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Synthesis and properties of glass-forming 2-substituted perimidines

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ABSTRACT

2-Substituted perimidine derivatives were synthesized by condensation of 1,8-diaminonaphthalene and the different formyl derivatives. Alkylation of the intermediate compounds was performed using microwave irradiation using potassium and cesium carbonate as a base. The synthesized compounds were characterised by UV and luminescence spectroscopies, cyclic voltammetry, thermogravimetry, differential scanning calorimetry. They exhibit relatively high thermal stability with the temperatures of the onset of thermal degradation ranging from 230 to 392°C. Most of the synthesized perimidines are capabale to form glasses with glass transition temperatures up to 197°C. The alkyl group attached to the perimidinyl moiety influences the conformation of the molecules and consequently the absorption and emission spectra. The values of ionization potential of the layers of the synthesized derivatives range from 5.26 to 5.52 eV.

KEYWORDS

perimidine; ionization potential; glass transition; solid state fluorescence

1. Introduction

The 1*H*-perimidine system has been known since 1874, when it was obtained by de Aguiar [1]. The peri-naphtho-fused perimidines have the characteristics both of π-deficient and π-excessive systems [2]. Therefore 2-naphthol perimidine (together with several 2,3-dihydroperimidines) can be used as charge-transporting materials [3]. The derivatives of perimidine have been used as dye intermediates and coloring materials for polyester fibers [4]. More recently it was shown that some of perimidine derivatives are potential near-infrared absorbing materials [5] and antibacterial compounds [6]. In addition, macroporous poly(aromatic amine) derived from oxidation of 1H,2H-dihyroperimidines was reported to have potential for sensing and electrochemical applications [7]. *1H*-perimidine tethered polysulfone was used for the preparation of blend membrane for direct methanol fuel cells [8]. It is evident that 1*H*-perimidine heterocyclic system is versatile and the derivatives can be applied in variety of fields. It was therefore of interest to synthesise new 2-substituted perimidines and to study their thermal, optical, photoelectrical and photophysical properties.

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2. Experimental

2.1. Instrumentation

^{1}H NMR spectra were obtained on Varian Unity Inova (300 MHz) instrument. Mass spectra were obtained on a Waters ZQ 2000 (Waters, Milford, USA). IR-spectroscopy was performed on Perkin Elmer Spectrum GX II FTIR, using KBr pellets. For the elemental analyses the CE-440 apparatus (Exeter Analytical) was used. Differential scanning calorimetry (DSC) measurements were performed on TA Instruments Q10 (heating/cooling rate 10 K/min). Thermogravimetric analysis (TGA) was done using NETZSCH STA 409 thermogravimeter at a heating rate of 10 K/min under N_2. Melting points were measured on a MEL – TEMP melting point apparatus. UV spectra were recorded with Perkin Elmer Lambda 35 spectrometer. Fluorescence emission spectra were recorded with a Hitachi MPF-4 luminescence spectrometer. The ionization potentials (I_p) of the films of the synthesized compounds were measured by the electron photoemission in air method as described earlier [9,10].

2.2. Materials

1,8-Diaminonaphthalene (95%), aniline (98%) were purchased from Fluka and used as received. Triphenylamine (98%), 4-iodoanisole (98%), $Na_2S_2O_5$ and Cs_2CO_3 (99.9%), copper powder (99%), 18-crown-6 (99%), o-dichlorobenzene, phosphorus oxychloride, 1-bromohexane (98%), 2-ethylhexylbromide (95%), 1-iodobutane (99%), N-methyl-2-pyrrolidinone, benzaldehyde, 9-ethyl-3-carbazolylaldehyde were purchased from "Aldrich" and used as received. 10-(2-Ethylhexyl)-10*H*-3-phenotiazine carbaldehyde was synthesized as described elsewhere [11].

2.2.1. 2-Phenylperimidine (1)

It was synthesized according the earlier reported procedure [12]. Yield of compound 1 was 84%. M.p. 186°C (DSC). MS (APCI$^+$, 20 V), m/z (%): 245.5 ([M+H]$^+$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 3.7 (s, 1H, NH), 6.68 (dd, 2H, $J_1 = 7.2$ Hz, $J_2 = 1.1$ Hz), 7.06–7.15 (m, 2H), 7.16–7.25 (m, 2H), 7.5–7.64 (m, 3H), 8.06–8.14 (m, 2H). IR, KBr, (cm^{-1}): 3628, ν (NH); 3049, ν (CH_{ar}) 1599, ν (C=C_{ar}); 1373, ν (C–N); 824, 770, 698, γ (CH). Elemental analysis: Calculated ($C_{17}H_{12}N_2$): C 83.58%; H 4.95%; N 11.47%; Found: C 83.61%; H 4.90%; N 11.49%.

2.2.2. 2-(9-Ethyl-3-carbazolyl)perimidine (2)

A mixture of 9-ethyl-3-carbazolylaldehyde (1.4 g, 6.3 mmol) and 1,8-diaminonaphthalene (1 g, 6.3 mmol) in 7 ml of 2-propanol was stirred at 65°C for 24 h. Then the solution of $Na_2S_2O_5$ (0.84 g, 4.4 mmol) in water (2 ml) was added to the reaction mixture and it was refluxed for 1 h. After that, the reaction mixture was poured into water, the product was precipitated, then washed with water, filtered and dried. The product was obtained as a orange crystals. Yield of 2 was 1.14 g (72%). M.p. 225°C (DSC). MS (APCI$^+$, 20 V), m/z (%): 362.5 ([M+H]$^+$). ^{1}H NMR (300 MHz, *d*-acetone, ppm, δ): 1.46 (t, 3H, $J = 7.2$ Hz, $CH_2\underline{CH_3}$), 3.46 (s, 1H, NH) 4.57 (q, 2H, $J = 7.2$ Hz, $\underline{CH_2}CH_3$), 6.73 (dd, 2H, $J_1 = 7.3$ Hz, $J_2 = 1.0$ Hz), 7.12 (dd, 2H, $J_1 = 8.4$ Hz, $J_2 = 1.0$ Hz), 7.2 (d, 1H, $J = 7.3$ Hz), 7.23 (d, 1H, $J = 7.2$ Hz), 7.27–7.38 (m, 1H), 7.5–7.61 (m, 1H), 7.67 (dt, 1H, $J_1 = 8.4$ Hz, $J_2 = 1.0$ Hz), 7.71 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 0.5$ Hz), 8.21–8.32 (m, 2H), 8.91 (dd, 1H, $J_1 = 1.9$ Hz, $J_2 = 0.5$ Hz). IR, KBr, (cm^{-1}): 3202, ν (NH); 3047, ν (CH_{ar}); 2983, ν (CH_{aliph}); 1630, ν (C=N); 1592, 1502, 1444, ν

(C=C_{ar}); 1383, ν (C–N); 816, 752, 704, γ (CH_{ar}). Elemental analysis: Calculated ($C_{25}H_{19}N_3$): C 83.08%; H 5.30%; N 11.63%; Found: C 83.12%; H 5.27%; N 11.61%.

2.2.3. 10-(2-Ethylhexyl)-3-(1H-perimidin-2-yl)-10H-phenothiazine (3)

The compound was prepared from 10-(2-ethylhexyl)-10*H*-3-phenothiazine carbaldehyde (1.1 g, 3.24 mmol), 1,8-diaminonaphthalene (0.51 g, 3.24 mmol), $Na_2S_2O_5$ (0.62 g, 3.3 mmol), and 8 ml of 2-propanol using the similar procedure as for 2. Compound 3 was obtained in the form of yellow crystals with the yield of 1.49 g (96%). M.p. 162°C (DSC). MS (APCl$^+$, 25 V), m/z (%): 478.6 ([M+H]$^+$). ^{1}H NMR (300 MHz, d_6-DMSO, ppm, δ): 0.75–0.9 (m, 6H, ($CH_2\underline{CH_3}$)$_2$), 1.12–1.48 (m, 8H, ($\underline{CH_2}$)$_4$), 1.78–1.95 (m, 1H, $\underline{CH}CH_2N$), 3.75–3.95 (m, 2H, $\underline{CH_2}N$), 6,54 (d, 1H, J = 7.2 Hz), 6.68 (d, 1H, J = 7.2 Hz), 6.95–7.30 (m, 9H), 7.8 (d, 1H, J = 2.1 Hz), 7.61 (dd, 1H, J = 8.6 Hz), 10.54 (s, 1H, NH). IR, KBr, (cm^{-1}): 3202, ν (NH); 3050, ν (CH_{ar}); 2926, ν (CH_{aliph}); 1634, ν (C=N); 1576, 1595, 1461, ν (C=C_{ar}); 1338, ν (C–N); 822, 769, 751, γ (CH_{ar}); 682, ν (C–S). Elemental analysis: Calculated ($C_{31}H_{31}N_3S$): C 77.95%; H 6.54%; N 8.8%; S 6.71% Found: C 77.90%; H 6,59%; N 8.85%.

2.2.4. N-(4-(1H-Perimidin-2-yl)phenyl)-N-phenylbenzenamine (4)

A mixture of *p*-(diphenylamino)benzaldehyde (1 g, 3.86 mmol) and 1,8-diaminonaphthalene (0.61 g, 3.86 mmol) in 30 ml of 2-propanol was reacted at 50°C for 20 h. Additionally the solution of $Na_2S_2O_5$ (0.73 g, 3.8 mmol) in 2.4 ml water was added to the reaction mixture and it was refluxed for 1.5 h. The crude product precipitated. It was collected by filtration and subjected to column chromatography using the mixture of ethyl acetate and hexane in a volume ratio of 1:4 as an eluent. The solid was recrystallized from mixture of chloroform and hexane. The product was obtained as a brown crystals. Yield of compound 4 was 1.45 g (95%). M.p. 242°C (DSC). MS (APCl$^+$, 25 V), m/z (%): 412.5 ([M+H]$^+$). ^{1}H NMR (300 MHz, d_6-DMSO, ppm, δ): 6.45 (d, 2H, J = 7.2 Hz), 7.01 (d, 2H, J = 8.8 Hz), 7.06–7.22 (m, 10H), 7.35–7.44 (m, 4H), 7.89 (d, 2H, J = 8.8 Hz). IR, KBr, (cm^{-1}): 3429, ν (NH); 3049, ν (CH_{ar}); 1633, ν (C=N); 1588, 1505, 1491, ν (C=C_{ar}); 1332, ν (C–N); 823, 757, 697, γ (CH_{ar}). Elemental analysis: Calculated, ($C_{29}H_{21}N_3$): C 84.64%; H 5.14%; N 10.21%; Found: C 84.61%; H 5.13%; N 10.26%.

2.2.5. N,N-Bis(4-(1H-perimidin-2-yl)phenyl)benzenamine (5)

A mixture of bis-(4-formylphenyl)phenylamino (1 g, 3.32 mmol)) and 1,8-diaminonaphthalene (1.76 g, 6.64 mmol) in 30 ml of 2-propanol was stirred at 60°C for 21 h. Then the solution of $Na_2S_2O_5$ (0.63 g, 3.3 mmol) in 2 ml of water was added to the reaction mixture and it was refluxed for 22 h. The crude product precipitated and was collected by filtration, washed with 2-propanol and subjected to column chromatography using the the mixture of diethyl ether and toluene in a volume ratio of 1/6. The solid was recrystallized from the eluent mixture of solvents. The product was obtained as a brown crystals. Yield of compound 5 was 1.72 g (96%). M.p. 264°C (DSC). MS (APCl$^+$, 25 V), m/z (%): 578.5 ([M+H]$^+$). ^{1}H NMR (300 MHz, d_6-DMSO, ppm, δ): 6.51–6.59 (m, 2H), 6.62–6.71 (m, 2H), 6.97–7.29 (m, 17H), 7.98 (d, 4H, J = 8.8 Hz), 10.59 (s, 2H, NH). IR, KBr, (cm^{-1}): 3418, 3239, 3208, ν (NH); 3045, ν (CH_{ar}); 1635, ν (C=N); 1590, 1505, ν (C=C_{ar}); 1333, ν (C–N); 822, 768, 694, γ (CH_{ar}). Elemental analysis: Calculated, ($C_{40}H_{27}N_5$): C 83.17%; H 4.71%; N 12.12%; Found: C 83.14%; H 4.75%; N 12.11%.

2.2.6 N-(4-(1H-Perimidin-2-yl)phenyl)-4-methoxy-N-(4-methoxyphenyl)benzenamine (6)

A mixture of 4-(bis(4-metoxyphenyl)amino)benzaldehyde (1.55 g, 4.65 mmol) and 1,8-diaminonaphthalene (0.74 g, 4.65 mmol) in 30 ml of 2-propanol was stirred at 60°C for 21 h. Then the solution of $Na_2S_2O_5$ (0.88 g, 4.6 mmol) in 2 ml of water was added to the reaction mixture and it was refluxed for 22 h. The crude product precipitated and was collected by filtration. Then it was washed with 2-propanol, dried. The product was obtained as a yellow crystals. Yield of compound 6 was 1.7 g. (79%). M.p. 188°C (DSC). MS ($APCl^+$, 25 V), m/z (%): 472.5 ($[M+H]^+$). ^1H NMR (300 MHz, $CDCl_3$, ppm, δ): 3.83 (s, 6H, OCH_3), 6.85–6.95 (m, 8H), 6.98–7.25 (m, 8H), 7.72 (d, 2H, $J = 9.0$ Hz), 8.05 (s, 1H, NH). IR, KBr, (cm^{-1}): 3282, ν (NH); 3047, 3010, ν (CH_{ar}); 2835, ν (CH_{aliph}); 1636, ν (C=N); 1591, 1504, 1441, ν ($C{=}C_{ar}$); 1326, ν (C–N); 827, γ (CH_{ar}). Elemental analysis: Calculated, ($C_{31}H_{25}N_3O_2$): C 78.96%; H 5.34%; N 8.91%, O 6.79%; Found: C 78.91%; H 5.38%; N 8.96%.

2.2.7. 1-Ethyl-2-phenylperimidine (7)

2-Phenylperimidine (1) (2 g, 8.19 mmol) was dissolved in 30 ml of dry acetone and KOH powder (0.92 g, 16.4 mmol) was added. After 15 min, ethyl iodide (1.66 g, 10.65 mmol) was added by syringe and the reaction mixture was stirred for 30 min at room temperature. The crude product was precipitated into 400 ml of water. The suspension was extracted with dichloromethane and after evaporation the crude product was subjected to column chromatography (eluent: chloroform). The solid was recrystallized from eluent. Yield of yellow crystals of 7 was 0.65 g (30%). M.p. 175°C (DSC). MS ($APCI^+$, 20 V), m/z (%): 273.4 ($[M+H]^+$). ^1H NMR (300 MHz,$CDCl_3$, ppm, δ): 1.23 (t, 3H, $J = 7.0$ Hz, $CH_2\underline{CH_3}$), 3.63 (q, 2H, $J = 7.0$ Hz, $\underline{CH_2}CH_3$), 6.36 (dd, 1H, $J_1 = 7.2$ Hz, $J_2 = 1.7$ Hz), 6.94 (dd, 1H, $J_1 = 7.2$ Hz, $J_2 = 1.7$ Hz), 7.13–7.44 (m, 4H), 7.46–7.69 (m, 5H). IR, KBr, (cm^{-1}): 3053, ν (CH_{ar}); 2983, ν (CH_{aliph}); 1624, ν (C=N); 1569, 1495, 1444, ν ($C{=}C_{ar}$); 1335, ν (C–N); 820, 769, 750, γ (CH_{ar}). Elemental analysis: Calculated ($C_{19}H_{16}N_2$): C 83.79%; H 5.92%; N 10.29%; Found: C 83.74%; H 5.96%; N 11.30%.

2.2.8. 1-Ethyl-2-(9-ethyl-3-carbazolyl)perimidine (8)

2-(9-Ethyl-3-carbazolyl)perimidine (2) (1 g, 2.77 mmol) was dissolved in 15 ml of dry THF and KOH powder (0.31 g, 5.54 mmol) was added. After 10 min, ethyl iodide (0.56 g, 3.6 mmol) was added by syringe and the reaction mixture was stirred for 30 min at room temperature. The reaction mixture was filtrated, solvent was evaporated and the crude product was subjected to column chromatography using chloroform as an eluent. The solid was recrystallized from eluent. Yield of yellow crystals of 8 was 0.52 g (48%). M.p. 282°C (DSC). MS ($APCI^+$, 20 V), m/z (%): 390.4 ($[M+H]^+$). ^1H NMR (300 MHz,$CDCl_3$, ppm, δ): 1.26 (t, 3H, $J = 7.0$ Hz, $CH_2\underline{CH_3}$(perimidine)), 1.49 (t, 3H, $J = 7.2$ Hz, $CH_2\underline{CH_3}$(carbazole)), 3.75 (q, 2H, $J = 7.0$ Hz, $\underline{CH_2}CH_3$(perimidine)), 4.46 (q, 2H, $J = 7.2$ Hz, $\underline{CH_2}CH_3$(carbazole)), 6.44 (dd, 1H, $J_1 = 7.0$ Hz, $J_2 = 1.5$ Hz), 6.97 (dd, 1H, $J_1 = 7.4$ Hz, $J_2 = 1.2$ Hz), 7.21–7.34 (m, 5H), 7.46–7.57 (m, 3H), 7.63 (dd, 1H, $J_1 = 8.4$ Hz, $J_2 = 1.5$ Hz), 8.15 (d, 1H, $J = 7.7$ Hz), 8.29 (d, 1H, $J = 1.2$ Hz). IR, KBr, (cm^{-1}): 3051, ν (CH_{ar}); 2978, ν (CH_{aliph}); 1628, ν (C=N); 1572, 1496, 1454, ν ($C{=}C_{ar}$); 1339, ν (C–N); 828, 762, 751, γ (CH_{ar}). Elemental analysis: Calculated ($C_{27}H_{23}N_3$): C 83.26%; H 5.95%; N 10.79%; Found: C 83.31%; H 5.91%; N 11.78%.

2.2.9. 10-(2-Ethylhexyl)-3-(1-hexyl-1H-perimidin-2-yl)-10H-phenothiazine (9)

10-(2-Ethylhexyl)-3-(1*H*-perimidin-2-yl)-10*H*-phenothiazine (3) (0.52 g, 1.1 mmol) was dissolved in *N*-methyl-2-pyrrolidone (2 ml). K_2CO_3 (1 g, 7.8 mmol) was added and the reaction mixture was stirred under an atmosphere of argon for 10 min. Subsequently hexyl bromide

(0.22 g, 1.3 mmol) was added and the reaction was carried out under microwave irradiation for 1.5 min (P = 320 W). Then the reaction mixture was extracted with ethyl acetate, the solvent was evaporated and the crude product was subjected to column chromatography using the mixture of ethyl acetate and hexane in a volume ratio of 1/10 as an eluent. Yield of the yellow liquid was 0.15 g, (27%). MS (APCl$^+$, 25 V), m/z (%): 562.6 ([M+H]$^+$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 0.81 (t, 3H, J = 6.8 Hz, CH_3), 0.91 (t, 6H, $CH_2CH_2\underline{CH_3}$), 1.14–1.50 (m, 14H, $(\underline{CH_2})_7$), 1.59–1.74 (m, 2H, $\underline{CH_2}CH_2N$), 1.96 (p, 1H, $\underline{CH}CH_2N$), 3.64 (t, 2H, J = 7.1 Hz, $\underline{CH_2}N$), 3.79 (d, 2H, J = 7.1 Hz, $\underline{CH_2}N$), 6.35 (dd, 1H, J_1 = 6.9 Hz, J_2 = 6.9 Hz), 6.90–7.02 (m, 5H), 7.15–7.26 (m, 4H), 7.27–7.34 (m, 3H). IR, KBr, (cm^{-1}): 3052, ν (CH_{ar}); 2925, ν (CH_{aliph}); 1625, ν (C=N); 1576, 1463, ν (C=C_{ar}); 1336, ν (C–N); 822, 767, 746, γ (CH_{ar}); 680, ν (C–S). Elemental analysis: Calculated, ($C_{37}H_{43}N_3S$): C 79.10%; H 7.71%; N 7.48%, S 5.71%; Found: C 79.14%; H 7.67%; N 7.53%.

2.2.10. 3-(1-Butyl-1H-perimidin-2-yl)-10-(2-ethylhexyl)-10H-phenothiazine (10)

10-(2-Ethylhexyl)-3-(1*H*-perimidin-2-yl)-10*H*-phenothiazine (3) (0.32 g, 0.67 mmol) was dissolved in *N*-methyl-2-pyrrolidone (2 ml). The Cs_2CO3 (0.5 g, 1.5 mmol) was added and the reaction mixture was stirred under an atmosphere of argon for 10 min. Subsequently butyl iodide (0.15 g, 0.80 mmol) was added and the reaction was carried out under microwave irradiation for 1 min (P = 320 W). Then the reaction mixture was extracted with ethyl acetate, the solvent was evaporated, the crude product was subjected to column chromatography using the mixture of ethyl acetate and hexane in a volume ratio of 1/8 as an eluent. Yield of the yellow liquid was 0.08 g (22%). MS (APCl$^+$, 25 V), m/z (%): 534.5 ([M+H]$^+$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 0.83 (t, 3H, J = 7.3 Hz, CH_3), 0.93 (t, 6H, $CH_2CH_2\underline{CH_3}$), 1.16–1.52 (m, 12H, $(\underline{CH_2})_6$), 1.97 (p, 1H, $\underline{CH}CH_2N$), 3.62 (t, 2H, J = 7.6 Hz, $\underline{CH_2}N$), 3.79 (d, 2H, J = 7.3 Hz, $\underline{CH_2}CH_2N$), 6.32 (dd, 1H, J_1 = 6.9 Hz, J_2 = 7.0 Hz), 6.89–7.03 (m, 5H), 7.17–7.26 (m, 4H), 7.27–7.34 (m, 3H). IR, KBr, (cm^{-1}): 3053, ν (CH_{ar}); 2927, ν (CH_{aliph}); 1625, ν (C=N); 1577, 1463, ν (C=C_{ar}); 1337, ν (C–N); 823, 767, 749, γ (CH_{ar}); 680, ν (C–S)). Elemental analysis: Calculated, ($C_{35}H_{39}N_3S$): C 78.76%; H 7.36%; N 7.87%, S 6.01%; Found: C 78.72%; H 7.40%; N 7.82%.

2.2.11. N-(4-(1-Hexyl-1H-perimidin-2-yl)phenyl)-N-phenylbenzenamine (11)

N-(4-(1*H*-Perimidin-2-yl)phenyl)-*N*-phenylbenzenamine (4) (0.27 g, 0.68 mmol) was dissolved in *N*-methyl-2-pyrrolidone (2 ml). K_2CO_3 (1 g, 7.8 mmol) was added and the reaction mixture was stirred under an atmosphere of argon for 10 min. Subsequently hexyl bromide (0.13 g, 0.82 mmol) was added and the reaction was performed under microwave irradiation for 3 min (P = 320 W). Then the reaction, reaction mixture was extracted with dichloromethane, the solvent was evaporated and the crude product was subjected to column chromatography using the mixture of ethyl acetate and hexane in a volume ratio of 1/8 as an eluent. Yield of the brown liquid was 0.08 g (28%). MS (APCl$^+$, 25 V), m/z (%): 496.6 ([M+H]$^+$). ^{1}H NMR (300 MHz, d_6-DMSO, ppm, δ): 0.8 (t, 3H, J = 6.9 Hz, CH_3), 1.02–1.25 (m, 6H, $CH_3(\underline{CH_2})_3$), 1.57 (p, 2H, $\underline{CH_2}CH_2N$), 3.66 (t, 2H, J = 7.4 Hz, $\underline{CH_2}N$), 6.49 (d, 1H, J = 7.1 Hz), 6.68 (dd, 1H, J_1 = 7.1 Hz, J_2 = 1.1 Hz), 7.04 (d, 2H, J = 8.7 Hz), 7.07–7.20 (m, 8H), 7.22–7.32 (m, 2H), 7.33–7.42 (m, 4H), 7.44 (d, 2H, J = 8.7 Hz). IR, KBr, (cm^{-1}): 3052, 3036, ν (CH_{ar}); 2926, ν (CH_{aliph}); 1625, ν (C=N); 1579, 1494, ν (C=C_{ar}); 1334, 1316, ν (C–N); 822, 754, 699, γ (CH_{ar}).). Elemental analysis: Calculated, ($C_{35}H_{33}N_3$): C 84.81%; H 6.71%; N 8.48%; Found: C 84.85%; H 6.70%; N 8.45%.

2.2.12. N-(4-(1-(2-Ethylhexyl)-1H-perimidin-2-yl)phenyl)-N-phenylbenzenamine (12)

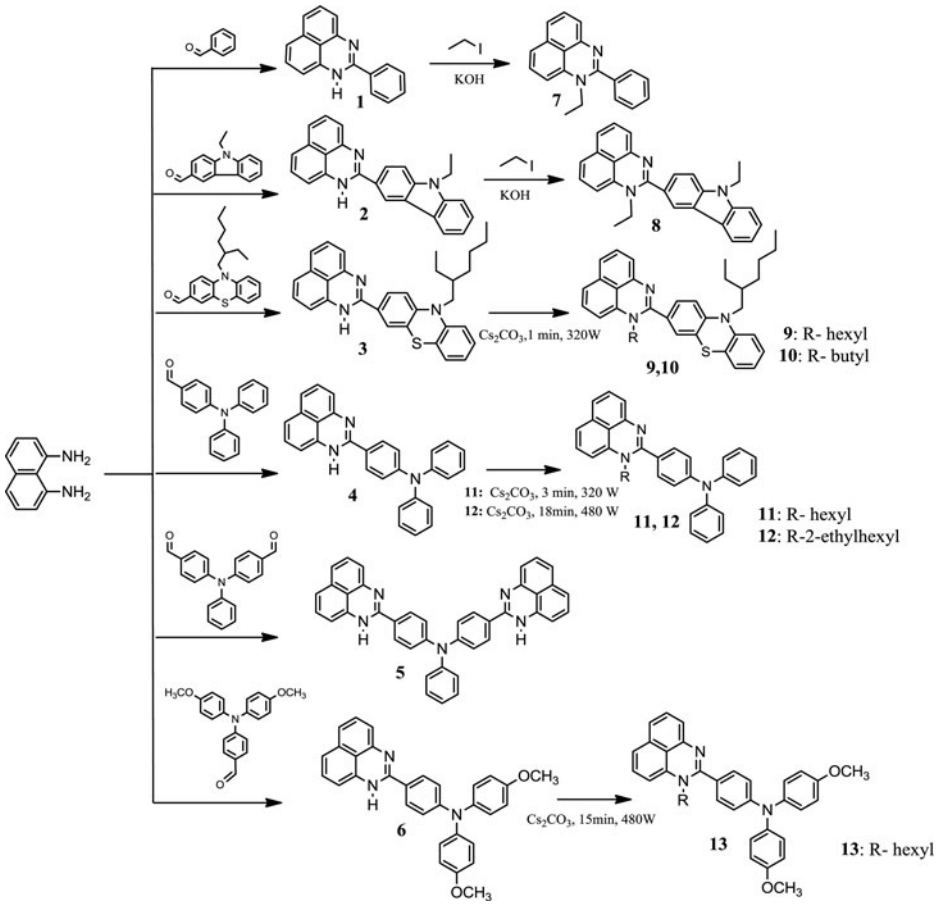
N-(4-(1*H*-Perimidin-2-yl)phenyl)-*N*-phenylbenzenamine (4) (1 g, 2.51 mmol) was dissolved in *N,N*-dimethylacetamide. Cs_2CO_3 (0.5 g, 1.5 mmol) was added and the reaction mixture was stirred under an atmosphere of argon for 10 min. Subsequently 2-ethylhexyl bromide (0.58 g, 3.02 mmol) was added and the reaction was carried out under microwave irradiation for 18 min (P = 480 W). Then the reaction mixture was extracted with ethyl acetate, the solvent was evaporated and the crude product was subjected to column chromatography using the mixture of ethyl acetate and hexane in a volume ratio of 1/5 as an eluent. Yield of the yellow liquid was 0.36 g (28%). MS (APCl$^+$, 25 V), m/z (%): 423.7 ([M+H]$^+$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 0.69 (s, 3H, $CH_2CH_2\underline{CH_3}$), 0.82 (t, 3H, J = 6.9 Hz CH_3), 0.98–1.37 (m, 8H, $(\underline{CH_2})_4$), 1.82–1.97 (m, 1H, $\underline{CH}CH_2N$), 3.55–3.85 (s(br), 2H, $\underline{CH_2}N$), 6.31 (dd, 1H, J_1 = 7.2 Hz, J_2 = 1.3 Hz), 6.90 (dd, 1H, J_1 = 7.2 Hz, J_2 = 1.3 Hz), 7.06 (d, 2H, J = 6.7 Hz), 7.08–7.22 (m, 8H), 7.22–7.32 (m, 6H), 7.35 (d, 2H, J = 8.3 Hz). IR, KBr, (cm^{-1}): 3052, ν (CH_{ar}); 2926, ν (CH_{aliph}); 1625, ν (C=N); 1584, ν (C=C_{ar}); 1331, 1315, ν (C–N); 823, 767, 695, γ (CH_{ar}). Elemental analysis: Calculated, ($C_{37}H_{37}N_3$): C 84.86%; H 7.12%; N 8.02%; Found: C 84.82%; H 7.17%; N 8.01%.

2.2.13. N-(4-(1-Hexyl-1H-perimidin-2-yl)phenyl)-4-methoxy-N-(4-methoxyphenyl) benzenamine (13)

N-(4-(1*H*-Perimidin-2-yl)phenyl)-4-methoxy-*N*-(4-methoxyphenyl)benzenamine (6) (0.8 g, 1.7 mmol) was dissolved in *N,N*-dimethylacetamide (2 ml). Cs_2CO_3 (0.5 g, 1.5 mmol) was added and the reaction mixture was stirred under an atmosphere of argon for 10 min. Subsequently hexyl bromide (0.35 g, 2.1 mmol) was added and the reaction was carried out under microwave irradiation for 15 min (P = 480 W). Then the reaction mixture was extracted with ethyl acetate, the solvent was evaporated and the crude product was subjected to column chromatography using hexane as an eluent. Yield of the yellow liquid was 0.2 g (34%). MS (APCl$^+$, 25 V), m/z (%): 556.4 ([M+H]$^+$). ^{1}H NMR (300 MHz, $CDCl_3$, ppm, δ): 0.9 (t, 3H, J = 7.2 Hz, CH_3), 1.18–1.34 (m, 6H, $CH_3(\underline{CH_2})_3$), 1.66 (p, 2H, $\underline{CH_2}CH_2N$), 3.67 (t, 2H, J = 7.2 Hz, $\underline{CH_2}N$), 3.84 (s, 6H, OCH_3), 6.32 (dd, 1H, J = 7.2 Hz, J = 1.4 Hz), 6.87–6.92 (m, 4H), 6.93 (dd, 1H, J = 7.2 Hz, J = 1.4 Hz), 6.99 (d, 2H, J = 8.8 Hz), 7.05–7.16 (m, 4H), 7.17–7.20 (m, 2H), 7.21–7.29 (m, 2H), 7.32 (d, 2H, J = 8.8 Hz). IR, KBr, (cm^{-1}): 3049, ν (CH_{ar}); 2927, 2833, ν (CH_{aliph}); 1625, ν (C=N); 1575, 1506, 1497, ν (C=C_{ar}); 1320, ν (C–N); 823, 767, γ (CH_{ar}). Elemental analysis: Calculated, ($C_{37}H_{37}N_3O_2$): C 79.97%; H 6.71%; N 7.56%, O 5.76%; Found: C 79.92%; H 6.75%; N 7.61%.

3. Results and discussion

2-Substituted perimidines (**1-6**) were obtained by the synthetic routes shown in Scheme 1. The first step was the condensation of 1,8-diaminonaphthalene with varoius aldehydes including benzaldehyde, 9-ethyl-9*H*-carbazole-3-carbaldehyde, 10-(2-ethylhexyl)-10*H*-3-phenothiazine carbaldehyde, 4-(diphenylamino)benzaldehyde, bis-(4-formylphenyl)phenylamino benzaldehyde and 4-(bis(4-metoxyphenyl)amino)benzaldehyde. These reactions preceed in two steps. The first step is the condensation to form Schiff base and the second step is the intramolecular nucleophilic attack of the amino group at the imino carbon to result in C–N coupling [13]. The imino (or azomethine, C=N) carbon is partially positively charged, and therefore is susceptible to intermolecular or intramolecular nucleophilic attack. The obtained dihydroperimidines were effectively aromatized with $Na_2S_2O_5$ and the corresponding perimidines (**1-6**) were formed in high yields. The obtained



Scheme 1. Synthesis of perimidine derivatives.

perimidine derivatives (**1**-**6**) were purified by column chromatography and characterized by IR, ^{1}H NMR spectroscopies, mass spectrometry and elemental analyses as described in experimental section. The usual alkylation conditions were used for the preparation of compounds **7** and **8**, while the alkylation reactions of **3**, **4** and **6** were perfomed using microwave irradation. The alkylated 2-substituted perimidine derivatives (**7**-**13**) were purified by column chromatography and characterized also by IR, ^{1}H NMR spectroscopies, mass spectrometry and elemental analysis as described in experimental section.

3.1. Thermal properties

Thermal properties of 2-substituted perimidine derivatives were examined by DSC and TGA. The glass transition (T_g) and melting temperatures (T_m) as well as 5% weight loss temperatures (T_{ID}) of the compounds are summarized in Table 1.

Compounds **1**-**8** and **11** were isolated after the synthesis as the crystalline substances. Compounds **1**, **3**-**6** and **11** could be transformed into molecular glasses by cooling from the melts. Compounds **9**, **10, 12, 13** were isolated after the synthesis as amorphous substances. Compound **9** exhibited glass transition below room temperature. The glass transition temperatures of perimidine derivatives containing triphenylamino moiety (**4**-**6**, **11**-**13**) varies from 2 to 197°C. Compound **5** having two perimidinyl moieties exhibit T_g by 96°C higher than the

Table 1. Thermal, optical and phothophysical characteristics of 2-substituted perimidines 1–13.

Compound	T_m[a]/T_g[a]/T_d[b] (°C)	[sol]Abs (nm)	[film]Abs (nm)	[sol]PL (nm)	[film]PL (nm)	Stokes shift in sol (nm)
1	186/70/246	328	331	388	—	60
2	225/–/238	326	329	386	—	60
3	162/69/363	348	350	520	556	172
4	242/101/392	350	351	540	558	190
5	264/197/345	355	355	404	—	49
6	188/126/265	363	370	520	561	157
7	175/–/265	336	340	414	—	78
8	232/–/270	336	341	414	—	78
9	–/–4/296	339	342	512	522	173
10	–/1/303	339	344	522	550	183
11	–/31/311	338	341	502	540	164
12	–/2/230	341	345	470	550	129
13	–/44/375	340	344	476	530	136

[a]Determined by DSC, scan rate 10°C/min, N_2 atmosphere. [b]$T_{dec\text{-}5\%}$-5% weight loss temperatures; scan rate 10°C/min, N_2 atmosphere.

derivative **4** having one perimidinyl group (Table 1). Such drastic increase of T_g can apparently be explained by the enhancement of intermolecular interaction (hydrogen bonding) in the glass of **5**. The comparison of T_g of **4** and **11** shows that alkylation resulted in the dramatic decrease of T_g. Compound **11** showed T_g lower by 69°C compared with that of **4**. Such a decrease of T_g of **11** can be explained by the plasticizing effect of alkyl chain and by disappearance of hydrogen bonding site (NH group).

Compounds **7**, **8** having short aliphatic chains (ethyl) did not show glass-forming property. Compound **1** exhibited glass-forming property which was apparently enhanced by hydrogen bonding. Methoxy substituents at triphenylamino moiety also influenced the glass transition temperature of the studied perimidine derivatives. Compound **6** containing methoxy groups exhibited T_g by 25°C higher than compound **4** (Fig. 1).

The temperatures of 5% weight loss temperatures of the compounds ranged from 230 to 392°C. Extremely high thermal stability with T_{ID} 392°C was observed for compound **4**.

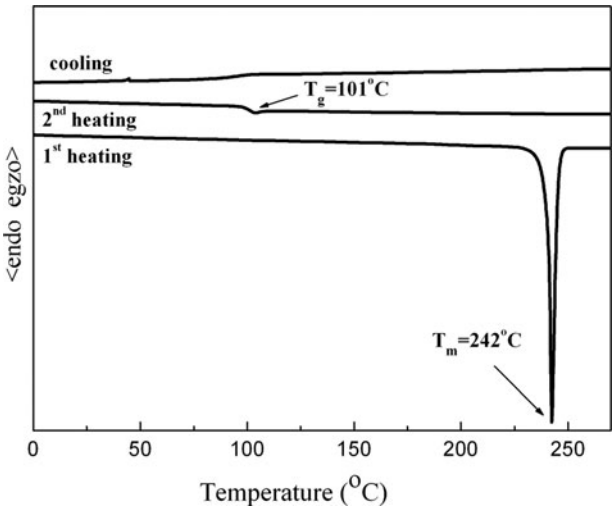


Figure 1. DSC curves of compound **4**. Heating rate 10°C/min, N_2 atmosphere.

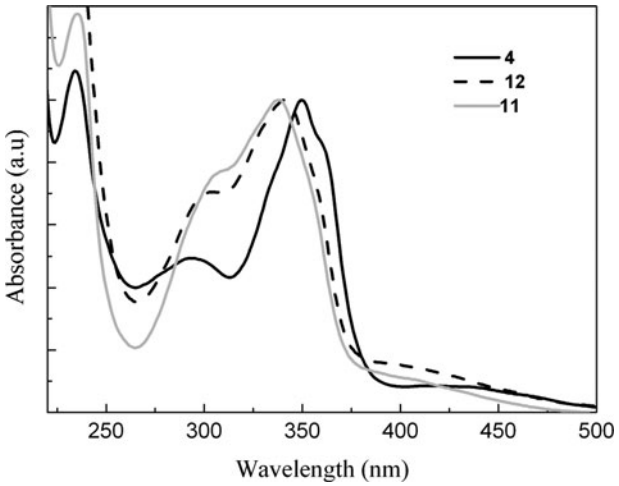


Figure 2. UV absorption spectra of diluted solutions in THF of **4**, **11** and **12** compounds.

3.2. Optical properties

The optical properties of dilute THF solutions and of the films of the synthesized compounds were studied by UV spectrometry. UV absorption spectra of the dilute solutions of the selected derivatives are given in Fig 2.

Comparison of the wavelengths of absorption bands of the compounds (Table 1) shows that the most red-shifted absorption spectrum belongs to compound **6** containing two methoxy groups. The alkylated compounds **7**-**13** both in solutions or in solid state exhibit blue shifts of the absorption spectra with respet to those the parent compounds **4, 11, 12** (Fig. 2). The alkyl substitution at the nitrogen atom apparently results in a loss of coplanarity between the perimidine and the (hetero)aromatic moiety. This observation is in agreement with previously described findings, which where supported by photophysical, X-ray and NMR data [14]. Moreover, the nature of alkyl substituents was found to have effect on the absorption spectra. UV absorptions bands of compound **12** having 2-ethylhexyl substituent was found to be blue shifted with respect to those of compound **11** having hexyl group. It seems that compound **12** having the branched alkyl substituent adopts les planar conformation than compound **11** having linear alkyl chain.

3.3. Photophysical properties

Photophysical characterization of the synthesized compounds in the form of diluted solutions and solid layers was performed by fluorescence spectroscopy. The wavelengths of emission maxima are presented in the Table 1.

The fluorescence spectra of the dilute solutions of alkylated compounds (**9**, **11**, **12** and **13**) were found to be blue shifted in respect of those of the solutions of non-alkylated compounds (**3**, **4**, **6**). This observation supports UV spectroscopy data that compounds **3**, **4** and **6** adopt planar conformations in contrast to their alkylated counterparts. In addition, it was found that the nature of alkyl substituent influences the position of the emmision band as it is shown in Fig. 3. The dependence of the Stokes shifts on the chemical structure of compounds was observed. Non-alkylated compounds **4** and **6** showed higher Stokes shifts than alkylated compounds (**11**, **12**, and **13**).

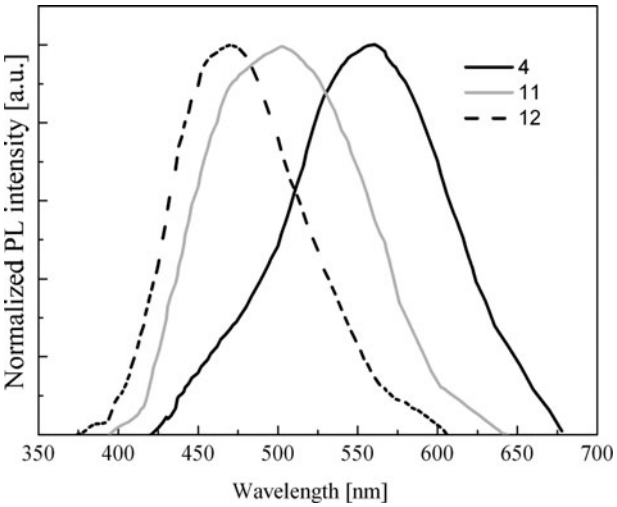


Figure 3. Photoluminescence spectra of dilute solutions of **4, 11** and **12** in THF.

Most of the synthesized 2-substituted perimidine derivatives exhibit detectable fluorescence in solid state (Fig. 4). Due to intermolecular interactions between the molecules in the solid state the emmision bands of the films are shifted to the longer wavelengths with respect to those of the dilute solutions.

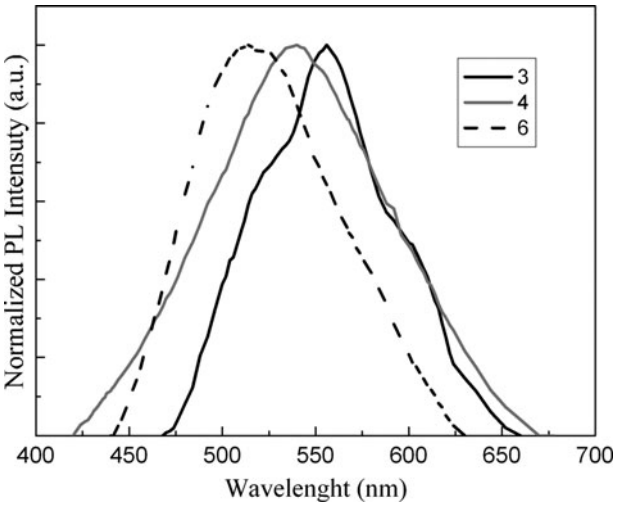


Figure 4. Photoluminescence spectra of solid-state samples of **3, 4** and **6.**

3.4. Photoelectrical properties

An important characteristic of electronically active compounds used in optoelectronic devices is ionization potential (I_p), which characterizes the electron releasing work under illumination. The I_p values for the films of the synthesized compounds were established by electron photoemission technique from the dependencies of photocurrent (I) on the incident light quanta energy, which are named as electron photoemission spectra and plotted as $I^{0.5} = f(h\nu)$. The linear part of this dependency was extrapolated to the hν axis and I_p value was determined

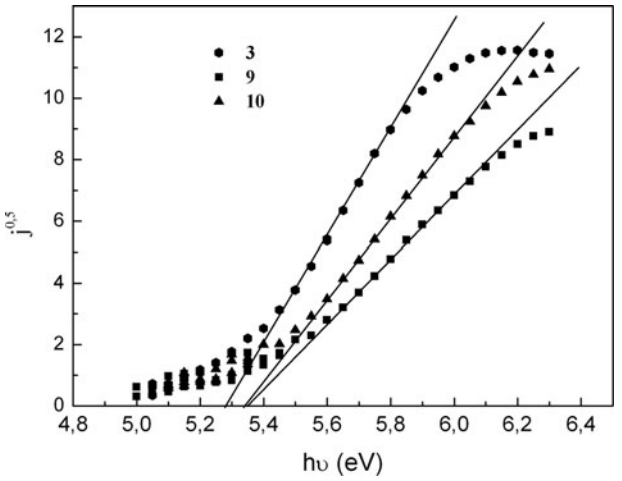


Figure 5. Electron photoemission spectra of the layers of **3**, **9**, **10**.

Table 2. Photoelectron spectroscopy data.

Compound	3	4	7	8	9	10	11	12	13
I_p, [eV]	5.28	5.28	5.52	5.26	5.35	5.34	5.35	5.33	5.26

as the photon energy at the interception point. The photoemission spectra of the films of the selected compounds **3, 9**, **10** recordeded at 25°C are shown in Fig. 5. The values of ionization potentials of all the synthesized compounds are summarised in Table 2. The ionization potentials of synthesized 2-substituted perimidine derivatives depend on the structure of the perimidine substituent at position C-2. Compound **7** containing phenyl substituent shows the highest I_p value.

Figure 5 shows electron photoemission spectra of alkylated (**9, 10**) and non-alkylated (**3**) perimidine derivatives containing phenothiazine substituent. Compound **3** possess slightly lower ionisation potential and these results correlate with UV spectroscopy data. Probably the lower ionization potential of **3** is related to the more planar structure of the molecule and therefore more efficient conjugation of π electrons.

4. Conclusions

The family of 2-substituted perimidine derivatives was synthesized by condensation reactions of 1,8-diaminonaphthalene and the different formyl derivatives. The alkylation of the intermediate compounds have been performed using microwave irradiation. Synthesized compounds exhibit higher thermal stability. The alkyl substituents attached to the perimidinyl moiety influence the conformation of the molecules and consequently their absorption and emission properties. The values of ionization potentials of the layers of the synthesized derivatives range from 5.26 to 5.52 eV.

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