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# The synthesis and characterisation of novel pyrazoline derivatives containing triphenylamine

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#### A R T I C L E I N F O

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## 1. Introduction

Since the report of the first high-efficiency, multi-layered, organic light-emitting diode (OLED) [1], much work has been carried out to improve device efficiency and stability. A very successful method for achieving such improvements is by doping a host organic layer with a fluorescent dye of high quantum yield [2,3]. However, the question as to how such dyes are selected and evaluated remains. Pyrazoline may be used as this material; pyrazoline derivatives are five-membered, nitrogen-containing heterocyclic compounds which have high hole-transport efficiency, excellent blue emission and high quantum yield [4,5]. Thus, pyrazoline derivatives have been widely used as fluorescent brightening agents, fluorescence chemosensors, hole-transport materials in electrophotography, OLED and as novel fluorescent materials [6-16]. Triphenylamine (TPA) and its derivatives has been widely investigated as hole-transporting, photovoltaic materials and electroluminescent materials for almost two decades [17–29]. Thus, in this work, it was considered that the incorporation of a triphenvlamine fragment within a pyrazoline molecule may increase excelsior efficiency. In this context, six pyrazoline compounds were synthesized (Fig. 1) and their structures determined by <sup>1</sup>H, <sup>13</sup>C NMR and HRMS. Fluorescence emission spectra were red-shifted in CHCl<sub>3</sub> from 6 to 7. The solvent

# ABSTRACT

Novel pyrazoline optical materials were synthesized and characterized using <sup>1</sup>H, <sup>13</sup>C NMR and HRMS; the thermal, optical and electrochemical properties of the compounds were also investigated. Solvent effects on the fluorescence of the six compounds indicated that the emission wavelength was red-shifted with increase in solvent polarity. Quantum chemical calculations were used to obtain optimized ground-state geometry as well as spatial distributions of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of the compounds.

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effect on the fluorescence characteristics of the six compounds was studied, which indicated that the emission wavelength of the compounds was red-shifted with increased solvent polarity. The fluorescence quantum yields of the six compounds were obtained and that of **7a** was largest. Quantum chemical calculations were used to obtain optimized ground-state geometry, spatial distributions of the highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) levels of the compounds.

# 2. Experimental section

#### 2.1. Chemicals and instruments

All materials were commercially available and used without further purification. Melting points were recorded on Electrothermal digital melting point apparatus and uncorrected. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at 295 K on a Varian INOVA 400 MHz or a Varian NMR System 300 MHz spectrometer using CDCl<sub>3</sub> or  $d_6$ -DMSO as solvent and TMS as internal standard. UV–vis spectra were recorded on a Shimadzu UV-2501PC spectrometer; Fluorescence spectra were obtained on an Hitachi FL-2500 spectrofluorimeter; Cyclic voltammetry were carried on a Chi 1200A electrochemical analyzer with three-electrode cell (Platinum was used as working electrode and as counter electrode, and SCE as reference electrode) at room temperature; HRMS data were measured using TOF-MS(El<sup>+</sup>) instrument; thermal properties were performed on a SDT 2960 and DSC 2010.



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Fig. 1. Synthetic routines for compounds. Reagents and conditions: (a) NaOH (15%), EtOH, 25  $^{\circ}$ C; (b) EtOH, 80  $^{\circ}$ C; HCI (37%).

### 2.2. Synthesis

**1**, **4**, **5** were prepared according to the published literature [30,31] as were the chalcones **3** (a–c) [32], which served as the starting materials for further synthesis. **6** and **7** were synthesized by reacting **4**, **5** with chalcones **3** (a–c) as follows. A mixture of **4** and **5** (1.0 mmol) and chalcone **3** (1.0 mmol) in ethanol (5.0 ml) and 37% HCl (0.5 ml) was refluxed for 6–12 h. The resulting mixture was cooled and the precipitate filtered to afford the crude products, which were recrystallized from ethanol/tetrahydrofuran ( $\nu/\nu = 1:1$ ) (Fig. 1).

#### 2.2.1. 4-(Diphenylamino)benzaldehyde (1)

Compound 1: yield 86%, white. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.81(s, 1H), 7.67–7.69 (d, *J* = 8.0 Hz, 2H), 7.32–7.36 (t, *J* = 7.8 Hz, 4H), 7.15–7.19 (m, 6H), 7.01–7.03 (d, *J* = 8.0 Hz, 2H).

2.2.2. 3-(4-(Diphenylamino)phenyl)-1-phenylprop-2-en-1-one (**3a**)

Compound **3a**: M.p.: 131 °C. yield 88%, yellow. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.00 (d, J = 7.6 Hz, 2H), 7.77 (d, J = 15.6 Hz, 1H), 7.48–7.57 (m, 5H), 7.39 (d, J = 15.6 Hz, 1H), 7.29–7.34 (m, 5H), 7.09–7.19 (m, 6H), 7.03 (d, J = 8.8 Hz, 2H).

HRMS [Found: m/z 375.1625 (M<sup>+</sup>), Calcd for C<sub>27</sub>H<sub>21</sub>NO: M, 375.1623].

# 2.2.3. 3-(4-(Diphenylamino)phenyl)-1-(4-methoxy-phenyl)prop-2-en-1-one (**3b**)

Compound **3b**: M.p.: 141 °C. yield 84%, yellow. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  8.02 (d, *J* = 8.8 Hz, 2H), 7.75 (d, *J* = 15.6 Hz, 1H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.40 (d, *J* = 15.6 Hz, 2H), 7.27–7.36 (m, 4H), 6.95–7.18 (m, 10H), 3.88 (s, 3H).

HRMS [Found: *m*/*z* 405.1725 (M<sup>+</sup>), Calcd for C<sub>28</sub>H<sub>23</sub>NO<sub>2</sub>: M, 405.1729].

## 2.2.4. 1-(4-Chloro-phenyl)-3-(4-(diphenylamino)phenyl)prop-2-en-1-one (**3c**)

Compound **3c**: M.p.: 119 °C. yield 90%, yellow. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.95 (d, *J* = 8.4 Hz, 2H), 7.77 (d, *J* = 15.6 Hz, 1H), 7.44–7.50 (m, 4H), 7.29–7.36 (m, 5H), 7.12–7.22 (m, 6H), 7.03 (d, *J* = 8.4 Hz, 2H).

HRMS [Found: m/z 409.1232 (M<sup>+</sup>), Calcd for C<sub>27</sub>H<sub>20</sub>NOCI: M, 409.1233].

#### 2.2.5. 2-Hydrazinyl benzothiazole (4)

Compound **4**: yield 91%, white. <sup>1</sup>H NMR ( $d_6$ -DMSO):  $\delta$  7.51–8.23 (m, 4H), 6.12 (s, 1H), 3.34 (s, 2H).

# 2.2.6. 2-Dodecyl-6-hydrazinyl-1H-benzo isoquinoline-

1,3(2H)-dione (5)

Compound **5**: yield 89%, yellow. <sup>1</sup>H NMR (CDCl<sub>3</sub>)<sup>:</sup>  $\delta$  8.61 (d, J = 6.4 Hz, 1H), 8.55 (d, J = 8.0 Hz, 1H), 8.04 (d, J = 7.6 Hz, 1H), 7. 67 (d, J = 7.2 Hz, 2H), 6. 58 (s, 1H), 4.17 (s, 2H), 3.51 (s, 2H), 1.49–1.71 (m, 20 H), 0.97 (s, 3H).

# 2.2.7. 1-(Benzothiazol-2-yl)-3-phenyl-5-(diphenylamino)phenyl-2-pyrazoline (**6a**)

Compound **6a**: M.p.: 95 °C. yield 66%, yellow. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.79 (d, *J* = 7.6 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 5.2 Hz, 3H), 7.29 (d, *J* = 7.2 Hz, 1H), 6.97–7.23 (m, 15H), 5.76–5.80 (m, 1H), 3.90–3.97 (m, 1H), 3.32–3.38 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  163.7, 153.1, 147.9, 147.7, 135.2, 132.1, 131.6, 130.5, 129.8, 129.6, 129.2, 129.1, 127.3, 126.9, 126.0, 125.5, 124.8, 123.9, 123.3, 122.2, 121.2, 120.4, 63.5, 44.0.

HRMS [Found: m/z 522.1883 (M<sup>+</sup>), Calcd for C<sub>34</sub>H<sub>26</sub>N<sub>4</sub>S: M, 522.1878].

#### 2.2.8. 1-(Benzothiazol-2-yl)-3-(4-methoxy-phenyl)-5-

(*diphenylamino*)*phenyl-2-pyrazoline* (**6b**)

Compound **6b**: M.p.: 101 °C. yield 78%, yellow. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.72 (d, J = 8.8 Hz, 2H), 7.64 (d, J = 7.6 Hz, 1H), 7.56 (d, J = 8.0 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.18–7.23 (m, 6H), 6.93–7.11 (m, 11H), 5.72–5.76 (m, 1H), 3.87–3.92 (m, 1H), 3.85 (s, 3H), 3.28–3.33 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  163.6, 161.1, 152.9, 152.8, 147.8, 147.4, 135.1, 131.9, 129.4, 128.3, 127.1, 125.8, 124.7, 124.6, 124.1, 123.8, 123.1, 121.8, 121.0, 120.0, 114.3, 63.2, 55.6, 44.0.

HRMS [Found: m/z 552.1988 (M<sup>+</sup>), Calcd for C<sub>35</sub>H<sub>28</sub>N<sub>4</sub>OS: M, 552.1984].

#### 2.2.9. 1-(Benzothiazol-2-yl)-3-(4-chloro-phenyl)-5-

(diphenylamino)phenyl-2-pyrazoline (**6c**)

Compound **6c**: M.p.: 133 °C. yield 67%, yellow. <sup>1</sup>H NMR ( $d_6$ -DMSO):  $\delta$  7.78–7.81 (d, J = 8.4 Hz, 3H), 7.53–7.56 (d, J = 8.1 Hz, 2H), 7.44–7.47 (d, J = 7.8 Hz, 1H), 7.21–7.28 (m, 7H), 7.08–7.13 (t, J = 7.7 Hz, 1H), 6.91–7.02 (m, 8H) 5.74–5.80 (m, 1H), 4.01–4.11 (m, 1H), 3.31–3.38 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  155.1, 143.5, 141.8, 133.1, 124.2, 123.8, 122.9, 122.5, 122.2, 120.0, 119.7, 118.5, 117.2, 116.4, 112.0, 59.4, 39.7.

HRMS [Found: *m*/*z* 556.1487 (M<sup>+</sup>), Calcd for C<sub>34</sub>H<sub>25</sub>N<sub>4</sub>SCI: M, 556.1488].

2.2.10. 1-(2-Benzyl-benzo isoquinoline-3-dione)-3-phenyl-5-

(*diphenylamino*)*phenyl-2-pyrazoline* (**7a**)

Compound **7a**: M.p.: 91 °C. yield 76%, red. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.64 (d, *J* = 8.8 Hz, 1H), 8.61 (d, *J* = 6.8 Hz, 1H), 8.35 (d, *J* = 8.8 Hz, 1H), 7.67–7.79 (m, 3H), 7.40–7.47 (m, 3H), 7.15–7.23 (m, 6H), 6.95–7.03 (m, 8H), 6.84 (d, *J* = 8.8 Hz, 1H), 5.60–5.64 (m, 1H), 4.14 (t, *J* = 7.6 Hz, 2H), 3.83–3.90 (m, 1H), 3.27–3.34 (m, 1H), 1.67–1.74 (m, 2H), 1.24 (m, 18H), 0.87 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  165.0, 164.3, 152.2, 148.0, 147.6, 145.9, 134.6, 133.6, 132.6, 131.9, 131.6, 130.1, 129.6, 129.1, 196.9, 126.5, 124.9, 123.7, 123.5, 122.6, 114.1, 110.9, 65.9, 42.6, 40.6, 32.2, 29.9, 29.7, 29.6, 28.5, 27.5, 23.0, 14.4.

HRMS [Found: m/z 752.4073 (M<sup>+</sup>), Calcd for C<sub>51</sub>H<sub>52</sub>N<sub>4</sub>O<sub>2</sub>: M, 752.4090].

Table <sup>•</sup>	1
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Optical, therma	l properties	of the	compounds	6a-c	: and	7a–	c
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Compounds	abs <sup>a</sup> (nm)		em (nm)		$\Phi^{b}$	$T_m/T_d/T_g(^{\circ}C)^c$		
	CHCl <sub>3</sub>	Solid	CHCl <sub>3</sub>	THF	Benzene	Solid		
6a	322	305	456	440	437	507	0.37	109/410/135
6b	352	340	436	427	425	453	0.93	170/475/140
6c	327	320	453	448	445	487	0.38	191/480/136
7a	613	466	535	524	505	600	0.96	189/400/133
7b	615	475	543	534	518	561	0.40	114/410/133
7c	581	462	523	519	504	622	0.41	140/450/130

<sup>a</sup> First absorption peak in dilute CHCl<sub>3</sub> solutions  $(1 \times 10^{-5} \text{ mol L}^{-1})$  and solid. <sup>b</sup> Quantum yields ( $\Phi$ ) in CHCl<sub>3</sub> solutions were determined using quinine sulfate

( $\Phi = 0.55$ ) as standard. ^ Measured by TG-DTA and DSC analysis under N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup>.

 $T_m$  is melting point,  $T_d$  is decomposition temperature,  $T_g$  is glass transition temperature.

# 2.2.11. 1-(2-Benzyl-benzoisoquinoline-3-dione)-3-(4-methoxy-phenyl)-5-(diphenylamino)phenyl-2-pyrazoline (**7b**)

Compound **7b**: M.p.: 167 °C. yield 65%, red. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.67–9.70 (d, *J* = 8.8 Hz, 1H), 8.61–8.63 (d, *J* = 7.2 Hz, 1H), 8.34–8.36 (d, *J* = 8.4 Hz, 1H), 7.67–7.75 (m, 3H), 7.16–7.24 (m, 6H), 6.96–7.04 (m, 10H), 6.82–6.83 (d, *J* = 8.0 Hz, 1H), 5.60–5.61 (m, 1H), 4.13 (t, *J* = 7.4 Hz, 2H), 3.88 (s, 3H), 3.81–3.86 (m, 1H), 3.26–3.32 (m, 1H), 1.25 (s, 20H), 0.88 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  165.0, 164.3, 161.3, 152.2, 147.9, 147.6, 146.2, 134.8, 133.7, 132.7, 131.5, 131.0, 129.6, 128.1, 126.9, 124.9, 124.8, 123.8, 123.5, 123.4, 122.6, 114.5, 113.7, 110.6, 65.7, 55.7, 42.8, 40.5, 32.2, 29.9, 29.7, 29.6, 28.4, 27.5, 23.0, 14.4.

HRMS [Found: m/z 782.4197 (M<sup>+</sup>), Calcd for C<sub>52</sub>H<sub>54</sub>N<sub>4</sub>O<sub>3</sub>: M,782.4196].

# 2.2.12. 1-(2-Benzyl-benzoisoquinoline-3-dione)-3-(4-chloro-phenyl)-5-(diphenylamino)phenyl-2-pyrazoline (**7c**)

Compound **7c**: M.p.: 152 °C. yield 56%, red. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  9.56 (d, *J* = 8.4 Hz, 1H), 8.63 (d, *J* = 7.2 Hz, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 3H), 7.43 (d, *J* = 8.4, Hz 2H), 7.16–7.24 (m, 6H), 6.96–7.04 (m, 8H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.63–5.67 (m, 1H), 4.14 (t, *J* = 7.6 Hz, 2H), 3.82–3.89 (m, 1H,), 3.26–3.33 (m, 1H), 1.69–1.73 (t, *J* = 7.4 Hz, 2H), 1.25 (s, 18H), 0.87 (t, *J* = 6.8 Hz, 3H); <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  164.9, 164.2, 152.3, 150.9, 148.0, 147.5, 145.8, 134.2, 132.5, 131.5, 130.9, 129.6, 129.5, 129.3, 127.6, 126.9, 125.4, 125.1, 124.9, 124.0, 123.6, 123.5, 121.8, 114.5, 111.2, 66.0, 42.5, 40.9, 40.5, 32.1, 29.8, 29.7, 29.6, 28.4, 27.4, 22.9, 14.4.



Fig. 2. The absorption spectra of Compound **6a–c**  $(1 \times 10^{-5} \text{ mol } L^{-1})$  in CHCl<sub>3</sub>.



Fig. 3. The absorption spectra of Compound 7a–c  $(1 \times 10^{-5} \text{ mol } L^{-1})$  in CHCl<sub>3</sub>.

HRMS [Found: m/z 786.3691 (M<sup>+</sup>), Calcd for C<sub>51</sub>H<sub>51</sub>N<sub>4</sub>O<sub>2</sub>Cl: M,786.3701].

## 3. Results and discussion

#### 3.1. Absorption and fluorescence spectra

The UV-vis absorption properties of compounds **6**  $(1 \times 10^{-5} \text{ mol})$  $L^{-1}$ ), **7** (1 × 10<sup>-5</sup> mol  $L^{-1}$ ) and photoluminescent (PL) of compounds  $6(1 \times 10^{-6} \text{ mol } \text{L}^{-1})$ ,  $7(1 \times 10^{-5} \text{ mol } \text{L}^{-1})$  in CHCl<sub>3</sub> were presented in Table 1. Absorption spectra of each compound exhibits intense absorption band which are attributed to the  $\pi - \pi^*$  transition of the conjugated backbone [33]. The absorption peaks could be observed in the absorption spectra of compounds **6a**–**c** in the wavelength ranging from 230 to 500 nm. It can be seen from Fig. 2, the spectral shape of the compounds 6a-c are very similar because these compounds possess the similar structure. The maximum absorption peaks are red-shifted from 322 nm (6a), to 327 nm (6c), to 352 nm (6b). In the case of compounds 7a-c. These compounds exhibit two prominent bands in the solution, appearing at 280-320 nm and 581-615 nm (Fig. 3), respectively. The former is ascribed to a localized aromatic  $\pi - \pi^*$  transition and the later is charge transfer character [34]. There are slightly differences among these compounds, although they are similar in the structure. Thus, these



Fig. 4. Fluorescence emission spectra of compounds 6a-c (1 × 10<sup>-6</sup> mol L<sup>-1</sup>) in CHCl<sub>3</sub>.



Fig. 5. Fluorescence emission spectra of compounds 7a-c (1  $\times$  10<sup>-5</sup> mol L<sup>-1</sup>) in CHCl<sub>3</sub>.

differences might be result from the different conjugation degree and different electron effect in these compounds [13].

Figs. 4 and 5 show the fluorescence spectra for these compounds in diluted chloroform solutions. Compounds 6a-c present a blue emission with the peaks varying from 436 to 455 nm. By comparison, the maximum emission peaks in the fluorescence spectra of compounds **7a–c** are located at 524–539 nm, indicating that they can emit green lights. This is due to the emission wavelength of naphthalimide derivatives which is from blue to red region [35]. It indicates that the pyrazoline derivatives emitting different colour fluorescence can be obtained by changing substitute radical of pyrazoline. As shown in Fig. 4, the emission peaks of 6a, 6c are at 456 and 453 nm, respectively. As for 6b, its emission peak is at 436 nm, which has been slightly blue-shifted by 20 nm with respect to that of **6a**. Compounds **7a–c** have similar fluorescence spectra, especially, the similar shape and position. The maximum emission peaks near 524 nm are observed for these molecules. The emission peak of **7b** is red-shifted by 19 nm, which might be attributed to the different conjugation degree and different electron effect in these compounds. The difference in absorption and fluorescence spectra of 6 and 7 is due to the fact that there is respectively a benzothiazole and a naphthalimide group at the 1-position of 6 and 7. Thenaphthalimide group enhances the extent of conjugation in compounds 7 and thus shifts the absorption and fluorescence spectra to longer wavelengths. In general, the absorption and



Fig. 6. Fluorescence emission spectra of compounds 6a-c in solid state.



Fig. 7. Fluorescence emission spectra of compounds 7a-c in solid state.

fluorescence spectra for these compounds are similar to pyrazoline derivatives reported in the literature [15,16].

The fluorescence and absorption spectra of these compounds in the solid are similar to the corresponding spectra measured in solution. Comparing to the fluorescence spectra of these compounds in solution, a red shift of 17–99 nm in the peak wavelength is observed in the solid (Figs. 6 and 7). Whereas to our surprised, comparing the absorption spectra of these compounds in solution, a blue shift of 7–140 nm in the peak wavelength was observed in the solid (Figs. 8 and 9). These relatively shifts in the spectra suggest that there is no big change in the molecular configuration of these compounds when they are dissolved in solution or in solid film [10].

The fluorescence quantum yields ( $\Phi$ ) were measured in CHCl<sub>3</sub> using quinine sulfate ( $\Phi = 0.55$ ) as standard [36]. The  $\Phi$  value of 0.96 is observed for **7a**, which is higher than that of other compounds. This might be due to the conjugation degree and non-planar configuration degree of **7a**. The PL quantum yields of the other compounds are in the range of 0.37–0.93. This difference of quantum yields might be due to the change of the molecular size and the change of the electronic push–pull substitution of the conjugated part in the molecules [10].

Moreover, the solvent effect on the fluorescence characteristics of these compounds was studied, which indicated that the emission wavelength of the compound was red-shifted with the increase of solvent polarity (Figs. 10 and 11) [37,38].

1.2 1.1 1.0 0.9 0.8 Absorbance 0.7 06 0.5 0.4 0.3 0.2 01 0.0 200 300 400 500 Wavelength / nm

Fig. 8. The absorption spectra of Compound 6a-c in solid state.



Fig. 9. The absorption spectra of Compound 7a-c in solid state.

#### 3.2. Thermal properties

The glass transition temperatures (T<sub>g</sub>) were obtained from differential scanning calorimeter. The compounds were heated at 10 °C/min under a nitrogen atmosphere. A second heating scan at the same rate was performed to detect the decomposition temperatures (T<sub>d</sub>) by thermogravimetric analysis (TGA), Melting points (T<sub>m</sub>) were recorded on Electrothermal digital melting point apparatus and the detailed data are listed in Table 1. The T<sub>g</sub> value of these compounds increases progressively on incorporating chromophores such as benzothiazole and naphthalimide. The six materials of **6a**, **6b**, **6c**, **7a**, **7b** and **7c** show distinct T<sub>g</sub> at 135, 140, 136, 133, 133 and 130 °C, respectively. The glass transition temperatures of **7** are reduced compared to **6**, which might be due to the close packing and intermolecular interaction. Furthermore, the six compounds show high thermal stabilities with decomposition temperatures (T<sub>d</sub>) from 400 to 480 °C, which indicate that the decomposition temperatures rise with the increase of conjugation degree and electron effect. Due to the thermal stability of the six compounds, thin films of the compounds could be prepared by vacuum deposition. Therefore, the introduction of TPA substituents at the C-5 position is beneficial for these compounds [39].



Fig. 10. The emission spectra of compounds **6a** in different solvents  $(1 \times 10^{-6} \text{ mol } L^{-1})$ .



**Fig. 11.** The emission spectra of compounds **7c** in different solvents  $(1 \times 10^{-5} \text{ mol } L^{-1})$ .

#### 3.3. Electrochemical properties

The electrochemical properties of compounds 6, 7 were analyzed by cyclic voltammetry in CHCl<sub>3</sub> in the presence of tetrabutylammonium hexafluorophosphate (0.10 mol  $L^{-1}$ ) as supporting electrolyte (Fig. 12) and the results are listed in Table 2. All CV measurements were recorded at room temperature with a conventional three-electrode configuration consisting of a platinum wire working electrode, a platinum counter electrode, and a SCE (saturated calomel electrode) reference electrode under argon. Electrochemical band gaps were calculated from onset potentials of the anodic and cathodic waves [40]. The cyclic voltammetry (CV) of compounds 6, 7 exhibit an irreversible oxidation process which shift positively from -0.73 to -0.45 V. As shown in Table 2, the HOMO ranges are from -5.13 to -4.85 eV, while the LUMO ranges are from -2.07 to -1.57 eV, which are in agreement with the calculated values (-5.17 to -4.95 eV for the HOMO, and -2.26 to -1.63 eV for the LUMO of compounds). The HOMO energy level is lower than that of the most widely used hole-transport material 4,4'-bis(1-naphthylphenylamino)biphenyl (NBP) (5.20 eV) and this might be beneficial for the hole-transport capacity [41]. Their LUMO levels represented a small barrier for electron injection from a commonly used cathode such as barium, which has a work function of 2.2 eV [42]. Therefore, these compounds might be used for hole-transporting and electron-transporting materials for OLEDs [10].



Fig. 12. Cyclic voltammetry of the compound **6b** in 0.1 mol L<sup>-1</sup> Bu<sub>4</sub>NPF<sub>6</sub>-CHCl<sub>3</sub>.

Table 2	
Electrochemical properties of the compounds <b>6a-c</b> and <b>7a-c</b>	ε.

Compound	Band gap <sup>a</sup>	HOMO/LUMO <sup>a</sup> (eV)	$E_g(eV)^b$	$E_{ox}^{c}(V)$	E <sub>HOMO</sub> /E <sub>LUMO</sub> <sup>d</sup> (eV)
6a	2.95	-5.12/-2.17	3.28	0.45	-4.85/-1.57
6b	2.92	-4.95/-2.03	3.17	0.73	-5.13/-1.96
6c	3.43	-5.06/-1.63	3.25	0.67	-5.07/-1.82
7a	2.93	-5.11/-2.18	3.12	0.55	-4.95/-1.83
7b	2.97	-5.07/-2.10	2.95	0.62	-5.02/-2.07
7c	2.91	-5.17/-2.26	3.12	0.57	-4.97/-1.85

<sup>a</sup> DFT/B3LYP calculated values.

Table 3

<sup>b</sup> Optical energy gaps calculated from the edge of the electronic absorption band. <sup>c</sup> Oxidation potential in CHCl<sub>3</sub> ( $10^{-3}$  M) containing 0.1 M ( $n-C_4H_9$ )<sub>4</sub>NPF<sub>6</sub> with a scan rate of 100 mV s<sup>-1</sup>.

 $^{d}$  E<sub>HOMO</sub> was calculated by E<sub>ox</sub> + 4.4 V (vs NHE), and E<sub>LUMO</sub> = E<sub>HOMO</sub> - E<sub>g</sub>.

## 3.4. Theoretical calculation

The ground-state geometry of compounds 6a and 7a as examples were optimized by hybrid densityfunctional theory (B3LYP) with 6–31G\* basis set in the Gaussian 03 program package [43] (Fig. 13). The dihedral angle of **6a** formed between the pyrazoline ring and a benzene ring of TPA is 85.3° and the whole molecule takes a non-planar configuration, which helps to impede the  $\pi$ – $\pi$ stacking interaction in solid state to some extent. In the case of compound **7a**, the dihedral angle formed between the pyrazoline ring and a benzene ring of TPA is 89.2° and the dihedral angle formed between the pyrazoline ring and naphthalimide group is 43.5°. Fig. 14 illustrates the calculated spatial distributions of the HOMO (the highest occupied molecular orbital), LUMO (the lowest unoccupied molecular orbital) levels of compounds 6a and 7a. As can be seen clearly, HOMO is a  $\pi$  orbital concentrated on the central triphenylamine moiety; LUMO is of  $\pi^*$  character distributed on the pyrazoline ring and benzene ring for **6a**, the pyrazoline ring and naphthalimide ring for **7a**.



Fig. 13. Optimized ground-state geometry of compounds **6a** and **7a** with B3LYP/6-31G\* in gas phase.



Fig. 14. Calculated spatial distributions of the HOMO, LUMO levels of compounds 6a and 7a.

#### 4. Conclusions

In summary, we have designed and synthesized a series of novel pyrazoline chromophores containing triphenylamine moieties. The synthetic strategy is straightforward, benefits from high yield and facile purification without tedious silica gel chromatography. The thermal, optical and electrochemical properties were also investigated. The fluorescence quantum yields of the six compounds were obtained. Further research is presently under study in our laboratory.

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