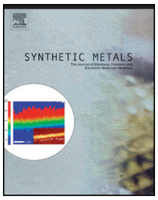
Synthetic Metals 212 (2016) 55–61

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet



Synthesis and properties of cross-linkable twin derivatives of 2-phenylindole

Rasa Keruckiene, Laura Peciulyte, Dmytro Volyniuk, Juozas Vidas Grazulevicius*

Department of Polymer Chemistry and Technology, Kaunas University of Technology, Radvilenu pl. 19, LT-50254 Kaunas, Lithuania

ARTICLE INFO

Article history:
Received 1 October 2015
Received in revised form 10 November 2015
Accepted 5 December 2015
Available online 17 December 2015

Keywords:
Indole
Ethenyl linkage
Self-polymerization

ABSTRACT

Synthesis and optical, thermal, electrochemical as well as photophysical properties of a series of new cross-linkable twin derivatives of 2-phenylindole with the different linkages are reported and compared. The compounds form molecular glasses with the glass transition temperatures in the range from 44 °C to 120 °C. They absorb electromagnetic radiation in the range of 225–420 nm and emit in the range of 400–600 nm. Compounds with ethenyl-containing linkages were found to exhibit very large Stokes shifts ranging from 142 nm to 159 nm for the dilute solutions and from 155 to 181 for the solid samples. The ionization potentials of the synthesized compounds were found to be in the range from 5.16 eV to 5.79 eV. Cyclic voltammetry showed that the synthesized diindolylethenes are electrochemically stable up to 1 V. The hole-drift mobility in the layers of the compounds exceeded 10^{-4} cm^2/Vs at high electric fields. The ability of thermally initiated polymerization in the solid state of the monomers was demonstrated by DSC and ATR-FTIR spectroscopy.

1. Introduction

Low-molar-mass and polymeric organic amorphous semiconductors are widely studied as the key components of organic optoelectronic devices such as organic light emitting diodes and organic and hybrid solar cells [1–3]. High efficiencies were recently reported for both organic light emitting diodes [4–6] and for organic solar cells [7,8]. However, there are still some challenges that suppress the smooth development of these technologies, such as performance stability or large area processing [9]. The limiting factors with respect of the performance stability can be inclination to crystallization of low-molar-mass organic semiconductors, diffusion of the molecules between the layers or the deficient resistance with respect of organic solvents. The stability of organic optoelectronic devices can be markedly increased if their active layers are cross-linked. For this purpose electroactive monomers with at least two photochemically or thermally polymerizable functional groups are required [10,11].

Effective charge transport and excellent thermal stability are the reasons why electron-rich moieties such as carbazole [12], triphenylamine [2,13] are widely used in the design of hole transporting materials. Much less investigations are reported on the derivatives having other electro-active moieties, such as indole [14]. and 2-phenylindole [15,16]. One common characteristic of the indole derivatives are large Stokes shift values, which lead to the suitable luminescence assays, for example, for developing of sensors [17] or optoelectronic devices [18]. In addition, indole derivatives usually show high triplet energy values and can be used as host materials in phosphorescent organic light emitting diodes (OLEDs). For example, Lee et al. [19] reported on pyrido-indole derivatives as bipolar host materials in efficient blue phosphorescent OLEDs with external quantum efficiencies exceeding 30%.

The aim of this study was the synthesis of two groups of new 2-phenylindole twin compounds containing reactive functional groups with the direct and double bond containing linkages between the chromophores. In addition, we explored the effect of the linking topology of the chromophores on the thermal, optical, photophysical and photoelectrical properties of the compounds. To our knowledge, this is the first article on synthesis and properties of the twin derivatives of 2-phenylindole with reactive functional groups.

2. Experimental

2.1. Materials

2-Phenylindole, 2-phenylindole-3-carbaldehyde, potassium *tert*-butoxide, iron(III) chloride, zinc, titanium tetrachloride, sodium carbonate, benzyltrimethylamonnium chloride (BTMAC), 4-vinylbenzyl chloride, bromoethane, benzyl chloride, epichlorohydrin, cyclopentadienyl(fluorene) iron(II) hexafluorophosphate

---

* Corresponding author.
E-mail address: juozas.grazulevicius@ktu.lt (J.V. Grazulevicius).

http://dx.doi.org/10.1016/j.synthmet.2015.12.005
0379-6779/

(all from Aldrich), 2-methylpropyl iodide (from Fluka), 3-bromomethyl-3-methyloxetane (from Chemada Fine Chemicals) were used as received.

1,2-Bis(2-phenyl-1*H*-indol-3-yl)ethene (**BPIE**) was synthesized by McMurry reaction according to the reported procedure [20]. Zinc (2.35 g, 36 mmol) was added to dry tetrahydrofuran (THF, 35 ml) and the mixture was cooled down to 0 °C. Titanium tetrachloride (2.17 ml, 19 mmol) was added dropwise and then the reaction mixture was slowly brought to room temperature. 2-Phenylindole-3-carbaldehyde (4 g, 18 mmol) was added dropwise and then the reaction mixture was refluxed for 1 h. The reaction was monitored by TLC using hexane: ethylacetate 1:1 as an eluent. The solution of sodium carbonate was poured in and stirred for 14 h. After extraction with chloroform, the organic layer was washed with water, dried with anhydrous sodium sulphate and filtered. The solvent was evaporated, the product was crystalized from methanol. Yield of greenish crystals was 75%. M_w = 412.0 g/mol $C_{30}H_{24}N_2$. T_m = 167–168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.72 (s, 2H, N—H), 7.43 (d, 8H, Ar, *J* = 8.9 Hz), 7.38–7.34 (m, 12H, Ar), 6.93 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 135, 134, 133, 129, 128, 127, 122, 119, 113, 110, 26. Elemental analysis for $C_{30}H_{24}N_2$.% Calc.: C 87.35; H 5.86; N 6.79% Found: C 87.30; H 5.91; N 6.74. MS: *m*/*z* 413 [$(M + H)^+$].

2-Phenyl-3-(2-phenyl-1*H*-indol-3-yl)-1*H*-indole (**PPII**) was synthesized according to the described procedure [21].

1,2-Bis(1-(4-vinylbenzyl)-2-phenylindol-3-yl)ethene (**1**) was prepared by the procedure similar to that described elsewhere [22]. To a mechanically stirred mixture of 2-phenyl-3-(2-phenyl-1*H*-indol-3-yl)-1*H*-indole (**PPII**) (1 g, 2.25 mmol), dimethyl sulphoxide (DMSO) (10 ml), potassium *tert*-butoxide (0.75 g, 6.75 mmol), BTMAC (0.01 mmol) and 4-vinylbenzylchloride (1.27 ml, 9 mmol) were added. The resulting mixture was stirred at room temperature for 2 h. The reaction was stopped by adding water and neutralized with 10% HCl (8 ml) to pH 6–7. The crude product was extracted with chloroform several times (50 ml × 3). The chloroform solution was washed with water, dried with anhydrous sodium sulphate, filtered and the solvent was evaporated. The product was purified by silica gel column chromatography using hexane as an eluent. Yield of yellow crystals was 59%. M_w = 558.62 g/mol. $C_{48}H_{38}N_2$. T_m = 201–203 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.43 (d, 8H, Ar, *J* = 8.9 Hz), 7.31–7.25 (m, 10H, Ar), 7.22–7.11 (m, 8H, Ar), 6.95 (s, 2H, CHCH), 6.73–6.64 (m, 2H, AMX system $CHCH_2$ proton H^A), 5.72 (dd, 2H, AMX system —$CHCH_2$ proton H^M trans J_{AM} = 5.75 Hz and gem J_{MX} = 5.80 Hz), 5.27–5.22 (m, 2H, AMX system of —$CHCH_2$ proton H^X *cis* J_{AX} = 14.1 Hz), 5.20 (s, 4H, CH_2). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 137, 136, 130, 128, 126, 122, 120, 119, 113, 110, 47. FT-IR (KBr) cm^{-1}: 3047 (ν C—H Ar), 2922, 2853 (ν C—H aliph.), 1463 (ν C=C Ar), 1366 (ν C—N Ar), 986, 899 (C—H of vinyl group), 831, 735 (γ C—H Ar). Elemental analysis for $C_{48}H_{38}N_2$. % Calc.: C 89.68; H 5.96; N 4.36; % Found: C 89.73; H 5.916; N 4.31. MS: *m*/*z* 559 [$(M + H)^+$].

1,2-Bis(1-isopropyl-2-phenylindol-3-yl)ethene (**2**). To a mechanically stirred mixture of 2-phenyl-3-(2-phenyl-1*H* -indol-3-yl)-1*H* -indole (**PPII**) (0.5 g, 1.12 mmol), dimethyl sulphoxide (DMSO) (10 ml), potassium *tert*-butoxide (0.375 g, 3.375 mmol), BTMAC (0.01 mmol) and 2-methylpropyl iodide (0.49 ml, 4.5 mmol) were added. The resulting mixture was stirred at room temperature for 2 h. The reaction was stopped by adding water and neutralized with 10% HCl (5 ml) to pH 6–7. The crude product was extracted with chloroform several times (50 ml × 3). The chloroform solution was washed with water, dried with anhydrous sodium sulphate, filtered and the solvent was evaporated. The product was purified by silica gel column chromatography using hexane as an eluent.Yield of yellowish powder was 89%. M_w = 498.60 g/mol. $C_{36}H_{34}N_2$. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.36–7.27 (m, 10H, Ar), 7.19–7.13 (d, 8H, Ar *J* = 27.5 Hz), 6.97 (s, 2H, CHCH), 4.66–4.39 (m, 2H, CH), 1.28 (s, 12H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 139, 138, 137, 136, 130, 128, 126, 122, 113, 110, 47. FT-IR (KBr) cm^{-1}: 3048 (ν C—H Ar), 2922, 2853 (ν C—H aliph.), 1493, 1462 (ν C=C Ar), 1363 (ν C—N Ar), 831, 807, 767 (γ C—H Ar). Elemental analysis for $C_{36}H_{34}N_2$. % Calc.: C 87.41; H 6.93; N 5.66; % Found: C 87.45; H, 6.88; N, 5.71. MS: *m*/*z* 522 [$(M + Na)^+$].

1,2-Bis(1-((3-methyloxetan-3-yl)methyl)-2-phenylindol-3-yl) ethene (**3**). To a mechanically stirred mixture of 2-phenyl-3-(2-phenyl-1*H* -indol-3-yl)-1*H* -indole (**PPII**) (0.3 g, 0.68 mmol), dimethyl sulphoxide (DMSO) (10 ml), potassium *tert*-butoxide (0.23 g, 2.00 mmol), BTMAC (0.01 mmol) and 3-bromomethyl-3-methyloxetane (0.47 ml, 3.38 mmol) were added. The resulting mixture was stirred at room temperature for 2 h. The reaction was stopped by adding water and neutralized with 10% HCl (5 ml) to pH 6–7. The crude product was extracted with chloroform several times (50 ml × 3). The chloroform solution was washed with water, dried with anhydrous sodium sulphate, filtered and the solvent was evaporated. The product was purified by silica gel column chromatography using hexane as an eluent.Yield of yellow crystals was 97%. M_w = 512.57 g/mol. $C_{40}H_{38}N_2O_2$. T_m = 184–186 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.53–7.43 (m, 10H, Ar), 7.36–7.25 (m, 8H, Ar), 7.13 (s, 2H, CHCH), 4.40 (s, 4H, CH_2), 4.15 (d, 4H, CH_2 *J* = 6.0 Hz), 3.97 (d, 4H, CH_2, *J* = 6.0 Hz), 1.28 (s, 6H, CH_3). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 138, 131, 128, 125, 122, 121, 118, 114, 110, 81, 41, 22. FT-IR (KBr) cm^{-1}: 3056 (ν C—H Ar), 2923, 2853 (ν C—H aliph.), 1489, 1457 (ν C=C Ar), 1346 (ν C—N Ar), 1235, 1181 (ν C—O—C), 822, 759 (γ C—H Ar). Elemental analysis for $C_{40}H_{38}N_2O_2$. % Calc.: C 83.01; H 6.62; N 4.84; O 5.53; % Found: C 83.06; H 6.57; N 4.89; O 5.48. MS: *m*/*z* 536 [$(M + Na)^+$].

1,2-Bis(1-(oxiran-2-yl)-2-phenylindol-3-yl)ethene (**4**). A solution of 2-phenyl-3-(2-phenyl-1*H*-indol-3-yl)-1*H*-indole (**PPII**) (0.2 g, 0.45 mmol) potassium in epichlorohydrin (4 ml, 51 mmol) was stirred at 120 °C for 24 h under argon atmosphere. Then epichlorhydrin was removed by distillation The product was purified by silica gel column chromatography using hexane as an eluent. Yield of yellow crystals 42.5%. M_w = 498.52 g/mol. $C_{36}H_{30}N_2O_2$. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.64–7.49 (m, 8H, Ar), 7.38–7.33 (m, 10H, Ar), 7.18 (s, 2H, CHCH), 4.34–4.30 (m, 4H, CH_2), 4.28 (d, 4H, CH_2, *J* = 4.1 Hz), 3.20 (m, 1H, CH), 2.73 (t, 1H, CH, *J* = 4.4 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 138, 137, 131, 128, 125, 122, 121, 119, 114, 110, 45. FT-IR (KBr) cm^{-1}: 3051 (ν C—H Ar), 2923, 2854 (ν C—H aliph.), 1460 (ν C=C Ar), 1362 (ν C—N Ar), 1226, 1195 (ν C—O—C), 840, 741 (γ C—H Ar). Elemental analysis for $C_{36}H_{30}N_2O_2$. % Calc.: C 82.57; H 5.30; N 5.66; O 6.47;% Found: C 82.52; H 5.35; N 5.61; O 6.52. MS: *m*/*z* 522 [$(M + Na)^+$].

1-Ethyl-3-(1-ethyl-2-phenylindol-3-yl)-2-phenylindole (**5**). To a mechanically stirred mixture of 1,2-Bis(2-phenyl-1*H*-indol-3-yl) ethene (**BPIE**) (0.6 g, 1.5 mmol), dimethyl sulphoxide (DMSO) (10 ml), potassium *tert*-butoxide (0.52 g, 4.6 mmol), BTMAC (0.01 mmol) and bromoethane (0.58 ml, 7.7 mmol) were added. The resulting mixture was stirred at room temperature for 2 h. The reaction was stopped by adding water and neutralized with 10% HCl (8 ml) to pH 6–7. The crude product was extracted with chloroform several times (50 ml × 3). The chloroform solution was washed with water, dried with anhydrous sodium sulphate, filtered and the solvent was evaporated. The product was purified by silica gel column chromatography using hexane as an eluent. Yield of greenish crystals was 31%. M_w = 440.58 g/mol. $C_{32}H_{28}N_2$. T_m = 143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm 7.61–7.42 (m, 10H, Ar), 7.47–7.36 (m, 8H, Ar) 4.26 (q, 4H, CH_2, *J* = 7.2 Hz), 1.38 (t, 6H, CH_3, *J* = 7.2 Hz). ^{13}C NMR (400 MHz, $CDCl_3$) δ ppm 137, 133, 130, 126, 125, 123, 117, 110, 38, 15. FT-IR (KBr) cm^{-1}: 3049 (ν C—H Ar), 2989 (ν C—H aliph.), 1479, 1457, 1446 (ν C=C Ar), 1350 (ν C—N Ar), 847, 797 (γ C—H Ar). Elemental analysis for $C_{32}H_{28}N_2$. % Calc.: C 87.24; H 6.41; N 6.36; % Found: C 87.24; H 6.41; N 6.36. MS: *m*/*z* 441 [$(M + H)^+$].