine derivatives exhibited glass-forming properties with glass-transition temperatures in the range of 10–98 °C and high thermal stability with decomposition temperatures placed between 231 and 337 °C. The photoluminescence (PL) studies showed that all investigated compounds both in solid state as blends with PMMA and in NMP solution emitted blue light, however, with different intensity. Relative PL intensity of azines was investigated in NMP in relation to rhodamine-B used as a standard. Moreover, the stability of azines during doping with acid and ferric chloride was spectroscopically demonstrated via repeated doping/dedoping in solution and in film. All compounds are electrochemically active. Depend on chemical structure of azines they undergo reversible or irreversible electrochemical oxidation and reduction processes. The LUMO levels were found in the range from −2.66 to −3.0 eV. They exhibited energy band gap (E_g) estimated electrochemically from 2.57 to 3.22 eV.

1. Introduction

The development of organic materials, both low molecular weight compounds and polymers, is the subject of recent research in the area of photonics and electronics. The important advantages of organic compounds are light-weight, good processability and tunability of their properties by structure modifications [1,2]. Significant advances have been reached in the field of organic electronics and optoelectronics based on low molecular weight compounds [3]. Small molecules in relation to polymers have advantages such as well-defined structure and molecular weight without any distribution, easier purification and more easily controllable properties. However, active layers in devices for organic electronics based on molecular materials are usually obtained by evaporation, thus limiting their use [3]. Thus, especially interesting are low molecular weight compounds that readily form glasses above room temperature which are called molecular glasses or amorphous molecular materials [4–8]. They combine the characteristic properties of small molecules with behavior of polymers, that is, the ability to access amorphous solid states. They may form uniform, transparent amorphous thin films by spin-coating methods contrary to low molar mass compounds with strong tendency for crystallization.

Organic azines (diimines) belong to a group of π-conjugated compounds, which seem to be promising for organic (opto)electronics. However, taking into account the literature review concerns aiznes it can be concluded that, they are rather seldom investigated for optoelectronic applications. They have been usually widely studied because of their numerous chemical and biological applications [9–11]. To the best of our knowledge, there are a few articles in which azines are proposed for applications in optoelectronic devices [12–18]: as potential nonlinear optical (NLO) materials [12–14], as liquid crystals [13,15] also as thermoluminescent materials [15] and as thermochromic compounds [16,17]. It should be mentioned that principal role with respect to NLO properties plays intramolecular charge transfer from the donor to the acceptor due to molecule became polarized [18]. Considering various π-spaces, that is, vinylene, azine, arylimine

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and ethynylene it was found that vinylene and azine have the more favorable effect on the absorption spectrum and redox properties [19]. Thus, azines seem to be promising compounds for optoelectronic devices. Inspired by the findings described above we have undertaken a preparation and investigation of four aromatic azines obtained from benzophenone hydrazone and one prepared from benzophenone and hydrazine. Considering chemical structure of these azines there is a one example of the same compounds in literature [20]. A synthesis of azine, described in this paper, that is, prepared from benzophenone and hydrazine has been reported [20]. However, such diimine was obtained from differ substrates than in our case, that is, in solvent-free resection of benzophenone hydrazone with benzophenone using sulfated titania as catalytic system [20]. The aim of mentioned work was to develop a simple method under mild conditions for the preparation of azines. Three azines described in this paper contain triphenylamine group (TPA), which is well-known for its hole-transporting properties. Low molecular weight compounds and polymers with triarylamine units are also expected to exhibit good solubility, stability and high photoluminescence efficiency and are therefore widely investigated as materials for organic light emitting diodes, solar cells and organic field-effect transistors [21–23]. Symmetrical azine obtained from hydrazine and 4-formyltriphenylamine has been described in literature, including our previous work [19,24,25]. This compound has proved to be convenient chromogenic sensor for the detection of mercury ions [24]. The azine forms molecular glass, which allows preparing uniform transparent thin films of the compound using spin-coating techniques [25]. Its optical and electrochemical properties have been examined [19,25] and compared with azomethine analogue [25] and azine with carbazole end-groups [19].

The nitrogen atom in imine linkages has lone pair electrons. It can form intra or inter molecular interactions, conduct protonation and complexation with metal ions, acids and iodine [26]. Therefore, compounds may possess novel optical properties because both absorption and photoluminescence can be modulated by chemical environment. 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 [25,27–33].

This paper describes the synthesis and thermal (DSC, TGA) and optical (UV–Vis, PL) and electrochemical properties of four new symmetrical and unsymmetrical azines synthesized from benzophenone hydrazone and one obtained from benzophenone and hydrazine. Additionally, the electronic properties of obtained compounds are described theoretically by density functional theory (DFT).

2. Experimental

2.1. Materials

4-Formyltriphenylamine, 4,4′-diformyltriphenylamine, tris (4-formylphenyl)amine, benzophenone hydrazone, hydrazine monohydrate (80% solution), trifluoroacetic acid, terephthaldicarboxaldehyde and *N*-methyl-2-pyrrolidone (NMP) were obtained from Aldrich. Ethanol and toluene were supplied from POCh.

2.2. Synthesis of azines (***AHs***)

2.2.1. Synthesis of ***AH-1***

4-Formyltriphenylamine (0.1367 g, 0.5 mmol) and benzophenone hydrazone (0.0981 g, 0.5 mmol) were dissolved in 5 ml ethanol and 2 drops of trifluoroacetic acid were added. The reaction mixture was stirred for 24 h at 80 °C and cooled to room temperature. The resulting precipitate was filtered, washed with hot ethanol and dried.

AH-1: Yellow powder. Yield: 29%. Elem. anal.: found(calcd)% C 84.62(85.11), H 5.50(5.58), N 9.67(9.31). ^{1}H NMR ($CDCl_3$, δ, ppm): 8.57–8.52 (d, —CH═N, 1H), 7.68 (d, 2H), 7.34–7.28 (m, 8H), 7.17–7.06 (m, 14H). ^{13}C NMR ($CDCl_3$, δ, ppm): 161.09 (—CH═N), 150.46, 147.13, 129.61, 127.49, 125.55, 124.10, 121.84. FTIR (cm^{-1}): 3061, 3035 (CH aromatic), 1617 (CH═N stretching), 1591 (C═C stretching deformations in phenyl ring).

2.2.2. Synthesis of ***AH-2***

4,4′-Diformyltriphenylamine (0.1506 g, 0.5 mmol) and benzophenone hydrazone (0.1962 g, 1 mmol) were dissolved in 5 ml ethanol and 2 drops of trifluoroacetic acid were added. The reaction mixture was stirred for 24 h at 80 °C and cooled to room temperature. The resulting precipitate was filtered, washed with hot ethanol and dried.

AH-2: Yellow powder. Yield: 45%. Elem. anal.: found (calcd)% C 83.08(83.99), H 5.22(5.36), N 11.02(10.65). ^{1}H NMR ($CDCl_3$, δ, ppm): 8.52–8.609 (m, —CH═N, 2H), 7.75–7.72 (m, 5H), 7.56 (m, 3H), 7.46–7.31 (m, 16H), 7.19–7.05 (m, 9H). ^{13}C NMR ($CDCl_3$, δ, ppm): 161.12 (—CH═N), 159.20 (—CH═N), 149.50, 146.49, 138.58, 135.69, 130.56, 130.30, 129.80, 129.25, 128.99, 128.36, 127.65, 126.23, 124.90, 123.31. FTIR (cm^{-1}): 3055, 3026 (CH aromatic), 1620 (CH═N stretching), 1594 (C═C stretching deformations in phenyl ring).

2.2.3. Synthesis of ***AH-3***

Tris(4-formylphenyl)amine (0.1647 g, 0.5 mmol) and benzophenone hydrazone (0.2944 g, 1.5 mmol) were dissolved in 5 ml ethanol and 2 drops of trifluoroacetic acid were added. The reaction mixture was stirred for 24 h at 80 °C and cooled to room temperature. The resulting precipitate was filtered, washed with hot ethanol and dried.

AH-3: Yellow powder. Yield: 52%. Elem. anal.: found(calcd)% C 83.61(83.40), H 5.18(5.25), N 11.36(11.35). ^{1}H NMR ($CDCl_3$, δ, ppm): 8.51–8.63 (m, —CH═N, 3H), 7.75–7.71 (m, 6H), 7.56 (m, 4H), 7.48–7.28 (m, 24H), 7.22–7.05 (m, 8H). ^{13}C NMR ($CDCl_3$, δ, ppm): 160.67 (—CH═N), 158.99 (—CH═N), 138.33, 135.52, 130.55, 129.73, 129.47, 129.29, 128.81, 128.39, 128.16, 128.01, 127.68, 124.38. FTIR (cm^{-1}): 3049, 3022 (CH aromatic), 1619 (CH═N stretching), 1594 (C═C stretching deformations in phenyl ring).

2.2.4. Synthesis of ***AH-4***

4 mmol (0.729 g) of benzophenone dissolved in 5 ml of toluene at room temp. and then solution of 2 mmol (0.1001 g)of hydrazine in 3 ml toluene was added dropwise and then 3 drops of acetic acid was added. This solution was heating to 110 °C under argon atmosphere. The reaction mixture was stirred for 28 h at 110 °C. This mixture was cooled to room temperature and precipitate was separated.

AH-4: White powder. Yield: 34.7%. Elem. anal.: found(calcd)% C 86.50(86.63), H 6.02(5.59), N 7.50(7.72). ^{1}H NMR ($CDCl_3$, δ, ppm): 7.48–7.46 (m, 4H), 7.41–7.36 (m, 4H), 7.34–7.31 (m, 8H), 7.30–7.28 (m, 4H). ^{13}C NMR ($CDCl_3$, δ, ppm): 158.91 (C═N), 129.73, 129.50, 128.81, 128.16, 128.01. FTIR (cm^{-1}): 3083–3023 (CH aromatic), 1587 (C═C stretching deformations in phenyl ring).

2.2.5. Synthesis of ***AH-5***

0.5 mmol (0.068 g) of terephthaldicarboxaldehyde and 1.5 mmol (0.2944 g) of benzophenone hydrazone dissolved in 5 ml ethanol. After few minutes yellow product started to precipitate. The reaction mixture was stirred for 5 h at room temperature under argon atmosphere. The precipitate was filtered, washed several times with ethanol and dried at 60 °C in vacuum.