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# The synthesis, crystal structures and photophysical properties of a series of novel 4,6-diphenyl-1,9-anthrazolines

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# 1. Introduction

Research on organic light-emitting diodes (OLEDs) received a boost by the development of conjugated  $\pi$ -electron materials using as light emitters and charge transporters [1-12]. However, for developing more efficient organic light-emitting devices, they are challenges to balance charge carrier injection from both cathode and anode and balance charge transport to the emissive layer [13–16]. Since hole mobility is typically orders of magnitude larger than electron mobility in most current OLED systems, the introduction of an electron-transport layer can dramatically reduce the hole current and thereby result in more efficient OLEDs [17–19]. Heterocyclic molecules, oligomers, and polymers have been used as electron-transport materials to varied degrees of success in improving device performance [6,17,18,20-24]. Among these materials, diphenylanthrazoline derivatives are of immense interest because these small molecules have high electron affinity and high thermal stability and are promising electron-transport materials for OLED [6]. Recently, our group has reported a series of thermally stable 4,8-diphenyl-1,5-anthrazolines, which also exhibit high decomposition temperature, high melt transitions, low optical band gaps and high electron affinity, suggesting that these

# ABSTRACT

The synthesis and properties of a series of nine new 4,6-diphenyl-1,9-anthrazolines molecules **1a**-**1i** are reported. Compounds **1a**-**1i** were synthesized by Friedländer condensation of 4,6-dibenzoyl-1,3-phenylenediamines and acetyl-functionalized compounds in the presence of polyphosphoric acid as catalyst, in yields ranging from 60% to 94%. The 4,6-diphenyl-1,9-anthrazolines are thermally robust with high decomposition temperatures (>371.0 °C) and high melt transitions (215.1-322.8 °C). Compounds **1a** and **1f** crystallized in the triclinic system with the space groups *P*-1. All of them show the lowest energy absorption bands ( $\lambda_{max}^{Abs}$ : 397-454 nm), revealing low optical band gaps (2.55-3.00 eV). The compounds emit blue fluorescence with  $\lambda_{max}^{Em}$  ranging from 432 to 493 nm in dilute toluene solution. 4,6-Diphenyl-1,9-anthrazolines **1a**-**1i** have a formal reduction potential in the range -1.02 to -1.19 V (versus SCE) and estimated electron affinities (LUMO levels) of 3.21-3.38 eV. These results demonstrate that the new 4,6-diphenyl-1,9-anthrazolines are promising thermally stable n-type semiconductors for organic electronics.

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molecules can be applicable as an electron-transporting electroluminescent material [11,12]. 4,6-Diphenyl-1,9-anthrazolines are the isomers of 4,8-diphenyl-1,5-anthrazolines, they may have similarly excellent photophysical properties. However, the reports concerning the photophysical properties of small molecules based on the 4,6-diphenyl-1,9-anthrazoline core are limited. In this context, we aim to develop new 4,6-diphenyl-1,9-anthrazoline molecules and do the further study of the underlying structure–property relationships.

In this paper, we report the synthesis, detailed structural characterization and investigation of the thermal stabilities, electrochemical and photophysical properties of a series of new n-type organic semiconductors based on 4,6-diphenyl-1,9-anthrazolines, that contain various aromatic substituents (Scheme 1). Their photophysical properties and crystal structures were investigated with the aim of understanding structure–physical property relationships in the context of novel organic light-emitting materials.

# 2. Experimental section

#### 2.1. Materials

Pyromellitic dianhydride was purchased from Zhejiang Shengxiao Chemical Company. Fluorene was purchased from Beijing Rizhaoshilide Chemical Company. Acetophenone (**a**), 4-iodoacetophenone and other reagents were purchased from Sinopharm



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Scheme 1. Synthesis of 4,6-diphenyl-1,9-anthrazolines (1a-1i).

Chemcial Reagent Co. Ltd and used as received. 4,6-Dibenzoyl-1,3phenylenediamine (1) [25], other acetylfunctionalized compounds d-f [26–28], g [29], h [30] and i [31], and 4,6-Diphenyl-1,9anthrazoline derivatives (1a–1i) [25] were synthesized according to the methods reported in literatures with some modification. The synthetic routines are shown in Figs. 1–5, respectively.

# 2.2. Measurements

<sup>1</sup>H NMR and <sup>13</sup>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<sub>3</sub> and trifluoroacetic acid (TFA) as the solvent, with tetramethylsilane as internal standard. Fourier transformation infrared (FTIR) spectra were recorded in KBr pellets using an AVATAR 370 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. 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). The electrochemical experiments were carried out using a CHI 660C electrochemistry workstation (CHI USA). A standard one-compartment three-electrode cell was used with a Pt electrode as the working electrode, a Pt wire as the counter electrode and a Ag/Ag^+ electrode (Ag in 0.1 M AgNO\_3 solution, from CHI, Inc.) as the reference electrode, TBAP (0.1 M) was used as the supporting electrolyte. The films of 4,6-diphenyl-1,9-anthrazolines were coated on the Pt working electrode and the scan rate was 40 mV s<sup>-1</sup> [20].

## 2.3. Synthesis

#### 2.3.1. 4,6-Dibenzoylisophthalic acid (5)

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 (17.0 ml). After removal of the benzene by steam distillation, a mixture of 4,6-dibenzoylisophthalic acid (5) and 2,5dibenzoylterephthalic acid (4) was obtained as 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. After 4 was obtained by recrystallization from acetic acid, the residual products were recrystallized twice from acetone to give 5 (4.8 g, 12.8 mmol) as block solids in 25.6% yield, m.p. 277–279 °C (lit. [25]: 277–278 °C). <sup>1</sup>H NMR (DMSO, 500 MHz): δ ppm 7.49 (s, 1H), 7.50–7.57 (m, 4H), 7.64 (t, 2H), 7.70 (d, 4H), 8.56 (s, 1H), 13.66 (s, 2H).



Fig. 1. Synthesis of 4, 6-Dibenzoyl- 1, 3-phenylenediamine (1).



Fig. 2. Synthesis of acetyl-functionalized compounds (d-f).



Fig. 4. Synthesis of acetyl-functionalized compounds (h).

#### 2.3.2. Pseudo-4,6-dibenzoylisophthaloyl chloride (3)

A mixture of 2,4-dibenzoylisophthalic acid (14.0 g, 37.4 mmol), thionyl chloride (90.0 ml) and dimethyl formamide (0.6 ml) was heated at the reflux temperature (76–78 °C) for 2 h with stirring. Then the excess thionyl chloride was removed by distillation. Benzene (2 × 50.0 ml) was added and distilled to remove the last traces of thionyl chloride. Pseudo-4, 6-dibenzoylisophthaloyl chloride was obtained as white crystals in 99.0% yield, m.p. 183–185 °C (recrystallized from 1:1 dichloromethane /cyclohexane solvent mixture). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  ppm 7.47–7.49 (m, 6H), 7.66–7.68 (m, 4H), 7.79 (s, 1H), 8.46 (s, 1H).

## 2.3.3. 4,6-Dibenzoylisophthalamide (2)

To a stirred solution of concentrated ammonium hydroxide (45.0 ml) and *N*-methyl-2-pyrrolidone (NMP) (60.0 ml) was added a solution of Pseudo-4, 6-dibenzoylisophthaloylchloride in NMP (50.0 ml) at 0–5 °C over a 30 min period. The mixture was further stirred for 5 h at 25 °C and then diluted with water (300 ml). The mixture was allowed to stand overnight. The white precipitate which formed was collected and dried to give **2** (13.4 g, 36.0 mmol) as a white powder in 96.2% yield, m.p. 289–293 °C (lit. [25]: 290–295 °C). <sup>1</sup>H NMR (DMSO, 500 MHz):  $\delta$  ppm 7.01 (s, 2H), 7.10 (d, 1H), 7.20–7.26 (m, 6H), 7.37–7.39 (m, 4H), 7.74 (d, 1H), 9.37 (s, 2H).

# 2.3.4. 4,6-Dibenzoyl- 1,3-phenylenediamine (1)

To a solution of potassium hydroxide (42.9 g, 766 mmol) in water (300 ml) cooled in an ice water bath, was added 4,6-dibenzoylisophthalamide (26.7 g, 71.8 mmol). The amide dissolved rapidly and completely. To the stirred solution was added 5.25% sodium hydrochlorite solution (215 ml, 249.8 mmol) at 5-7 °C during a period of 30 min. The pale yellow, clear solution was then warmed rapidly on a water bath to 80 °C. The solution became orange and a precipitate began to separate within 15 min. The mixture was heated for an additional hour at 76-80 °C. After cooling the mixture to room temperature, the precipitate was filtered, washed thoroughly with hot water, and dried to give the crude 4,6-dibenzoyl- 1,3-phenylenediamine (18.5 g, 58.2 mmol) in 81.6% yield. Recrystallization from chloroform and subsequently from methanol gave pale yellow powder, m.p. 253–254 °C (lit. [25]: 255–257 °C). <sup>1</sup>H NMR (DMSO, 500 MHz): δ ppm 6.02 (s, 1H), 7.34-7.42 (m, 6H), 7.44-7.46 (m, 6H), 7.56 (s, 1H), 7.59 (s, 4H).

## 2.3.5. Synthesis of acetyl-functionalized compounds (d-f, g-i)

2.3.5.1. (4-Acetylphenyl)diphenylamine (**d**). Triphenylamine (4.42 g, 18.0 mmol), zinc chloride (2.45 g, 18.0 mmol) and dichloromethane (36.0 ml) were added slowly to a solution of acetyl chloride (1.42 g, 18.0 mmol) in dichloromethane (4.0 ml) with vigorous stirring at room temperature over 5 min. The mixture was refluxed for 20 h. After cooling to room temperature, it was poured into aqueous HCl

(2.0 M, 150 ml). The dichloromethane layer was separated and washed with water to pH 7. The dichloromethane was removed using a rotary evaporator and the residue purified by column chromatography (petroleum ether/chloroform = 3:1 as elution) to afford **d** (4.37 g, 15.0 mmol) as yellow crystals in 83.3% yield, m.p. 146–147 °C. (lit. [26]: 143–145 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  ppm 2.52 (s, 3H), 6.97–6.99 (m, 2H), 7.11–7.16 (m, 6H), 7.29–7.33 (m, 4H), 7.79 (d, 2H).

2.3.5.2. 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 (20.0 ml) with stirring. A yellow solid material was formed when the mixture was cooled to room temperature. After filtration, the vellow solid material was recrystallized from ethyl alcohol twice to give e (32.4 g, 165 mmol) as yellow plates in 82.5% yield, m.p. 121–122 °C (lit. [27]: 121 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ ppm 2.63 (s, 3H), 7.40–7.41 (m, 1H), 7.45–7.48 (m, 2H), 7.61-7.63 (m, 2H), 7.68 (d, d, 2H), 8.03 (d, d, 2H).

2.3.5.3. *p*-*Phenoxyacetophenone* (*f*). Compound **f** was synthesized according to the method described for compound **e**. Yield was 81.5% as yellow plates; m.p. 47–49 °C (lit. [28]: 49 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  ppm 2.56 (s, 3H), 7.00 (d, d, 2H), 7.06–7.08 (m, 2H), 7.19 (q, 1H), 7.37–7.41 (m, 2H), 7.94 (d, d, 2H).

2.3.5.4. 1-(4-(9H-carbazol-9-yl)phenyl)ethanone (**g**). A mixture of carbazole (33.4 g, 200 mmol), Cu (17.0 g, 26.8 mmol), 18-crown-6 (17.3 g, 65.5 mmol), 4-iodoacetophenone (50.2 g, 210 mmol), K<sub>2</sub>CO<sub>3</sub> (111.0 g, 803 mmol) and DMF (400 ml) was heated at the reflux temperature (152–153 °C) for 50 h with stirring. After cooling to room temperature, it was poured into water. After filtered, the solution was extracted with chloroform. Organic layer was separated and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The precipitate was purified by column chromatography (petroleum ether/dichloromethane = 1:1 as the elution) to give **g** (39.0 g, 136.5 mmol) as a yellow powder in 68.3% yield [29], m.p. 208–209 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  ppm 2.70 (s, 3H), 7.30–7.33(m, 2H), 7.41–7.44 (m, 2H), 7.48 (d, 2H), 7.71 (d, d, 2H), 8.14 (d, 2H), 8.21 (d, d, 2H).

2.3.5.5. 2-Acetylfluorene (**h**). Fluorene (20.0 g, 120 mmol) and carbon disulfide (250 ml) were added in a three-necked flask



Fig. 3. Synthesis of acetyl-functionalized compounds (g).



Fig. 5. Synthesis of acetyl-functionalized compounds (i).

equipped with a mechanical stirrer, stirring until fluorene was dissolved, anhydrous aluminum chloride (32.0 g, 240 mmol) was added in. Keeping the carbon disulfide refluxing slowly, acetic anhydride (12.2 g, 120 mmol) was added drop-by-drop. Then the reaction was kept 2 h in 46–47 °C water bathe. After filtration, the precipitate was transferred to a beaker and 40 ml of carbon disulfide was added, stirred for 30 min (to dissolve the fluorene which did not react and other impurities) and filtration was done. 200 ml of dilute hydrochloric acid solution (1000 g water: 40.0 g concentrated hydrochloric acid) was added in and fully stirred, then the first hydrolysis was coupled with the second hydrolysis. Then a light orange solid was obtained by water washing and drying after filtration. The precipitate was recrystallized from ethyl alcohol twice to give **h** (14.5 g, 69.6 mmol) in 58.0% yield, m.p. 126–129 °C (lit. [30]: 124–126 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  ppm 2.66 (s, 3H), 3.96 (s, 2H), 7.26–7.43 (m, 2H), 7.59 (d, 1H), 7.83–7.86 (m, 2H), 8.01 (d, d, d, 1H), 8.15 (d, 1H).

2.3.5.6. *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 (60.0 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** (23.3 g, 0.12 mol) as white needles in 75.0% yield, m.p. 67–68 °C (lit. [31]: 72–74 °C).

2.3.5.7. 3-Acetyl-N-ethylcarbazole (**i**). A mixture of **j** (31.2 g, 160 mmol) and acetic anhydride (16.3 g, 160 mmol) in boron trifluoride diethyl etherate (BF<sub>3</sub>·Et<sub>2</sub>O) (400 ml) was stirred at room temperature for 4 h. Then the mixture was hydrolyzed by pouring into a mixture of ice and water (1600 ml) containing concentrated hydrochloric acid (5.0 ml) with stirring. Then diethyl ether was removed by distillation, and brown precipitate was got by filtration. The precipitate was recrystallized from ethyl alcohol twice to give **i** (30.5 g, 128.6 mmol) as a shallow pink powder in 80.4% yield, m.p. 113–115 °C. (lit. [31]: 116–118 °C). <sup>1</sup>HNMR (CDCl<sub>3</sub>, 500 MHz):  $\delta$  ppm 1.45 (s, 3H), 2.72 (s, 3H), 4.38 (q, 2H), 7.30 (t, 1H), 7.40 (d, 1H), 7.44 (d, 1H), 7.51 (t, 1H), 8.12 (d, d, 1H), 8.15 (d, 1H), 8.74 (d, 1H).

#### 2.3.6. General procedure for synthesis of 1a-1i

A mixture of 4,6-dibenzoyl-1,3-phenylenediamine (2.0 mmol), acetyl-functionalized compound (**a**–**i**) (4.2 mmol), polyphosphoric acid (PPA) (4.0 g), and m-cresol (10.0 ml) was heated at 130–140 °C for 48 h. The reaction mixture was then diluted with methanol and poured into 1.0 M potassium hydroxide solution (500 ml) and collected by vacuum filtration. The precipitate was washed with hot water (3 × 500 ml), and dried at 80 °C. The resulting product was then recrystallized from tetrahydrofuran (THF)/methanol solutions ranging from 30% to 50% methanol. Each was recrystallized twice.

2.3.6.1. 2,4,6,8-Tetraphenyl-1.9-anthrazoline (1a). Yield was 80.5% as orange crystals; m.p.  $265.4 \,^\circ$ C. <sup>1</sup>H NMR (CDCl<sub>3</sub> and TFA,

500 MHz):  $\delta$  ppm 7.66–7.67 (m, 8H), 7.50–7.73 (m, 2H), 7.61–7.80 (m, 4H), 7.88–7.92 (m, 2H), 8.18–8.20 (m, 4H), 8.31 (s, 2H), 9.23 (s, 1H), 9.56 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub> and TFA, 500 MHz):  $\delta$  ppm 160.03, 138.68, 136.29, 133.66, 132.59, 132.36, 130.85, 130.29, 129.92, 129.63, 129.40, 128.07, 127.71, 125.40, 122.01. FTIR (KBr, cm<sup>-1</sup>): 3052, 1576, 1532, 1492, 1449, 883, 844, 762, 695. Anal. Calcd. (%) for C<sub>36</sub>H<sub>24</sub>N<sub>2</sub>: C, 89.23; H, 4.99; N, 5.78. Found: C, 89.29; H, 5.01; N, 5.68.

2.3.6.2. 2,8-Bis(4-tert-butylphenyl)-4,6-diphenyl-1,9-anthrazoline (**1b**). Yield was 60.4% as orange plates; m.p. 280.9 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub> and TFA, 500 MHz):  $\delta$  ppm 1.43(s, 18H), 7.65–7.70 (m, 10H), 7.79 (d, 4H), 8.13 (d, 4H), 8.26 (s, 2H), 9.12 (s, 1H), 9.46 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub> and TFA, 300 MHz):  $\delta$  ppm 159.71, 159.11, 138.57, 133.90, 132.06, 131.48, 130.59, 129.67, 129.55, 129.36, 127.82, 126.48, 125.02, 121.53, 120.09, 35.71, 30.73. FTIR (KBr, cm<sup>-1</sup>): 3053, 2958, 2955, 2902, 2865, 1571, 1522, 1457, 890, 842, 765, 701. Anal. Calcd. (%) for C<sub>44</sub>H<sub>40</sub>N<sub>2</sub>: C, 88.55; H, 6.76; N, 4.69. Found: C, 88.49; H, 6.68; N, 4.73.

2.3.6.3. 2,8-Bis(4-methoxyphenyl)-4,6-diphenyl-1,9-anthrazoline (**1c**). Yield was 64.3% as yellow needles; m.p. 266.5 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub> and TFA, 500 MHz):  $\delta$  ppm 4.03(s, 6H), 7.27(q, 4H), 7.61–7.70 (m, 10H), 8.21 (s, 2H), 8.23 (d, d, 4H), 9.02 (s, 1H), 9.32 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub> and TFA, 300 MHz):  $\delta$  ppm 160.18, 153.30, 147.52, 139.67, 132.60, 131.36, 129.99, 129.67, 127.81, 126.86, 125.43, 122.10, 121.77, 120.90, 119.95, 58.82. FTIR (KBr, cm<sup>-1</sup>): 3050, 2833, 1598, 1569, 1513, 1446, 884, 836, 758, 701. Anal. Calcd. (%) for C<sub>38</sub>H<sub>28</sub>N<sub>2</sub>O<sub>2</sub>: C, 83.80; H, 5.18; N, 5.14; O, 5.88. Found: C, 83.87; H, 5.19; N, 5.16; O, 5.82.

2.3.6.4. 2,8-Bis(4-triphenylamino)-4,6-diphenyl-1,9-anthrazoline (**1d**). Yield was 81.2% as orange crystals; m.p. 294.1 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub> and TFA, 500 MHz):  $\delta$  ppm 7.12 (d, 4H), 7.29 (d, 8H), 7.35 (t, 4H), 7.47 (t, 8H), 7.55 (d, 4H), 7.59–7.65 (m, 6H), 8.00 (s, 2H), 8.03 (d, 4H), 8.71 (s, 1H), 8.99 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub> and TFA, 300 MHz):  $\delta$  ppm 160.47, 157.56, 155.36, 155.28, 144.29, 139.38, 134.26, 131.55, 131.14, 130.21, 129.80, 129.51, 129.12, 127.20, 126.90, 124.02, 120.26, 119.90, 119.09. FTIR (KBr, cm<sup>-1</sup>): 3036, 1584, 1450, 1455, 883, 838, 755, 697. Anal. Calcd. (%) for C<sub>44</sub>H<sub>40</sub>N<sub>2</sub>: C, 87.99; H, 5.17; N, 6.84. Found: C, 88.36; H, 5.03; N, 6.73.

2.3.6.5. 2,8-Bis(biphenyl)-4,6-diphenyl-1,9-anthrazoline (**1e**). Yield was 94.5% as yellow plates; m.p. 267.2 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub> and TFA, 500 MHz):  $\delta$  ppm 7.50–7.57 (m, 6H), 7.68–7.75 (m, 14H), 8.03 (d, 2H), 8.31 (d, 2H), 8.36 (s, 2H), 9.20 (s, 1H), 9.52 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub> and TFA, 500 MHz):  $\delta$  ppm 160.94, 159.21, 149.93, 138.94, 138.27, 137.77, 132.59, 132.20, 130.04, 129.98, 129.86, 129.61, 129.48, 129.40, 127.66, 127.54, 125.38, 121.77, 117.86. FTIR (KBr, cm<sup>-1</sup>): 3027, 1568, 1486, 1449, 890, 842, 763, 731, 696. Anal. Calcd. (%) for C<sub>48</sub>H<sub>32</sub>N<sub>2</sub>: C, 90.54; H, 5.06; N, 4.40. Found: C, 90.50; H, 5.13; N, 4.25.

2.3.6.6. 2,8-Bis(4-phenoxylphenyl)-4,6-diphenyl-1,9-anthrazoline (**1f**). Yield was 75.6% as yellow needles; m.p. 215.1 °C. <sup>1</sup>H NMR

 Table 1

 Physical properties of 1a–1i.

• •	•						
Compd.	<i>T</i> <sub>m</sub> (°C)	<i>T</i> <sub>d</sub> (°C)	$^{\epsilon}(10^4{ m M}^{-1}{ m cm}^{-1})$	λ <sup>Abs</sup> (nm)	λ <sup>Em</sup> (nm)	Stokes shift (nm)	E <sup>opt</sup> (eV)
1a	265.4	371.0	1.89	397	432	35	3.00
1b	280.9	403.6	2.27	401	435	34	2.96
1c	266.5	406.2	2.54	411	463	52	2.89
1d	294.1	>450	3.82	454	493	39	2.55
1e	267.2	435.5	2.87	408	458	50	2.90
1f	215.1	425.0	2.51	406	448	42	2.92
1g	225.8	>450	2.72	414	450	36	2.79
1h	307.6	>450	3.31	419	469	50	2.84
1i	322.8	>450	4.20	435	458	23	2.71

(CDCl<sub>3</sub> and TFA, 500 MHz):  $\delta$  ppm 7.10 (d, 4H), 7.14–7.19 (m, 6H), 7.39 (q, 4H), 7.45–7.51 (m, 6H), 7.58 (q, 4H), 7.81 (s, 2H), 8.30 (d, 4H), 8.56 (s, 1H), 9.11 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub> and TFA, 300 MHz):  $\delta$  ppm 159.25, 157.87, 156.81, 149.46, 147.97, 138.18, 134.44, 129.97, 129.61, 129.54, 128.94, 128.74, 128.61, 124.56, 124.35, 123.84, 119.45, 118.93, 118.75. FTIR (KBr, cm<sup>-1</sup>): 2975, 1582, 1486, 873, 835, 782, 698. Anal. Calcd. (%) for C<sub>48</sub>H<sub>32</sub>N<sub>2</sub>O<sub>2</sub>: C, 86.20; H, 4.82; N, 4.19; O, 4.79. Found: C, 86.26; H, 4.95; N, 4.17; O, 4.76.

2.3.6.7. 2,8-Bis(4-(9H-carbazol-9-yl)phenyl)-4,6-diphenyl-1,9-anthrazoline (**1g**). Yield was 64.5% as a yellow powder; m.p. 225.8 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub> and TFA, 500 MHz):  $\delta$  ppm 7.32 (t, 4H), 7.44–7.47 (m, 4H), 7.48–7.55 (m, 10H), 7.64 d, 4H), 7.81 (d, 4H), 7.96 (s, 2H), 8.17 (d, 4H), 8.58 (d, 4H), 8.67 (s, 1H), 9.27 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub> and TFA, 300 MHz):  $\delta$  ppm 159.69, 157.85, 154.56, 149.82, 147.96, 140.70, 139.36, 138.35, 137.98, 129.58, 129.42, 128.84, 128.64, 127.30, 126.11, 124.87, 124.59, 123.65, 120.40, 120.23, 118.93. FTIR (KBr, cm<sup>-1</sup>): 3048, 1595, 1516, 1449, 887, 847, 746. Anal. Calcd. (%) for C<sub>60</sub>H<sub>38</sub>N<sub>4</sub>: C, 88.43; H, 4.70; N, 6.87. Found: C, 88.30; H, 4.72; N, 6.92.

2.3.6.8. 2,8-Bis(2-flourenyl)-4,6-diphenyl-1,9-anthrazoline (**1h**). Yield was 61.4% as a yellow powder; m.p. 307.6 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub> and TFA, 500 MHz):  $\delta$  ppm 4.11 (s, 4H), 7.52 (t, 4H), 7.63–7.70 (m, 12H), 7.97 (q,

#### Table 2

Crystallographic data f	or 4,6-diphenyl-1,9-anthrazoline	1a and 1f.
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Compound	1a	1f
Chemical formula	C <sub>36</sub> H <sub>24</sub> N <sub>2</sub>	C <sub>48</sub> H <sub>32</sub> N <sub>2</sub> O <sub>2</sub>
Formula weight	484.57	668.77
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	10.111(2)	9.668 (16)
b (Å)	10.750(2)	14.808(2)
<i>c</i> (Å)	12.736(3)	15.150(4)
α (°)	107.12(3)	115.43(3)
β(°)	96.36(3)	106.26(3)
γ (°)	96.68(3)	97.39(2)
V (Å <sup>3</sup> )	1298.6(5)	1801.3(6)
D <sub>calc</sub> (gcm <sup>-3</sup> )	1.239	1.266
$\mu ({ m mm^{-1}})$	0.072	0.079
F (000)	508	720
$\theta$ range (°)	1.7–25.3	1.6-27.1
Index range	$0 \le h \le 12$	$-12 \le h \le 12$
	$-12 \le k \le 12$	$-18 \le k \le 18$
	$-15 \le l \le 15$	$-18 \le l \le 19$
Reflns collected	4999	13,786
Unique reflns (R <sub>int</sub> )	4711 (0.028)	7913 (0.039)
Refinement method on $F^2$	Full-matrix least-squares	Full-matrix least-squares
GOF on F <sup>2</sup>	1.000	1.001
$R_1 \left[ I > 2\sigma \left( I \right) \right]$	0.0600	0.1359
$wR_2 [I > 2\sigma (I)]$	0.1660	0.2003
$R_1$ (all data)	0.1161	0.0772
wR <sub>2</sub> (all data)	0.2014	0.1687
Residual (e Å <sup>-3</sup> )	0.235 and -0.191	0.723 and -0.766



Fig. 6. Single crystal structure of 1a (a), view down the *a* axis (b).

2H), 8.11 (d, 2H), 8.26 (d, d, 2H), 8.29 (s, 2H), 8.43 (s, 2H), 9.03 (s, 1H), 9.56 (s, 1H).  $^{13}$ C NMR (CDCl<sub>3</sub> and TFA, 500 MHz):  $\delta$  ppm 159.33, 151.07, 146.14, 145.42, 139.25, 139.08, 133.89, 132.42, 131.75, 130.40, 129.92, 129.52, 129.23, 128.17, 127.94, 126.81, 125.78, 125.72, 125.48, 125.17, 122.11, 121.87, 121.38, 36.90. FTIR (KBr, cm<sup>-1</sup>): 3050, 1573, 1472, 1493, 885, 830, 765, 736, 701. Anal. Calcd. (%) for C<sub>50</sub>H<sub>32</sub>N<sub>2</sub>: C, 90.88; H, 4.88; N, 4.24. Found: C, 90.77; H, 4.86; N, 4.29.

2.3.6.9. 2,8-Bis(3-(*N*-ethyl-carbazole))-4,6-diphenyl-1,9-anthrazoline (**1i**). Yield was 70.3% as yellow plates; m.p. 322.8 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub> and TFA, 500 MHz):  $\delta$  ppm 1.57 (t, 6H), 4.52 (q, 4H), 7.44–7.47 (m, 2H), 7.58 (d, 2H), 7.65-7.74 (m, 14H), 8.23 (d, 2H), 8.33 (d, d, 2H), 8.37 (s, 2H), 8.92 (s, 1H), 8.98 (d, 2H), 9.22 (s, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub> and TFA, 500 MHz):  $\delta$  ppm 158.81, 158.45, 145.01, 141.43, 139.53, 134.22, 132.03, 130.88, 129.82, 129.33, 128.56, 126.51, 125.77, 124.55, 123.22, 177.73, 122.22, 121.36, 121.21, 121.11, 118.80, 117.81, 38.57, 13.59. FTIR (KBr, cm<sup>-1</sup>): 3048, 2972, 1570, 1486, 876, 814, 750, 701. Anal. Calcd. (%) for C<sub>52</sub>H<sub>38</sub>N<sub>4</sub>: C, 86.88; H, 5.33; N, 7.79. Found: C, 86.76; H, 5.43; N, 7.68.

## 2.4. X-ray diffraction crystallography

Crystals of **1a** and **1f** suitable for single crystal X-ray diffraction were obtained by slow evaporation of THF/methanol solutions. The diffraction data were collected on a Nonius CAD4 single crystal diffractometer equipped with a graphite-monochromated MoK $\alpha$ radiation ( $\lambda = 0.71073$  Å) by using an  $\omega/2\theta$  scan mode at 293 K. The



Fig. 7. Single crystal structure of 1f (a), view down the *a* axis (b).

crystal structures were solved by the direct method and refined by the full-matrix least-squares procedure on  $F^2$  using SHELXL-97 program [32]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were introduced at calculated



Fig. 8. UV-vis absorption spectra of 1a-1i in toluene solution ( $10^{-5}$  M).



**Fig. 9.** PL spectra of **1a**–**1i** in toluene solution  $(10^{-8} \text{ M})$ .

positions. The crystal and structure refinement data of **1a** and **1f** are listed in Table 2.

#### 3. Results and discussion

## 3.1. Synthesis and characterization

The synthetic route of 4.6-dibenzovl-1.3-phenylenediamine is shown in Fig. 1. According to the recrystallization method reported in literature [25], the pure 4,6-dibenzoylisophthalic acid (5) could not be obtained. When 5 were recrystallized from acetone, instead of a mixture of acetic acid and water (1:3), we succeeded in getting the pure product. Scheme 1 outlines the synthesis of the series of 4,6-diphenyl-1,9-anthrazolines. The acid-catalyzed Friedländer condensation reactions [25] yielded the desired products in 60-94% yields. The polyphosphoric acid catalyst was readily removed by precipitation into a 1.0 M potassium hydroxide solution. The precipitation was washed by hot water three times. They were subsequently recrystallized in THF/methanol mixture ranging from 30% to 50% methanol. Compounds 1a and 1d were obtained as orange crystals; 1b was obtained as orange plates; 1c and 1f were obtained as yellow needles; 1e and 1i were obtained as yellow plates; **1g** and **1h** were obtained as a yellow powder. <sup>1</sup>H NMR spectra, <sup>13</sup>C NMR spectra, FTIR spectra and element analysis on 1a-1i confirmed the proposed structures. All the 4,6-diphenyl-1,9anthrazolines were soluble in common organic solvents in varying degrees such as tetrahydrofuran, chloroform, toluene and formic acid.

The thermal properties, including melting and decomposition temperatures, of these molecules are shown in Table 1. Differential scanning calorimetry (DSC) was used to investigate phase transitions. No glass transitions events were observed by DSC scans of the molecules. All compounds had melting transitions ranging from 215.1 to 322.8 °C, with p-phenoxyl phenyl substituted **1f** melting at the lowest temperatures, 215.1 °C, and *N*-ethylcarbazolyl substituted **1i** melting at the highest temperature, 322.8 °C, respectively. Compared to 4,8-diphenyl-1,5-anthrazolines [6,11], the melting temperatures of 4,6-diphenyl-1,9-anthrazolines are lower due to their lower lattice energy. Also, it is evident that the solubility of 4,6-diphenyl-1,9-anthrazolines is better than 4,8-diphenyl-1,5-anthrazolines.

The decomposition temperatures determined by thermogravimetric analysis (TGA) were above 371.0 °C. Compared to **1a**, with electron-donating moiety substituted **1b–1i** are more thermally



Fig. 10. Cyclic voltammograms of thin films of 1a-1i coated on a Pt wire electrode. Scan rate = 40 mV/s.

stable. All of these results demonstrate that the series of 4,6diphenyl-1,9-anthrazolines **1a**–**1i** are very robust molecules.

#### 3.2. X-ray crystal structures

Crystals were grown by slow evaporation of THF/methanol solutions. Single crystals from two of the nine 4,6-diphenyl-1,9-anthrazolines (**1a** and **1f**) were suitable for the determination of X-ray crystal structures. **1a** was obtained as orange prisms, and **1f** was obtained as thin yellow needles. In the molecule of **1f**, it contains two molecules of H<sub>2</sub>O. **1a** and **1f** were found to have the same triclinic crystal systems, with a space group *P*-1. The unit cell parameters of a = 10.111 (2) Å, b = 10.750 (2) Å, c = 12.736 (3) Å,  $\alpha = 107.12^{\circ}$  (3),  $\beta = 96.36^{\circ}$  (3), and  $\gamma = 96.68^{\circ}$  (3) for **1a** are reported for the molecules, while **1f** forms the unit cell dimensions of a = 9.668 (16) Å, b = 14.808 (2) Å, c = 15.150 (4) Å,  $\alpha = 115.43$  (3),  $\beta = 106.26$  (3), and  $\gamma = 97.39$  (2). The detailed crystallographic data for **1a** and **1f** are collected in Table 2.

The single crystal structures and packing diagrams of **1a** and **1f** are shown in Figs. 6 and 7. In **1a** and **1f**, the crystal structures reveal that the 1,9-anthrazoline units are relatively planar. The pendant 4,6-diphenyl groups have a twist angle of 67° and 130° in **1a**, 49° and 128° in **1f**, respectively, from the plane of the 1,9-anthrazoline unit. The  $\alpha$ -linked phenyl groups are twisted 14° and 21° in **1a**, 9° and 29° in **1f** from the plane of the 1,9-anthrazoline unit. In the molecular packing of **1a**, the edge-to-face  $\pi$ -stacking interactions between neighboring molecular units are observed; 4,6-diphenyl groups and  $\alpha$ -linked phenyl groups are contacted via C–H... $\pi$  stacking interactions, which are separated by a distance of 2.94 Å. However, in the molecular packing of **1f**, it exhibits face-to-face  $\pi$ -stacking interactions between neighboring molecular units; the intermolecular distance is 3.39 Å.

#### 3.3. Optical properties

The absorption spectra of the nine 4,6-diphenyl-1,9-anthrazolines in toluene solution  $(10^{-5} \text{ M})$  are shown in Fig. 8. The lowest energy absorption bands are from the  $\pi - \pi^*$  transitions by virtue of their large molar extinction coefficients ( $\varepsilon = 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ). All the solution absorption spectra of 1a-1i are structured. Unsubstituted 1a and alkyl substituted 1b have nearly identical absorption maxima ( $\lambda_{max}^{Abs}$ ) at 397 nm and 401 nm, respectively. The absorption  $\lambda_{max}^{Abs}$  of methoxyl substituted **1c** and phenoxyl substituted 1f are red shifted by 14 nm and 9 nm compared to 1a as a result of the electron-donating methoxyl and phenoxyl moiety, respectively. Phenyl substituted 1e and N-carbazolyl substituted 1g have absorption  $\lambda_{max}^{~Abs}$  that are red shifted 11 nm and 17 nm compared to 1a as the phenyl and N-carbazolyl moiety extend the conjugated backbone, respectively. The increase in conjugation length and the increased electron density associated with triphenylamino groups in **1d**, fluoryl groups in **1h** and *N*-ethylcarbazolyl groups in **1i** lead to a large bathochromic shift of absorption maximum in 1d to 454 nm, in 1h to 419 nm and in 1i to 435 nm, respectively.

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 2.55 eV in **1d** to 3.00 eV in **1a**, which is lightly bigger than 4,8-diphenyl-1,5-anthrazolines [6,11].

The dilute solution  $(10^{-8} \text{ M})$  photoluminescence (PL) spectra of **1a**–**1i** are shown in Fig. 9. All nine compounds emit blue light with the emission maximum ranging from 432 nm for **1a** to 493 nm for **1d**. All the  $\lambda_{\text{max}}^{\text{Em}}$  of **1b**–**1i** are slightly red shifted compared to **1a**. Triphenylamino substituted **1d** has the maximum red shift (61 nm). The Stoke shifts are small for all the compounds, ranging from 23 to 52 nm. Of the nine compounds synthesized, **1d** showed the lowest

band gap (2.55 eV) and the largest  $\lambda_{max}^{Em}$  (493 nm) with high thermal stability ( $T_m = 294.1 \,^{\circ}$ C,  $T_d > 450 \,^{\circ}$ C) and is expected to be applicable as an electron-transporting electroluminescent material.

# 3.4. Electrochemical properties

Cyclic voltammetry was done on thin films of 1a-1i. The cyclic voltammograms (CVs) of these nine molecules are shown in Fig. 10. Irreversible reduction peaks were seen in CVs of 1a-1i. Molecules 1c, 1d had one irreversible oxidation peak. In the case of 1a, 1b, 1e, 1f, 1g, 1h, 1i, the irreversible oxidation peak was not seen when scanned to 2.0 V.

Table 3 shows the solid-state electrochemical data for **1a**–**1i**. HOMO and LUMO levels were estimated from the onset potentials by using an SCE energy level of 4.4 eV versus a vacuum [12,20]. Electron affinities (LUMO) were estimated from the onset of the reduction wave ( $EA = E^{onset}_{red} + 4.4$ ). **1a**–**1i** have electron affinities between 3.21 and 3.38 eV (below vacuum), revealing the promising electron-transport properties (n-type) for OLEDs. The reduction potentials of all the molecules are relatively unchanged by the substituent (R groups), indicating that the LUMOs lie on the 1,9anthrazoline moiety. Even the electron-rich carbazole substituted molecule (**1i**), which as expected has the lowest oxidation potential, has essentially the same LUMO level as the other molecules.

The formal reduction potential ( $E_{red}^{peak}$ ) varies from -1.34 V (vs SCE) for **1i** to -1.64 V for **1e** (Table 3). The electron-donating strength of the 2,8-substituents on the 1,9-anthrazoline unit (R group) shifts the formal reduction potential to less positive values. As a result the estimated ionization potential (IP =  $E_{ox}^{onset} + 4.4$  eV) is reduced from 6.05 eV in **1a** to 5.60 eV in **1d**. Also shown in Table 3 are the electrochemically derived band gap ( $E_g^{el}$ ) of thin films of **1a**-**1i**. The  $E_g^{el}$  varies from 2.31 eV for **1d** to 2.76 eV for **1f**. The electrochemical band gap is the smallest in **1d** as expected from the large delocalization length facilitated by the substituted groups of triphenylamino. The measured electrochemical band gap of each 4,6-diphenyl-1,9-anthrazolines is higher than the corresponding optical band gap ( $E_g^{opt}$ ). Such a difference between  $E_g^{opt}$  and  $E_g^{el}$  has been observed in the literature [11,20,33] and arises from the finite binding energy of excitons in the material.

Comparison of the  $E_{\rm red}^{\rm peak}$  values of the 4,6-diphenyl-1,9anthrazolines to other nitrogen heterocycles [6] confirms the expected progression of reduction potential and thus electron affinity. The average  $E_{\rm red}^{\rm peak}$  value of 1a-1i,  $-1.49 \pm 0.15$  V, is similar to 4,8-diphenyl-1,5-anthrazolines' [6,11], and falls between acridine and phenazine. This average reduction potential of 1a-1iis also significantly more positive compared to those of oxadiazole and benzothiadiazole, both which have been widely explored as building blocks for electron-transport materials for OLEDs [34–38]. The formal reduction potentials for 1a-1i suggest that these small molecules are expected to be applicable as an electron-transporting electroluminescent material. These results show that a series of

Table 3
Electrochemical properties of 1a-1i.

Compd.	$E_{\rm red}^{\rm peak}$ (V)	$E_{red}^{onset}(V)$	EA (eV)	$E_{\mathrm{ox}}^{\mathrm{peak}}\left(V\right)$	$E_{\mathrm{ox}}^{\mathrm{onset}}\left(V\right)$	IP (eV)	$E_{g}^{el}\left( eV ight)$
1a	-1.37	-1.11	3.29	*	1.65	6.05	2.76
1b	-1.39	-1.08	3.32	*	1.61	6.01	2.69
1c	-1.41	-1.12	3.28	1.60	1.38	5.78	2.50
1d	-1.41	-1.11	3.29	1.26	1.20	5.60	2.31
1e	-1.60	-1.19	3.21	*	1.44	5.84	2.63
1f	-1.64	-1.19	3.21	*	1.55	5.95	2.74
1g	-1.39	-1.10	3.30	*	1.58	5.98	2.68
1h	-1.36	-1.06	3.34	*	1.61	6.01	2.67
1i	-1.34	-1.02	3.38	*	1.58	5.98	2.60

4,6-diphenyl-1,9-anthrazolines have high electron affinity and are promising electron-transport materials for OLED.

#### 4. Conclusions

We have synthesized and investigated the thermal stabilities, electrochemical and photophysical properties of a series of nine new n-type organic semiconductors based on 4,6-diphenyl-1,9anthrazolines core. TGA and DSC measurements indicated that **1a–1i** were thermally robust with high decomposition temperature (above 371.0 °C) and high melt transitions (215.1–322.8 °C). Single crystal X-ray structures of **1a** and **1f** showed that they crystallized in the triclinic system with the space groups P-1. The 2,7-linked phenyl groups were twisted 14° and 21° from the plane of the anthrazoline unit, respectively, demonstrating the high degree of planarity of the molecules. Compared to 1a, both maximum peaks of the UV-vis absorption (from 401 to 454 nm) and PL emission peaks in toluene solution (from 435 to 493 nm) are slightly red shifted due to the electron-donating effect in 1b, 1c, 1f and the extension of the conjugated backbone of 1,9-anthrazoline in 1d, 1e, 1g, 1h and 1i. The high electron affinities of the new compounds (3.21-3.38 eV) together with their robust thermal stability suggested that they have promising electron-transport properties for OLEDs.

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