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Synthesis and optical properties of a series of thermally stable diphenylanthrazolines

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ABSTRACT

A series of diphenylanthrazolines were synthesized by Friedländer condensation of 2,5-dibenzoyl-1,4-phenylenediamine and acetyl-functionalized compounds in the presence of polyphosphoric acid as catalyst, in yields ranging from 61% to 88%. The diphenylanthrazolines are thermally robust with high decomposition temperatures (>380.0 °C) and high melt transitions (317–462 °C). All of them show the lowest energy absorption bands (λ_{max}^{Abs}: 394–433 nm) from the π–π^* transitions by virtue of their large molar extinction coefficients ($\varepsilon \approx 10^4\ M^{-1}\ cm^{-1}$), revealing low optical band gaps (2.59–2.80 eV). The compounds emit blue fluorescence with λ_{max}^{Em} ranging from 430 to 466 nm in dilute toluene solution.

1. Introduction

The electronic structure, optical, nonlinear optical and charge transport properties of numerous conjugated polyanthrazolines have recently attracted much attention in the context of electronic and optoelectronic devices [1–10]. Although over several polyanthrazolines have been reported over the past 20 or so years [1–3,5–7,11–13], reports concerning the photophysical properties of small molecules based on the 4,8-diphenylanthrazoline core are limited. However, in 2003, five diphenylanthrazoline derivatives were reported by Jenekhe [14] who showed that these small molecules had high electron affinity and high thermal stability and were promising electron-transport (n-type) materials for organic light-emitting diodes (OLED). In this context, the development of new anthrazoline molecules and the further study of the underlying structure–property relationships presented an interesting challenge.

In this paper, a series of new diphenylanthrazolines: 2,4,6,8-tetraphenylanthrazoline (**1a**), 2,6-bis(4′-methylphenyl)-4,8-diphenylanthrazoline (**1b**), 2,6-bis(4′-ethylphenyl)-4,8-diphenylanthrazoline (**1c**), 2,6-bis(4′-isopropylphenyl)-4,8-diphenylanthrazoline (**1d**), 2,6-bis(biphenyl)-4,8-diphenylanthrazoline (**1e**), 2,6-bis(4′-phenoxyl phenyl)-4,8-diphenylanthrazoline (**1f**), 2,6-bis(2-fluorenyl)-4,8-diphenylanthrazoline (**1g**), 2,6-bis(2-pyridyl)-4,8-diphenylanthrazoline (**1h**) and 2,6-bis(3-(*N*-ethylcarbazole))-4,8-diphenylanthrazoline (**1i**) (Fig. 1) were synthesized and characterized. The thermal stabilities and optical properties of these compounds were also investigated. Compound **1a** has been reported in the literature [14] and was synthesized as a reference compound.

2. Experimental section

2.1. Measurements

Melting points were measured on an X-4 microscope electrothermal apparatus (Taike China) and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-500 spectrometer at 500 MHz or a Bruker AV-300 spectrometer at 300 MHz using $CDCl_3$ and trifluoroacetic acid (TFA) as the solvent, with tetramethylsilane as internal standard. Fourier transformation infrared (FTIR) spectra were recorded in KBr pellets using an AVARTE360 FTIR spectrometer (Thermo Nicolet). The elemental analyses were performed with a Vario El III elemental analyzer. Thermogravimetric analysis (TGA) of the molecules and differential scanning calorimetry (DSC) were conducted on a TA Instruments NETZSCH TG 209 and a DSC Instruments NETZSCH DSC 204, respectively. A heating rate of 10 °C/min under air condition was used with runs being conducted from room temperature to 450 °C. Optical absorption spectra were obtained by using a HP-8453 UV/vis/near-IR Spectrophotometer (Agilent). Photoluminescence spectra were carried out on a LS-55 spectrofluorometer (Perkin–Elmer).

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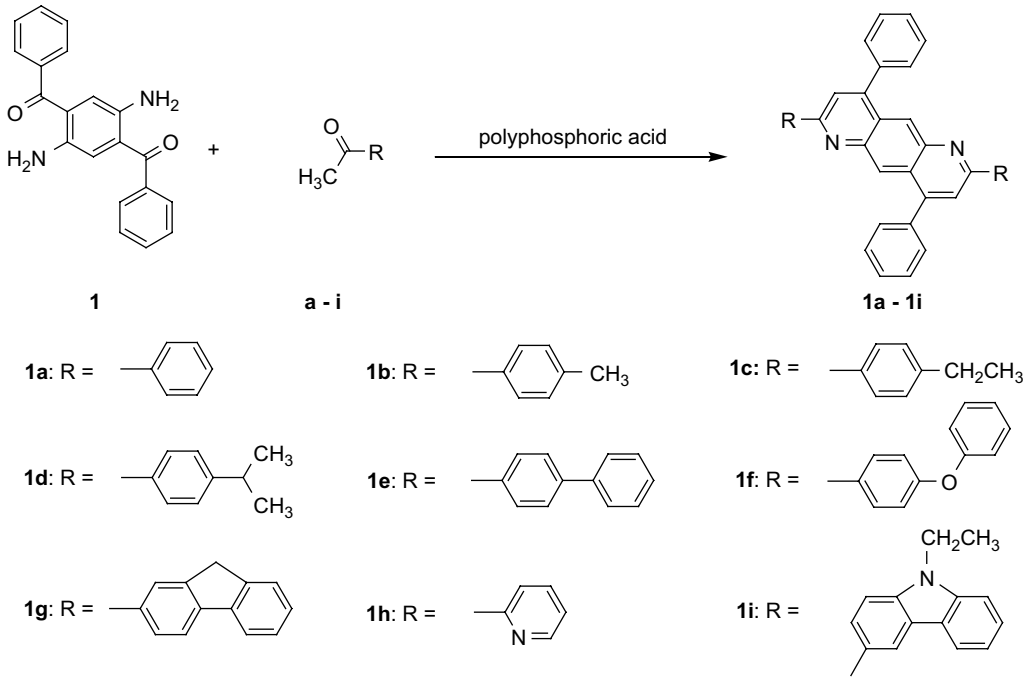

Fig. 1. Synthesis of diphenylanthrazolines (**1a**–**1i**).

2.2. Synthesis

Pyromellitic dianhydride was purchased from Zhejiang Shengxiao Chemical Company. 2-Acetylfluorene (**g**) and 2-acetylpyridine (**h**) were purchased from J&K Chemical Ltd. Acetophenone (**a**), *p*-methylacetophenone (**b**) and other reagents were purchased from Sinopharm Chemcial Reagent Co. Ltd and used as received. 2, 5-Dibenzoyl-1,4-phenylenediamine (**1**) [13,15], other acetyl-functionalized compounds **c**–**f** and **i** [16,17], and diphenylanthrazoline derivatives (**1a**–**1i**) [13] were synthesized according to the methods reported in literatures with some modification. The synthetic routines are shown in Figs. 1–4, respectively.

2.2.1. 2,5-Dibenzoylterephthalic acid (*4*)

A mixture of finely ground pyromellitic dianhydride (10.9 g, 50.0 mmol), powdered anhydrous aluminum chloride (30.0 g, 225 mmol) and benzene (250 ml) was heated with stirring at 65–70 °C for 4 h. During the period, hydrogen chloride gas was evolved, and the suspension turned brown. The reaction mixture was then poured into water (200 ml) containing concentrated hydrochloric acid (17 ml). After removal of the benzene by steam distillation, a mixture of **4** and its isomers (4,6-dibenzoylisophthalic acid) were obtained as an off-white, granular material. The acids were collected by filtration, washed with water, and dissolved in dilute potassium hydroxide solution. After filtration to remove a small amount of insoluble matter, the acids were reprecipitated with hydrochloride acid, washed with water, and dried at 80 °C for 8 h. Then the dried acids were recrystallized twice from acetic acid to give **4** (5.2 g, 14 mmol) as white needles in 28.0% yield, m.p. 318–321 °C (lit. [13]: 335–339 °C). The molecular structure of **4** was characterized by X-ray single crystal diffraction and reported by us elsewhere [18–20].

2.2.2. Pseudo-2,5-dibenzoylterephthalic chloride (*3*)

A mixture of **4** (28.0 g, 74.9 mmol), thionyl chloride (100 ml) and dimethyl formamide (1.2 ml) was heated at the reflux temperature (76–78 °C) for 2 h. Then the excess thionyl chloride was removed by distillation. Benzene (2 × 30 ml) was added and distilled to remove the last traces of thionyl chloride. Compound **3** (30.5 g, 74.2 mmol) was obtained as fine white plates in 99.2% yield, m.p. 206–208 °C (recrystallized from cyclohexane) (lit. [13]: 205–208 °C), and was used directly for the subsequent reaction without further purification. The molecular structure of **3** was characterized by X-ray single crystal diffraction and reported by us elsewhere [21].

2.2.3. 2,5-Dibenzoylterephthalamide (*2*)

To a stirred solution of concentrated ammonium hydroxide (108 ml) in *N*-methyl-2-pyrrolidinone (NMP) (200 ml) was added dropwise a solution of **3** (30.5 g, 74.2 mmol) in NMP (300 ml) at 0–5 °C over a period of 30 min. The mixture was further stirred for 5 h at 25 °C and then diluted with water (300 ml). The white precipitate was collected by filtration, washed with hot water (500 ml) for 1 h, and then dried at 80 °C for 8 h to give **2** (19.6 g, 52.6 mmol) as a white powder in 70.1% yield, m.p. 275–278 °C (recrystallized from methanol) (lit. [13]: 290–295 °C). Compound **2** was used directly for the subsequent reaction without further purification.

2.2.4. 2,5-Dibenzoyl-1,4-phenylenediamine (*1*)

To a cooled (8–10 °C) solution of potassium hydroxide (46.1 g, 822.4 mmol) in water (395 ml) was added **2** (25.0 g, 67.1 mmol), and the resulting suspension was cooled in an ice water bath. To this was added with stirring 5.25% sodium hypochlorite solution (224 ml) at 8–10 °C during a period of 30 min. The cooling bath was then removed, and the mixture gave a clear yellow solution, which was subsequently warmed on a water bath to 80 °C. The solution turned deep brown in color, and a precipitate began to separate within 30 min. The mixture was stirred at 76–78 °C for additional 1 h. The precipitate was collected, washed with hot water (3 × 500 ml) thoroughly, and dried to give the crude product of **1** (17.0 g, 53.7 mmol) in 80.0% yield. The product was recrystallized twice from ethyl acetate to give **1** (13 g, 41.1 mmol) as crimson prisms in 61.2% yield, m.p. 212–215 °C (lit. [13]: 216–218 °C). The molecular structure of **1** was characterized by X-ray single crystal diffraction and reported by us elsewhere [22].

2.2.5. Synthesis of acetyl-functionalized compounds (*c–f, i*)

*p-Ethylacetophenone (**c**).* To a suspension of powdered anhydrous aluminum chloride (93.4 g, 700 mmol) in carbon tetrachloride

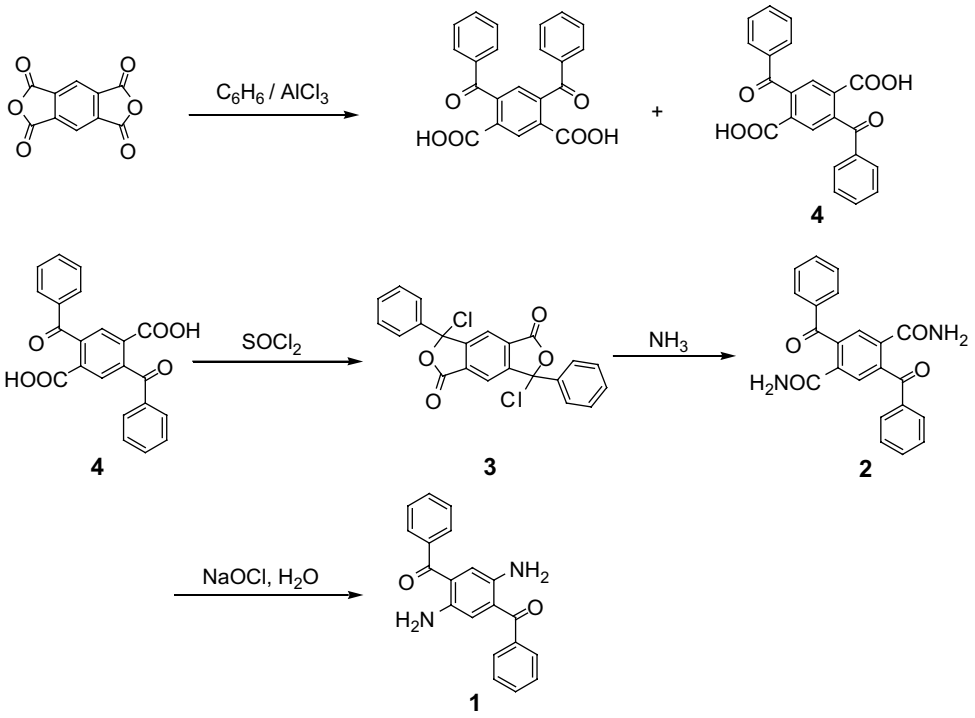

Fig. 2. Synthesis of 2,5-dibenzoyl-1,4-phenylenediamine (**1**).

(400 ml) was added dropwise acetyl chloride (49.8 ml, 700 mmol) ($c = 1.104$ g ml^{-1}) during 30 min with vigorous stirring and cooling in an ice-bath. *p*-Ethylbenzene (73.2 ml, 600 mmol) was then added dropwise over a period of 40 min, keeping the temperature below 5 °C. After the addition was complete, the mixture was stirred for another hour before hydrolyzing by pouring into a mixture of ice and water (500 ml) containing concentrated hydrochloric acid (20 ml) with stirring. The pale yellow carbon tetrachloride solution was washed with successive portion of dilute hydrochloric acid, sodium carbonate solution and water, and distilled through a 30 cm Vigreux column to give **c** (67.3 g, 454 mmol) as colorless liquid in 75.7% yield, b.p. 109–113 °C at 1.4 kPa (lit. [16]: 116–117 °C at 1.7 kPa). ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 1.25 (t, 3H), 2.56 (s, 3H), 2.64 (q, 2H), 7.27 (d, 2H), 7.88 (dd, 1H).

p-Isopropylacetophenone (***d***). Compound **d** was synthesized using the method reported in **c**. Yield was 64.0% as colorless liquid; b.p. 122–123 °C at 1.3 kPa (lit. [16]: 122–124 °C at 1.3 kPa). ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 1.27 (d, H), 2.57 (s, 3H), 2.93–2.99 (m, 1H), 7.31 (d, 2H), 7.89 (d, 2H).

p-Phenylacetophenone (***e***). To a suspension of powdered anhydrous aluminum chloride (29.3 g, 220 mmol) in carbon disulfide (150 ml) was added dropwise acetyl chloride (15.6 ml, 220 mmol) during 30 min with vigorous stirring and cooling in an ice-bath. A solution of biphenyl (30.8 g, 200 mmol) in carbon disulfide (100 ml) was then added dropwise over a period of 30 min. After the addition was complete, the mixture was stirred at the reflux temperature for additional 4 h. Carbon disulfide was removed by distillation and the residue was hydrolyzed by pouring into a mixture of ice and water (500 ml) containing concentrated hydrochloric acid (20 ml) with stirring. A yellow solid material was formed when the mixture was cooled to room temperature. After filtration, the yellow solid material was recrystallized from ethyl alcohol twice to give **e** (33.4 g, 170 mmol) as yellow plates in 85.0% yield, m.p. 120–121 °C (lit. [23]: 120 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 2.64 (s, 1H), 7.39–7.42 (m, 1H), 7.46–7.49 (m, 2H), 7.62–7.64 (m, 2H), 7.69 (d, 2H), 8.03 (d, 2H).

p-Phenoxyacetophenone (***f***). Compound **f** was synthesized according to the method described for compound **e**. Yield was 80.9% as yellow plates; m.p. 47–49 °C (lit. [16]: 49 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 2.56 (s, 3H), 7.00 (d, 2H), 7.06 (d, 2H), 7.19 (t, 1H), 7.39 (t, 2H), 7.93 (d, 2H).

N-Ethylcarbazole (***j***). A mixture of carbazole (26.4 g, 0.16 mol), potassium hydroxide (56.0 g, 1.0 mol) and DMF (320 ml) was stirred at room temperature for 40 min. A solution of bromoethane (18.0 ml, 0.24 mol) in DMF (60 ml) at room temperature was added dropwise over a period of 30 min, with stirring. After the addition was complete, the mixture was stirred at room temperature for additional 10 h. The mixture was then poured into water (4000 ml), and white precipitate was formed immediately. After filtration, the precipitate was recrystallized from ethanol to give **j** (25 g, 0.128 mol) as white needles in 80% yield, m.p. 69 °C (lit. [17]: 72–74 °C).

3-Acetyl-N-ethylcarbazole (***i***). A mixture of **j** (1.95 g, 10.0 mmol) and acetic anhydride (1.02 g, 10.0 mmol) in boron trifluoride diethyl etherate ($BF_3 \cdot Et_2O$) (50 ml) was stirred at room temperature for 4 h. Then the mixture was hydrolyzed by pouring into a mixture of ice and water (100 ml) containing concentrated hydrochloric acid

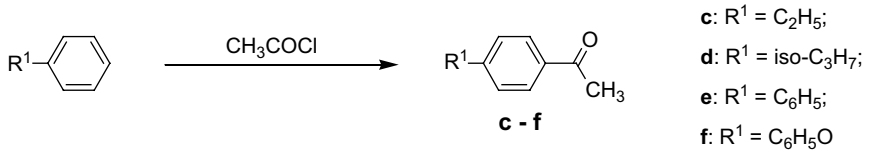

Fig. 3. Synthesis of acetyl-functionalized compounds (**c**–**f**).

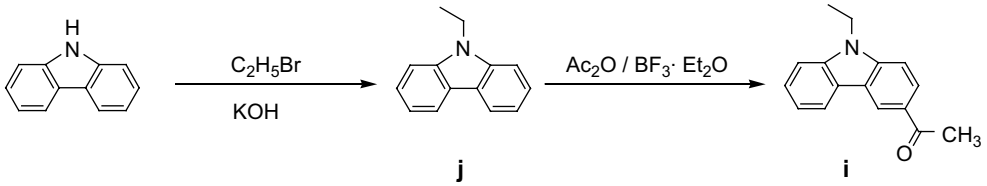

Fig. 4. Synthesis of 3-acetyl-*N*-ethylcarbazole (**i**).

(5 ml) with stirring. Then diethyl ether was removed by distillation, and brown precipitate was got by filtration. The precipitate was purified by column chromatography (petroleum ether/ethyl acetate = 2:1 as the elution) to give **i** (1.9 g, 8.0 mmol) as a yellow powder in 80.1% yield, m.p. 113–115 °C. (lit. [17]: 116–118 °C). ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 1.44 (s, 3H), 2.74 (s, 3H), 4.37 (q, 2H), 7.27–7.31 (m, 1H), 7.39 (d, 1H), 7.43 (d, 1H), 7.49–7.52 (m, 1H), 8.12 (d, d, 1H), 8.15 (d, 1H), 8.73 (d, 1H). ^{13}C NMR ($CDCl_3$, 500 MHz): δ ppm 197.63, 142.72, 140.70, 128.84, 126.45, 126.43, 123.30, 122.74, 121.90, 120.68, 119.98, 108.98, 108.02, 37.78, 26.54, 13.71.

*2.2.6. General procedure for synthesis of **1a–1i***

A mixture of 2,5-dibenzoyl-1,4-phenylenediamine (2 mmol), acetyl-functionalized compound (**a–i**) (4.2 mmol), polyphosphoric acid (PPA) (4 g), and *m*-cresol (10 ml) was heated at 130–140 °C for 48 h. The reaction mixture was then diluted with methanol and poured into 1 M potassium hydroxide solution (500 ml) and collected by vacuum filtration. The precipitate was washed with hot water (3 × 500 ml), once with hot methanol (250 ml), and dried at 80 °C. The resulting product was then recrystallized from tetrahydrofuran (THF)/methanol solutions ranging from 5% to 20% methanol. Each was recrystallized twice.

*2,4,6,8-Tetraphenylanthrazoline (**1a**).* Yield was 61.6% as orange crystals; m.p. 377.1 °C (lit. [14]: 380 °C). ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ ppm 9.35 (s, 2H), 8.35 (s, 2H), 8.12 (q, 4H), 7.85 (m, 4H), 7.82 (m, 2H), 7.76 (m, 12H). ^{13}C NMR ($CDCl_3$ and TFA, 300 MHz): δ ppm 161.46, 159.38, 136.29, 136.11, 133.97, 132.84, 131.06, 130.31. 129.83, 129.62. 129.41, 128.84, 123.37, 122.20. FTIR (KBr, cm^{-1}): 1591, 1533, 1487, 1443, 1358, 1180, 1026, 883, 831, 763, 706, 687. Anal. Calcd. (%) for $C_{36}H_{24}N_2$: C, 89.23; H, 4.99; N, 5.78. Found: C, 89.35; H, 5.24; N, 5.61.

*2,6-Bis(4′-methylphenyl)-4,8-diphenylanthrazoline (**1b**).* Yield was 68.4% as orange crystals; m.p. 395.8 °C. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ ppm 2.54 (s, 6H), 7.56 (d, 4H), 7.76 (m, 10H), 8.02 (d, 4H), 8.31 (s, 2H), 9.24 (s, 2H). ^{13}C NMR ($CDCl_3$ and TFA, 300 MHz): δ ppm 160.53, 158.59, 148.84, 135.82, 133.87, 132.47, 131.73, 130.07, 129.35, 129.23, 128.49, 126.65, 122.89, 121.55, 21.49. FTIR (KBr, cm^{-1}): 2918, 2860, 1595, 1533, 1485, 1446, 1354, 1182, 1043, 1026, 881, 818, 762, 706. Anal. Calcd. (%) for $C_{38}H_{28}N_2$: C, 89.03; H, 5.51; N, 5.46. Found: C, 89.45; H, 5.60; N, 5.32.

*2,6-Bis(4′-ethylphenyl)-4,8-diphenylanthrazoline (**1c**).* Yield was 64.8% as orange plates; m.p. 332.3 °C. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ ppm 1.33 (m, 6H), 2.84 (q, 4H), 7.57 (d, 4H), 7.75 (m, 10H), 8.05 (d, 4H), 8.29 (s, 2H), 9.27 (s, 2H). ^{13}C NMR ($CDCl_3$ and TFA, 300 MHz): δ ppm 158.40, 154.56, 135.76, 133.81, 132.35, 130.46, 130.00, 129.58, 129.38, 129.31, 128.35, 126.78, 122.82, 121.54, 29.13, 14.36. FTIR (KBr, cm^{-1}): 2958, 2925, 2360, 2341, 1591, 1560, 1531, 1490, 1351, 1182, 1056, 881, 835, 764, 708, 669. Anal. Calcd. (%) for $C_{40}H_{32}N_2$: C, 88.85; H, 5.97; N, 5.18. Found: C, 89.01; H, 5.53; N, 5.76.

*2,6-Bis(4′-isopropylphenyl)-4,8-diphenylanthrazoline (**1d**).* Yield was 88.0% as orange plates; m.p. 338.8 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ ppm 1.30 (d, 12H), 2.99 (m, 2H), 7.38 (d, 4H), 7.60 (m, 6H), 7.70 (d, 4H), 7.85 (s, 2H), 8.13 (d, 4H), 8.84 (s, 2H). ^{13}C NMR ($CDCl_3$ and TFA, 300 MHz): δ ppm 160.32, 158.41, 148.55, 135.74, 133.80, 132.37, 131.64, 130.00, 129.29, 129.21, 128.35, 126.63, 122.76, 121.51, 77.20, 21.61. FTIR (KBr, cm^{-1}): 2957, 2923, 2868, 1595, 1568, 1554, 1184, 1053, 883, 839, 771, 702. Anal. Calcd. (%) for $C_{42}H_{36}N_2$: C, 88.69; H, 6.38; N, 4.93. Found: C, 89.10; H, 6.03; N, 5.07.

*2,6-Bis(biphenyl)-4,8-diphenylanthrazoline (**1e**).* Yield was 67.1% as a yellow powder; m.p. 440.2 °C. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ ppm 7.52 (m, 6H), 7.71–7.81 (m, 14H), 8.00 (d, 4H), 8.22 (d, 4H), 8.37 (s, 2H), 9.29 (s, 2H). ^{13}C NMR ($CDCl_3$ and TFA, 300 MHz): δ ppm 160.62, 158.17, 149.61, 138.35, 135.97, 133.87, 132.56, 130.13, 129.85, 129.79, 129.46, 129.39, 128.63, 127.85, 127.54, 122.97, 121.67. FTIR (KBr, cm^{-1}): 1591, 1487, 1350, 1053, 887, 843, 766, 698. Anal. Calcd. (%) for $C_{48}H_{32}N_2$: C, 90.54; H, 5.07; N, 4.40. Found: C, 90.21; H, 4.80; N, 4.81.

*2,6-Bis(4′-phenoxyl phenyl)-4,8-diphenylanthrazoline (**1f**).*Yield was 68.6% as yellow plates; m.p. 317.1 °C. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ ppm 7.07 (d, 4H), 7.15 (m, 6H), 7.37 (t, 4H), 7.60 (m, 6H), 7.70 (d, 4H), 7.83 (s, 2H), 8.20 (d, 4H), 8.81 (s, 2H). ^{13}C NMR ($CDCl_3$ and TFA, 300 MHz): δ ppm 165.97, 160.20, 157.56, 154.36, 135.98, 134.08, 132.54, 131.85, 130.72, 130.19, 129.41, 128.55, 126.36, 122.81, 121.27, 120.99, 119.17. FTIR (KBr, cm^{-1}): 1588, 1536, 1489, 1454, 1351, 1242, 1166, 1026, 885, 849, 749. Anal. Calcd. (%) for $C_{48}H_{32}N_2O_2$: C, 86.20; H, 4.82; N, 4.19. Found: C, 86.46; H, 4.35; N, 4.03.

*2,6-Bis(2-flourenyl)-4,8-diphenylanthrazoline (**1g**).*Yield was 63.0% as a yellow powder; m.p. 431.5 °C. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ ppm 4.10 (s, 4H), 7.52 (m, 4H), 7.68 (t, 2H), 7.80 (m, 10H), 7.98 (t, 2H), 8.13 (d, 2H), 8.19 (d, 2H), 8.32 (s, 2H), 8.41 (s, 2H), 9.23 (s, 2H). ^{13}C NMR ($CDCl_3$ and TFA, 500 MHz): δ ppm 160.14, 158.49, 150.92, 146.31, 145.44, 139.42, 136.08, 134.10, 132.52, 130.37, 130.18, 129.44, 128.99, 128.71, 128.99, 128.71, 128.00, 127.06, 125.77, 125.69, 123.20, 122.17, 122.10, 121.31, 36.94. FTIR (KBr, cm^{-1}): 1591, 1491, 1415, 1361, 1049, 895, 843, 742. Anal. Calcd. (%) for $C_{50}H_{32}N_2$: C, 90.88; H, 4.88; N, 4.24. Found: C, 90.15; H, 4.31; N, 4.56.

*2,6-Bis(2-pyridyl)-4,8-diphenylanthrazoline (**1h**).* Yield was 61.6% as yellow plates; m.p. 462.1 °C. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ ppm 7.74 (m, 10H), 8.64 (t, 2H), 8.35 (s, 2H), 8.71 (m, 4H), 9.06 (d, 2H), 9.23 (s, 2H). ^{13}C NMR ($CDCl_3$ and TFA, 300 MHz): δ ppm 157.77, 148.28, 146.76, 145.92, 145.20, 142.28, 135.01, 131.44, 129.89, 129.81, 129.45, 129.12, 127.72, 125.62, 118.93. FTIR (KBr, cm^{-1}): 2926, 1591, 1568, 1534, 1491, 1473, 1445, 1354, 1062, 1038, 896, 798, 766, 708. Anal. Calcd. (%) for $C_{34}H_{22}N_4$: C, 83.93; H, 4.56; N, 11.51. Found: C, 83.47; H, 4.70; N, 11.95.

*2,6-Bis(3-(N-ethylcarbazole))-4,8-diphenylanthrazoline (**1i**).*Yield was 65.6% as yellow plates; m.p. 348.1 °C. ^{1}H NMR ($CDCl_3$ and TFA, 500 MHz): δ ppm 1.55 (t, 6H), 4.50 (q, 4H), 7.43 (t, 2H), 7.57 (d, 2H), 7.65 (t, 2H), 7.71 (d, 2H), 7.75–7.81 (m, 10H), 8.20 (d, 2H), 8.22 (dd, 2H), 8.43 (s, 2H), 8.91 (d, 2H), 9.02 (s, 2H). ^{13}C NMR ($CDCl_3$ and TFA, 300 MHz): δ ppm 158.26, 157.55, 144.84, 141.52, 136.03, 134.39, 132.07, 129.20, 128.47, 128.39, 126.19, 125.73, 122.91, 122.81, 122.05, 121.17, 120.13, 120.07, 118.98, 116.36, 38.50, 13.45. FTIR (KBr, cm^{-1}): 2972, 2931, 2871, 1589, 1571, 1533, 1491, 1470, 1449, 1434, 1349, 1233, 1045, 1025, 890, 801, 767, 745, 732, 700. Anal. Calcd. (%) for $C_{52}H_{38}N_4$: C, 86.88; H, 5.33; N, 7.79. Found: C, 87.33; H, 5.05; N, 7.40.

3. Results and discussion

3.1. Synthesis and characterization

Fig. 1 outlines the synthesis of the series of diphenylanthrazolines. The acid-catalyzed Friedländer condensation reactions [13]

Table 1
Physical properties of diphenylanthrazolines (**1a–1i**).

Compound	T_m/T_d (°C)	ε (10^4 M^{-1} cm^{-1})	λ_{max}^{Abs} (nm)	λ_{max}^{Em} (nm)	Stokes shift (nm)	E_g^{Opt} (eV)
1a	337.1/396.4	1.79	396	430	34	2.80
1b	395.8/408.0	1.51	401	431	30	2.79
1c	332.3/400.0	1.73	401	431	30	2.77
1d	338.8/380.0	2.08	401	432	31	2.79
1e	440.2/>450.0	1.45	408	438	30	2.64
1f	317.1/400.0	2.00	410	439	29	2.76
1g	431.5/>450.0	1.22	417	445	28	2.65
1h	462.1/462.0	1.82	394	433	39	2.74
1i	348.3/>450.0	3.09	433	466	33	2.57

yielded the desired products in 61–88% yields. The PPA catalyst was readily removed by precipitation into a 1 M potassium hydroxide solution. The precipitation was washed by hot water three times, and hot methanol once, respectively. They were subsequently recrystallized in THF/methanol mixture ranging from 5% to 20% methanol. Compounds **1a** and **1b** were obtained as small orange crystals; **1c** and **1d** were obtained as orange plates; **1e** and **1g** were obtained as a yellow powder; **1f** and **1h** were obtained as yellow plates. ^{1}H NMR spectra, ^{13}C NMR spectra, FTIR spectra and element analysis on **1a–1i** confirmed the proposed structures. Compounds **1a–1i** were soluble in chloroform, tetrahydrofuran, toluene and formic acid in varying degrees.

The thermal properties, including melting and decomposition temperatures, of these molecules are shown in Table 1. DSC was used to investigate phase transitions. No glass transitions or crystallization events were observed by DSC, which is in good agreement with other compounds containing diphenylanthrazoline backbones reported in literature [14]. All compounds had melting transitions ranging from 317 to 462 °C, with *p*-phenoxyl phenyl substituted **1d** melting at 317 °C, and pyridyl substituted **1h** melting at 462 °C, respectively. The decomposition temperatures determined by thermogravimetric analysis (TGA) were above 380 °C, demonstrating that the series of diphenylanthrazolines **1a–1i** are very robust molecules.

3.2. Optical properties

The absorption spectra of the nine diphenylanthrazolines in toluene solution (10^{-5} M) are shown in Fig. 5. The lowest energy absorption bands are from the π–π^* transitions by virtue of their large molar extinction coefficients ($\varepsilon \approx 10^4$ M^{-1} cm^{-1}). All the solution absorption spectra of **1a–1i** are structured. Unsubstituted **1a**, **1h** and alkyl substituted **1b**, **1c** and **1d** have nearly identical

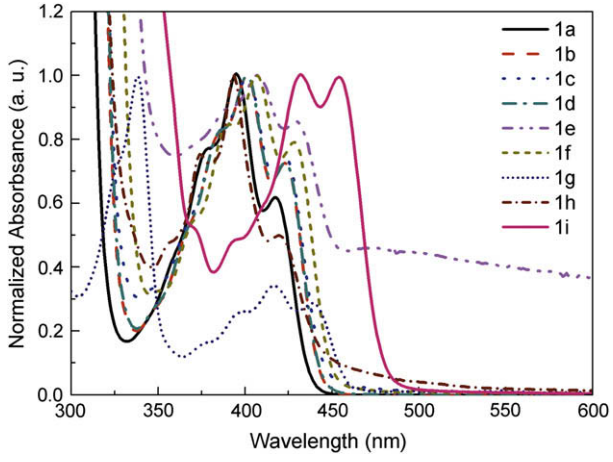

Fig. 5. UV–vis absorption spectra of **1a–1i** in toluene solution (10^{-5} M).

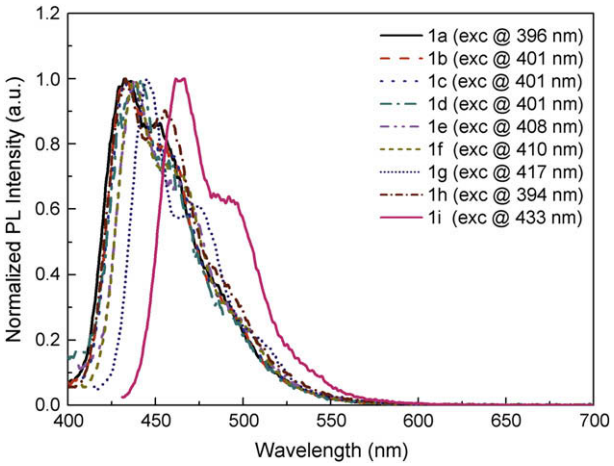

Fig. 6. PL spectra of **1a–1i** in toluene solution (10^{-8} M).

absorption maxima (λ_{max}^{Abs}) at 396, 394, 401, 401, 401 nm, respectively. Phenyl substituted **1e** has absorption λ_{max}^{Abs} that is red shifted 12 nm compared to **1a** as the phenyl moiety extends the conjugated backbone. The absorption λ_{max}^{Abs} of phenoxyl substituted **1f** is red shifted by 14 nm compared to **1a** as a result of the electron-donating phenoxyl moiety. The increase in conjugation length and the increased electron density associated with fluoryl groups in **1g** and *N*-ethylcarbazolyl groups in **1i** lead to a large bathochromic shift of absorption maximum in **1g** to 417 nm and in **1i** to 433 nm, respectively. For all the diphenylanthrazoline compounds, the absorption λ_{max}^{Abs} corresponds to the 0–1 optical transition. Although the 0–0 transition in compounds of **1a–1h** is a distinct peak, its oscillator strength is much smaller than the 0–1 transition (absorption maximum). However, in the case of **1i**, the oscillator strength of the 0–0 transition is nearly equal to the one of the 0–1 transition. We suppose that this arises from the greater molecular planarity and π-electron delocalization in **1i** compared to the other compounds. For **1g**, there is an additional absorption band in the 300–370 nm range with a maximum at 337 nm ($\varepsilon = 2.9 \times 10^4$ M^{-1} cm^{-1}), which is likely due to the optical transitions localized on the fluoryl chromophores.

Optical band gaps (E_g^{Opt}) determined from the absorption edge of the solution spectra are given in Table 1. The optical band gap varies from 2.57 eV in **1i** to 2.80 eV in **1a**.

The dilute solution (10^{-8} M) photoluminescence (PL) spectra of **1a–1i** are shown in Fig. 6. All nine compounds have structured emission bands and emit blue light with the emission maximum in the 430–466 nm ranges. All the λ_{em} of **1b–1i** are slightly red shifted compared to **1a** ($\lambda_{em} = 430$ nm). Similarly, **1i** has the maximum red shift (36 nm). If the 0–0 transitions in the emission and corresponding absorption bands are considered, the Stokes shift is small for all the compounds, ranging from 28 to 39 nm.

4. Conclusions

A series of nine diphenylanthrazoline derivatives were synthesized, and their thermal stabilities and optical properties were investigated. TGA and DSC measurements indicate that **1a–1i** were thermally robust with high decomposition temperature (above 380 °C) and high melt transitions (317–462 °C). Compared to **1a**, both the UV–vis absorption maximum peaks (from 394 to 433 nm) and PL emission peaks (from 430 to 466 nm) are slightly red shifted due to the electron-donating effect of alkyl substitutes in **1b–1d**, and the extension of the conjugated backbone of anthrazoline in **1g** and **1i**. Of the nine compounds synthesized, **1i** showed the lowest band gap (2.57 eV) and the largest λ_{max}^{Em} (466 nm) with high thermal

stability ($T_m = 348\ ^\circ C$, $T_d > 450\ ^\circ C$) and is expected to be applicable as an electron-transporting electroluminescent material. This series of new diphenylanthrazolines may also serve as model systems for investigating structure–property relationships with respect to the electronic, electrochemical, photoconductive, and nonlinear optical properties of π-conjugated polymers.

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