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# Luminescent columnar liquid crystals based on AIE tetraphenylethylene with hydrazone groups bearing multiple alkyl chains

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A series of novel tetraphenylethylene aromatic acylhydrazone derivatives **11**, **12** and **13** with 4, 8 or 12 alkyl chains were designed and synthesized in yields of 82-85%.

<sup>15</sup> Studies on the mesomorphic properties suggested the ordered hexagonal columnar mesophase for compounds 11, 12 and 13. The increase in the number of alkyl chains was favourable for decreasing the phase-transition temperatures and extending the mesophase temperature range. Further, samples 11, 12 and 13
<sup>20</sup> presented an excellent AIE effect. The fluorescence intensities increased by 70, 84 and 43 times for samples 11, 12 and 13, respectively. The absolute fluorescence quantum yields were 18.7%, 27.4% and 23.8% in solid films at room temperature and 6.7%, 24.2% and 17.3% in the mesophase. These results
<sup>25</sup> suggested that the number of alkyl chains greatly influenced the fluorescence emission and sample 12 with 8 alkyl chains exhibited the strongest fluorescence performance on OLED

device.

<sup>30</sup> Keywords: Tetraphenylethylene; Hydrazone; Fluorescence; Mesophase; Aggregation-induced emission

#### 1. Introduction

Since the aggregation-induced emission (AIE) effect was discovered by Tang's group in 2001 [1-3], the AIE <sup>35</sup> luminogens have been studied widely and applied in various research fields such as optoelectronic devices, chemical sensors, solid-state dyes, fluorescence probes and bio-imaging [4–15]. Especially, due to the excellent solid-state lightemitting efficiency, the AIE-based multifunctional materials <sup>40</sup> exhibited great application potential in OLED devices [16-18]. By decorating flexible chains on the AIE luminogens, the so-called AIE liquid crystals could be prepared [19]. This kind of luminescent liquid crystals had been paid considerable attention because of the effective fusion of intrinsic <sup>45</sup> luminescent characteristic, the supramolecular organization and self-healing properties within a mesophase [20, 21]. As a

## result, some AIE liquid crystals based on AIE cores, such as tetraphenylethylene and diphenylacrylonitrile, were investigated and exhibited interesting AIE luminescent and mesomorphic properties [22-40].

Among all types of liquid crystals, columnar discotic liquid crystals have attracted much commercial and academic research interest over the years [41]. They possess unique cores with  $\pi$ - $\pi$  stacking structures, displaying high ordered columnar mesophase with fast charge carrier mobility and 10 extensive application prospects in organic field-effect transistors, organic light-emitting diodes, organic photovoltaic cells and gas sensors, etc [42-45]. Generally, the columnar liquid crystals possessed symmetric and big coplanar aromatic cores. However, the AIE luminogens are usually the 15 asymmetric and noncoplanar structures against effective  $\pi$ - $\pi$ packing in columnar mesophase, resulting in smectic or nematic mesophases in most cases [22-40]. On the other hand, it was well known that the hydrogen bond and the extended aromatic structure were favourable for producing the 20 columnar mesophase [46-48], but these strategies were not applied in columnar AIE liquid crystals up to now. In this paper, in order to assure the columnar mesophase, the hydrazone groups with NH groups and aromatic units bearing multiple alkyl chains were successfully introduced on the 25 tetraphenylethylene core for the first time. The novel columnar AIE liquid crystals were readily constructed based on the positive influences of these hydrazone groups on columnar mesophase. Moreover, the influences of different numbers of alkyl chains (4, 8 and 12) on fluorescence 30 properties and mesomorphic properties were also first investigated in detail. The results suggested that the

alkyl chains exhibited not only excellent AIE fluorescence properties but also a good hexagonal columnar mesophase.

tetraphenylethylene with hydrazone groups bearing multiple

#### 35 2. Experimental

#### 2.1 General

The chemical reagents were obtained from Aladdin Co. Ltd. The inorganic reagents were used directly. The organic solvents were purified by standard process before use. TLC 40 analysis was done on pre-coated glass plates. Silica gel (200-300 mesh) was used for column chromatography. NMR spectra were measured on a Bruker-ARX 400 instrument at 26 °C with tetramethylsilane (TMS) as internal standard. Mass spectra were detected by Bruker mass spectrometer. UV-Vis 45 spectra were examined on Varian spectrometer. Fluorescence spectra were measured in a conventional quartz cell (10×10×45 nm) at 25°C on a Hitachi F-4500 spectrometer equipped with a constant-temperature water bath. The fluorescence absolute  $\Phi_F$  values were obtained on FLS920 <sup>50</sup> Fluorescence spectrometer with a 6-inch integrating sphere. POM (Leica DMRX) was obtained on a hot stage (Linkam THMSE 600) to observe phase transitions. Thermal analysis of the materials was carried out on DSC (Thermal Analysis Q100). XRD data were obtained from SEIFERT-FPM <sup>55</sup> (XRD7) with Cu Kα 1.5406 Å as the radiation source under 40 kV, 30 mA power. The particle size and distribution were measured by an ALV-5000 laser light scattering spectrometer (DLS). Benzaldehyde derivatives 2, 4, 6 were synthesized by the reported procedures [49]. Tetraphenylethylene 60 tetrahydroxyl derivative 8 was prepared by reacting 2,4'dihydroxybenzophenone in Zn,TiCl<sub>4</sub>/THF system according to the published literature [23].



Scheme 1 The synthetic route of compounds 11, 12 and 13

<sup>5</sup> 2.2. Synthesis of tetraphenylethylene tetraester derivative 9 Tetrahydroxy-tetraphenylethylene 8 (0.396 g, 1 mmol), anhydrous potassium carbonate (5.0 g, 36.2 mmol) and ethyl bromoroacetate (2.0 mL) were added in dried acetonitrile (40mL). After refluxing and stirring overnight, the TLC
<sup>10</sup> detection suggested that the starting material almost disappeared completely. After reaction, HCl solution (50 mL, 1 M) was dropped in reaction system, and the mixture was extracted with CHCl<sub>3</sub> (50 mL). The organic phase was separated and concentrated. The residue was recrystallized in <sup>15</sup> CHCl<sub>3</sub>/MeOH to give tetraphenylethylene tetraester derivative tetraester derivative **9**: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δppm: 6.83 (d, J = 8.0 Hz, 8H, ArH), 6.54 (d, J = 8.0 Hz, 8H, ArH), 4.44 (s, 8H, OCH<sub>2</sub>), 4.14(q, 8H, OCH<sub>2</sub>), 1.17(t, J = 8.0 Hz, <sup>20</sup> 12H, CH<sub>3</sub>); MALDI-TOF-MS (C<sub>42</sub>H<sub>44</sub>O<sub>12</sub>) Calcd. for m/z =740.8, found: m/z = 740.7 (M<sup>+</sup>).

- 2.3 Synthesis of tetraphenylethylene tetraacylhydrazine derivative 10
- Tetraphenylethylene tetraester derivative 9 (0.740 g, 1 mmol) <sup>25</sup> and N<sub>2</sub>H<sub>4</sub>-H<sub>2</sub>O (1 mL) were refluxed in CHCl<sub>3</sub>/MeOH (V/V = 1:1(20 mL)) for 10 h. The TLC detection indicated that the starting materials were consumed. The solvents were evaporated under reduced pressure. The residue was recrystallized in CHCl<sub>3</sub>/MeOH (V/V = 1:3) to give <sup>30</sup> tetraphenylethylene tetraacylhydrazine derivative **10** as white powder in the yield of 90%. Tetraphenylethylene tetraacylhydrazine derivative 10: <sup>1</sup>H NMR (400 MHz, DMSO) δppm: 9.32 (s, 4H, NH), 6.84 (d, J = 8.0 Hz, 8H, ArH), 6.72 (d, J = 8.0 Hz, 8H, ArH), 4.39 (s, 8H, OCH<sub>2</sub>), 35 4.31(bs, 8H, NH<sub>2</sub>); MALDI-TOF-MS (C<sub>34</sub>H<sub>36</sub>N<sub>8</sub>O<sub>8</sub>) Calcd.for m/z = 684.3, found: m/z = 684.3 (M<sup>+</sup>).

# 2.4 Synthesis of target tetraphenylethylene tetrahydrazone derivative 11, 12 and 13

The mixture of tetraphenylethylene tetraacylhydrazine <sup>40</sup> derivative **10** (0.342 g, 0.5 mmol) and benzaldehyde derivative **2** (**4** or **6**) (2 mmol) were refluxed in 20 mL of CHCl<sub>3</sub>/MeOH (V/V = 2:1) for 12 h with three drops of glacial acetic acid as catalysts. After reaction, the solvents was evaporated under reduced pressure and the residue was <sup>45</sup> recrystallized in CHCl<sub>3</sub>/MeOH (V/V = 1:5) for three times. Only one dot was found on TLC plate under various solvents, indicating the good purification for product. Compounds **11**, **12** and **13** were obtained as white powder in the yields of 82%, 84% and 85%, respectively. Compound **11**: FT-IR (KBr, cm<sup>-1</sup>):

MAsNdiscussed Pabove, the	2923, 2853, 1681, 1602, 1508, 1269, 1177, 808. <sup>1</sup> H NMR
acylhydrazone derivatives 1	(400 MHz, $CDCl_3$ ) $\delta ppm$ : <sup>1</sup> H NMR (400 MHz, $CDCl_3$ ) $\delta ppm$ :
target compounds due to	9.39 (bs, 4H, NH), 8.13 (s, 4H, CH), 7.71 (d, $J = 8.0$ Hz, 8H, ArH) 6.91-7.02 (m 16H ArH) 6.72 (d $I = 8.0$ Hz 8H
45 aromatic acylhydrazone stru	<sup>5</sup> ArH), 4.61 (s, 8H, OCH <sub>2</sub> ), 3.99 (s, 8H, OCH <sub>2</sub> ), 4.14(q, 8H,
NH group were favourable	OCH <sub>2</sub> ), 0.85-1.80 (m, 92H, $C_{11}H_{23}$ ); <sup>13</sup> C NMR (100 MHz,
different numbers of periph	CDCl <sub>3</sub> ) δppm: 164.37, 155.64, 148.34, 140.37, 132.40, 131.66, 120.67, 125.70, 114.68, 114.01, 105.06, 68.13, 67.03, 21.02
were decorated on hydraz	29.64, 29.58, 29.41, 29.19, 29.06, 26.02, 25.96, 22.63, 14.11;
influence of multiple alkyl	<sup>10</sup> MALDI-TOF-MS ( $C_{110}H_{148}N_8O_{12}$ ) Calcd. for $m/z = 1774.4$ ,
50 and mesomorphic properties.	found: $m/z = 1774.0$ (M <sup>+</sup> ), 1797.1 (MNa <sup>+</sup> ). HR-MS(ESI)
compounds 11, 12 and 13 we	$(C_{110}H_{148}H_8O_{12})^+$ [M+Na] · Calcu. 1797.1148. Found. 1797.0751(M+Na) <sup>+</sup> . Anal. calcd. for $C_{110}H_{148}N_8O_{12}$ : C, 74.46;
by reacting 1-bromododecar	H, 8.41; N, 6.32. found: C, 74.51; H, 8.48; N, 6.21.
3,4-dihydroxybenzaldehyde	<sup>15</sup> Compound <b>12</b> : FT-IR (KBr, cm <sup>-1</sup> ): 2923, 2853, 1681, 1602,
in K <sub>2</sub> CO <sub>3</sub> /MeCN system [4	9.48 (bs, 4H, NH), 8.11 (s, 4H, CH), 7.45 (s, 4H, ArH), 7.10
55 conveniently prepared in y	(d, <i>J</i> = 8.0 Hz, 4H, ArH), 6.84-6.97 (m, 12H, ArH), 6.71 (d, <i>J</i>
respectively. On the other	= 8.0 Hz, 8H, ArH), 4.60 (s, 8H, OCH <sub>2</sub> ), 4.00-4.05 (m, 16H,
method [23], tetraphenyleth	<sup>20</sup> OCH <sub>2</sub> ), 0.05-1.84 (iii, 1841), C <sub>11</sub> H <sub>23</sub> ), C NWK (100 WHZ, CDCl <sub>3</sub> ) δppm: 164.16, 155.55, 151.72, 150.09, 149.45, 145.54,
was synthesized by reacting	132.77, 125.79, 123.07, 121.66, 114.07, 112.34, 110.54, 69.25,
Zn,TiCl <sub>4</sub> /THF system in	69.04, 67.07, 31.94, 29.68, 29.49, 29.45, 29.39, 29.28, 29.17, 26.04, 22.71, 14.13; MALDI-TOF-MS (Cree Herrin Correlation) Calcid
	= 0.0.1, = 0.7.1, 1, 1.1.0, 1.1.0 = 1.01 1.10 (0.000, 0.

<sup>25</sup> for m/z = 2511.6, found: m/z = 2511.6 (M<sup>+</sup>). Anal. calcd. for C<sub>158</sub>H<sub>244</sub>N<sub>8</sub>O<sub>16</sub>: C, 75.55; H, 9.79; N, 4.46. found: C, 75.61; H, 9.73; N, 4.38. Compound **13**: FT-IR (KBr, cm<sup>-1</sup>): 2924, 2853, 1684, 1593, 1502, 1297, 1180, 803. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ ppm: 9.36 (bs, 4H, NH), 8.38 (s, 4H, CH), 7.01 (d, *J* <sup>30</sup> = 8.0 Hz, 8H, ArH), 6.68-6.76 (m, 16H, ArH), 4.61 (s, 8H, OCH<sub>2</sub>), 3.95-4.10 (m, 24H, OCH<sub>2</sub>), 0.86-1.86 (m, 276H, C<sub>11</sub>H<sub>23</sub>); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$ ppm: 164.09, 155.88, 152.76, 145.62, 141.13, 132.83, 132.44, 124.35, 121.81, 113.95, 108.59, 74.75, 73.53, 68.80, 31.93, 30.32, 30.21, <sup>35</sup> 29.66, 29.36, 29.31, 26.15, 26.11, 22.69, 14.10; MALDI-TOF-MS(C<sub>206</sub>H<sub>340</sub>N<sub>8</sub>O<sub>20</sub>) Calcd.for m/z = 3248.9, found: m/z = 3247.6 (M<sup>+</sup>). Anal. calcd. for C<sub>206</sub>H<sub>340</sub>N<sub>8</sub>O<sub>20</sub>: C, 76.15; H,10.55; N, 3.45. found: C, 76.10; H, 10.62; N,3.38.

#### 40 **3. Results and discussion**

3.1. Synthesis and characterization

1, 12 and 13 were designed as the feature that the extended cture and the hydrogen bond of for columnar mesophase. The eral alkyl chains (4, 8 and 12) cone groups to investigate the chains on fluorescence properties The synthetic routes to the target ere illustrated in Scheme 1. Firstly, ne with 4-hydroxy benzaldehyde, or 2,3,4-trihydroxybenzaldehyde 6], compounds 2, 4 and 6 were vields of 86%, 88% and 80%, hand, according to the literature ylene tetrahydroxyl derivative 8 2,4'-dihydroxybenzophenone in yield of 88%. Further, the 60 tetraphenylethylene derivative 9 was prepared in the yield of 75% by reacting compound 8 with ethyl bromoacetate in K<sub>2</sub>CO<sub>3</sub>/MeCN system. After the aminolysis reaction of compound 9 with  $N_2H_4$ , the tetraphenylethylene hydrazide derivative 10 was obtained in yield of 90%. Finally, based on 65 the Schiff-base condensation, the target tetraphenylethylene hydrazone derivatives 11, 12 and 13 were prepared by refluxing compound 10 with compounds 2, 4 and 6 in CHCl<sub>3</sub> / MeOH (1: 5, V/V) system. The purification process was simple with recrystallization due to the high reaction 70 efficiency of Schiff-base condensation and the yields were as high as 82%, 84% and 85%, respectively. The structures of compounds were characterized by FT-IR the new

tetraphenylethylene aromatic

spectrometry, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, MALDI-TOFMAN The phase transition behavior of compounds **11**, **12** and **13** mass spectrometry and elemental analysis (see SI). All the characterization data were in accordance with their structures. For example, a pair of doublet in <sup>1</sup>H NMR spectra was <sup>5</sup> observed for the tetraphenylethylene skeleton, indicating the symmetric tetra-substituted structure for these new compounds.

#### 3.2. Mesomorphic properties



Figure 1 The DSC traces of compounds 11, 12 and 13 for cooling and second heating at a rate of  $10 \,^{\circ}$ C / min.

<sup>15</sup> Table 1 Transition temperatures (°C) and enthalpy changes (kJ/mol) of compounds 11, 12 and 13

compound	Phase	Heating scan	Ieating scan Cooling scan			
	transition <sup>[a]</sup>	T( <i>ΔH</i> )	$T(\Delta H)$			
11	Cr-Col	137.8(18.5)	133.7(22.6)			
	Col-Iso	164.9(1.8)	162.6(2.1)			
12	Cr-Col <sub>h</sub>	108.9(20.3)	99.9(18.9)			
	Col <sub>h</sub> -Iso	181.3(3.3)	177.1(2.6)			
13	Cr-Col <sub>h</sub>	36.1(19.8)	34.7(18.6)			
	Col <sub>h</sub> -Iso	152.6(1.2)	141.6(1.3)			
[a] Cr-arvetalling Col-bayegonal columner mesonhase						

[a] Cr=crystalline,  $Col_h=hexagonal$  columnar mesophase, Iso=isotropic. 20 were firstly investigated by differential scanning calorimetry (DSC) under a nitrogen blanket at a scan rate of 10 °C / min. The DSC curves and the corresponding phase transition temperatures and enthalpy changes were shown in Figure 1 and Table 1, respectively. It was observed that compound 11 25 exhibited two endothermic peaks at 137.8 °C and 164.9 °C on heating and two exothermic peaks at 133.7 °C and 162.6 °C upon cooling, respectively. Compound 12 also had two endothermic peaks at 108.9 °C and 181.3 °C for the heating process and two exothermic peaks at 99.9 °C and 177.1 °C for 30 the cooling process. Compound 13 exhibited broad thermic peaks at low temperatures at 36.1 °C on heating and 34.7 °C on cooling, and a small thermic peak at 152.6 °C for heating process and 141.6 °C for cooling process, respectively. These results certainly implied the reversible phase transition for 35 compounds 11, 12 and 13 with the crystal phase-mesophaseisotropic phase process. Moreover, one can see that the melting points of compounds 11, 12 and 13 presented the orderly change of 11 (137.8 °C) > 12 (108.9 °C) > 13 (36.1 <sup>o</sup>C). After calculation, the mesophase temperature ranges of 40 compounds 11, 12 and 13 also displayed the orderly changes of 11 (27.1 °C) < 12 (72.4 °C) < 13 (116.5 °C). These results were in accordance with the order of the number of alkyl chains of 11 (4 chains) < 12 (8 chains) < 13 (12 chains), suggesting that the multiple alkyl chains influenced greatly 45 the mesomorphic behavior. The more peripheral alkyl chains favourable for decreasing the phase-transition were temperatures and extending the mesophase temperature range. The broad peaks and obvious hysteresis phenomena for compound 13 on thermic process could be attributed to this kind of viscous material with 12 long alkyl chains. Based on these DSC data, it could be summarized that compounds 11, 12 and 13 possessed good liquid crystalline behavior, and the more alkyl chains contributed to decrease the phase-transition <sup>5</sup> temperatures and extend the mesophase temperature ranges.

The mesomorphic textures of compounds 11, 12 and 13 were further observed by using polarising optical microscopy (POM). Upon heating and cooling process, the phase transitions of Cr-Col and Col-Iso phase were distinguished 10 clearly. Their phase transition temperatures were approximately in accordance with the thermic peaks of DSC curves. During slowly cooling form the isotropic phase, the mesophase textures can be observed as shown in Figure 2. All of them exhibited the orderly textures, which could be seen as 15 the type of pseudo-confocal conic texture for columnar mesophase. This proposal was further supported by XRD analysis.



Figure 2 The POM textures of compounds 11, 12 and 13 <sup>20</sup> upon cooling at 150 °C for 11, 120 °C for 12, 60 °C for 13 (Zooming in 200 times)

The XRD analyses for mesophase were carried out at the liquid crystalline phase of samples **11**, **12** and **13**. The <sup>25</sup> corresponding XRD curves were illustrated in Figure 3. In the small-angle region, sample **11** exhibited two strong reflections and one weak reflection at 2.69°, 4.67° and 5.39°, respectively. Samples **12** and **13** showed one strong reflection and two

Weak reflections at 2.46°, 4.26°, 5.92° and 2.24°, 3.88°, 4.48°, <sup>30</sup> respectively. Based on the Bragg equation  $d = 1.5406/(2\sin\theta)$ , the corresponding distances for these reflections were calculated as 32.80 Å, 18.91 Å, 16.39 Å for sample 11, 35.88 Å, 20.71 Å, 17.94 Å for sample 12, and 39.40 Å, 22.75 Å, 19.71 Å for sample 13. These data were in agreement with the  $_{35}$  ratios of  $1:1/\sqrt{3}:1/\sqrt{4}$ , suggesting the  $[d_{100}]$ ,  $[d_{110}]$  and  $[d_{200}]$ reflections for hexagonal columnar liquid crystals. In the wide-region, the broad halos at  $2\theta = 15 \sim 30^{\circ}$  could be attributed to the reflections of the molten alkyl chains. A small reflection at 21.38° for sample 11, 21.80° for sample 12, 40 20.94° for sample 13 could be observed. These reflections suggested the distances of 4.15 Å for sample 11, 4.07 Å sample 12 and 4.24 Å sample 13, which corresponded to the intracolumnar distances of  $\pi$ - $\pi$  interaction for the ordered hexagonal columnar liquid crystal. Moreover, the lattice 45 parameter (a) for samples 11, 12 and 13 could be calculated as 37.82 Å, 41.44 Å and 45.50 Å, respectively. These data were smaller than the diameter of samples 11, 12 and 13 (~60 Å) estimated by the CPK molecular model. These results might suggest that the soft alkyl chains for these samples adopted 50 the folding conformation and/or the interdigitation in the neighbouring columns. Thus, the possible molecular stacking of hexagonal columns for these samples could be proposed in Figure 3 (using sample 13 as representative one). Based on all the analyses of DSC, POM and XRD results, it could be 55 concluded that samples 11, 12 and 13 possessed the ordered hexagonal columnar mesophase. The more alkyl chains resulted in the lower phase-transition temperatures and wider mesophase temperature scopes.



<sup>10</sup> **Figure 3** XRD traces tested at 150 <sup>0</sup>C for **11**, 120 <sup>o</sup>C for **12** and 60 <sup>o</sup>C for **13**, and the proposed molecular stacking model for hexagonal columnar mesophase of compound **13**.

#### 3.3. photophysical properties

TPE is a well-known aggregation induced emission luminogen (AIEgen). To investigate the fluorescence properties of samples 11, 12 and 13, their UV-vis spectra and the fluorescence spectra in THF and THF / water mixtures were measured. Compounds 11, 12 and 13 showed similar 20 UV-vis signals with absorption at 300-350 nm and fluorescence emission at 400-600 nm based on the same TPE cores. The fluorescence changes in different THF / water mixtures are presented in Figure 4 and the comparison changes for fluorescences  $(I/I_0)$  were summarised in Figure 5. 25 As shown in Fig 4, the fluorescence spectra clearly showed the enhancement with the increase of H<sub>2</sub>O fractions in THF/H<sub>2</sub>O mixtures. Samples 11, 12 and 13 almost did not emit in pure THF solution. But fluorescence gradually became stronger when the  $H_2O$  fractions > 30%, reaching their 30 maximum emission at 95%. One can see that sample 12 exhibited the strongest fluorescence at 95% with the intensity

indicated that, compared with the fluorescence in pure THF solutions, the fluorescence intensities of samples 11, 12 and 35 13 increased by 70, 84 and 43 times in THF/H<sub>2</sub>O mixtures with 95% of H<sub>2</sub>O fractions, respectively. All these results suggested that the multiple alkyl chains influenced on the AIE effect obviously and the sample 12 with eight alkyl chains presented the strong AIE effect. The hydrodynamic size 40 distribution of compounds 11, 12 and 13 in solution of H<sub>2</sub>O/THF (5:95) was also evaluated by dynamic light scattering (DLS). The results showed that the hydrodynamic average size distribution of the compounds 11, 12 and 13 were 254 nm, 400 nm and 600 nm, which increased orderly 45 with the increase of number of alkyl chains. These phenomena could be explained by that the multiple alkyl chains decreased dramatically the solubility in H<sub>2</sub>O/THF solution and enhanced the aggregation abilities.



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**Figure 4** The fluorescence spectra of samples **11**, **12** and **13** in THF/H<sub>2</sub>O mixtures with different fractions of H<sub>2</sub>O ( $1 \times 10^{-5}$  M) excited at  $\lambda = 320$  nm. (Their pictures in pure THF and <sup>5</sup> THF/H<sub>2</sub>O (5:95) solutions were inserted).





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Figure 6 Hydrodynamic size distribution of samples 11, 12 and 13  $(1 \times 10^{-5} \text{ M})$  based on DLS measurements in solution of <sup>25</sup> H<sub>2</sub>O/THF (5:95).



Figure 7 The fluorescence spectra ( $\lambda_{ex} = 320$  nm) of solid films of samples 11, 12 and 13 before and after heating at mesophase temperatures (150 °C for 11, 120 °C for 12 and 50 s °C for 13). (Their pictures before and after heating for 12 were inserted)

Furthermore, the fluorescence behavior of samples 11, 12 and 13 in solid films at room temperature and mesophase <sup>10</sup> were investigated. Figure 7 illustrated the fluorescence spectra of samples 11, 12 and 13 before and after heating the mesophase. It can be seen that, compared with the fluorescence spectra in solution (Figure 4), no obvious red shift or blue shift occurred. Samples 11, 12 and 13 exhibited 15 strong fluorescence in solid films. The absolute fluorescence quantum yields of samples 11, 12 and 13 in solid films were as high as 18.7%, 27.4% and 23.8%, respectively. Also, the fluorescence spectra of samples 11, 12 and 13 in the mesophase showed some red shifts in comparison with that 20 before heating. The fluorescence intensities also decreased a little after heating with the absolute fluorescence quantum yields of 6.7%, 24.2% and 17.3% for samples 11, 12 and 13, respectively. These results suggested that the numbers of alkyl chains influenced greatly on fluorescence quantum yields. The 25 alkyl chains could enhance the steric hindrance and produce

films. On the other hand, the multiple alkyl chains were also favourable for the orderly  $\pi$ - $\pi$  stacking for TPE cores, producing the ACQ effect and resulting in the red shift and 30 decrease of fluorescence. Nevertheless, sample **12** with 8 alkyl chains still displayed strong fluorescence with good fluorescence quantum yields at both room temperature and mesophase temperature.



Figure 8 Molecular theoretical orbital amplitude plots of HOMO and LUMO energy levels of compounds 11, 12 and 13

In order to further study the relationship of structures and <sup>40</sup> properties, a density functional theory (DFT) calculation to better understand geometry and electronics through the Gaussian 03 program was performed. The optimized geometry and space diagrams for the highest occupied molecular orbital (HOMO) and the lowest unoccupied <sup>45</sup> molecular orbital (LUMO) were shown in Figure 8. It can be seen that the orbital electrons of the molecule were mainly distributed on the plane of the conjugated skeleton of the TPE nucleus, indicating that the charge transfer between tetraphenylethylene unit and hydrazone groups was very weak

#### 3.4 Electroluminescence properties

As sample 12 exhibited the strongest fluorescence emission, 10 the electroluminescence (EL) performance of sample 12 as representative one was investigated in an OLED device. Sample 12 was employed as the emitter with the configuration of ITO / PEDOT / emissive layer (~40 nm) / TPBI (20 nm) LiF (10 nm) / Al (100 nm). The key device performance data 15 were summarized in Table 2. Figures 9 (a-b) depicted the current density-voltage-luminance (J-V-L) characteristics of the OLED produced. The OLED of the device showed a high driving voltage of 14V (Vonset, equivalent to 1 cdm<sup>-2</sup>) probably due to the unbalanced charge carrier mobility in <sup>20</sup> these devices. A low luminance (Lmax) of 4.54 cdm<sup>-2</sup> for current efficiency ( $\eta_c$ ) was 3.898 cd A<sup>-1</sup>, and the power efficiency  $(\eta_p)$  was 0.0059 lmW<sup>-1</sup>. The steady-state EL spectrum of the device at a driving voltage of 15 V (Figure 9c) showed an emission peak at 582 nm. The device exhibited 25 excellent spectral stability over a wide range of operating voltages (Figure 9d). The EL spectrum of the device at 15V was used to determine the CIE chromaticity coordinates. International Commission on Illumination (CIE) color coordinates was shown in Figure 9e. The CIE coordinates 30 (0.4338, 0.4277) listed in Table 2 correspond to bright yellow emission. Although this device was not optimized for better

v performance including brightness and efficiency, this electroluminescence performance certainly suggested that this kind of AIE liquid crystal possessed the potential application <sup>35</sup> prospect for OLED device.

#### Table 2 Electroluminescent performance data of OLEDs<sup>a</sup>

V <sub>onset</sub> <sup>b</sup> (V)	$L_{max}^{c}$ (cd m <sup>-2</sup> )	$\eta_{c,}{}^d(cd\;A^{\text{-}1})$	$\eta_{p,}^{d}$ (Im W <sup>-1</sup> ) 7	em <sup>e</sup> (nm)	$CIE_{(x,\ y)}{}^f$		
14	4.541	3.898	0.0095	582	0.4338, 0.4277		
<sup>a</sup> Device configuration: ITO / PEDOT / emissive layer / TPBI							
(20nm) LiF (10nm) / Al (100nm) <sup>b</sup> V <sub>onset</sub> : turn-on voltage							
at luminance of 1 cd m <sup>-2</sup> . <sup>c</sup> L <sub>ma</sub> x: luminance at 20 V. <sup>d</sup> Current							
40 efficien	cy(η <sub>c</sub> ), po	ower effic	tiency $(\eta_p)$	. <sup>e</sup> λ <sub>em</sub> :	emission		
waveler	ngth maximu	n at 15 V. <sup>f</sup>	CIE color c	oordina	te.		





## 10 In

summary, three novel tetraphenylethylene aromatic acylhydrazone derivatives 11, 12 and 13 with 4, 8 or 12 alkyl chains were designed and synthesized in 82-85% yields. Their structures were confirmed by FT-IR spectrometry, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, MALDI-TOF mass spectrometry and 15 elemental analysis. The mesomorphic properties were investigated by DSC, POM and XRD analysis, suggesting they had the ordered hexagonal columnar mesophase. The more alkyl chains contributed to decrease the phase-transition temperatures and extend the mesophase range of the mesophase. 20 The studies on photophysical properties implied that compounds 11, 12 and 13 exhibited the excellent AIE effects and the fluorescence intensities increased by 70, 84 and 43 times for samples 11, 12 and 13, respectively. Compounds 11, 12 and 13 also showed good fluorescence with moderate 25 absolute fluorescence quantum yields in solid films at room temperature and mesophase temperature. The absolute fluorescence quantum yields of sample 12 were as high as 27.4% in solid film at room temperature and 24.2% in the mesophase. The OLED test suggested that sample 12 30 possessed the electroluminescence properties, indicating the potential application prospect of these novel AIE liquid crystals in the field of OLED device.



0.4 x 0.5

0.6

0.7

0.8

0.3

0.1

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### ACCEPTED MANUSCRIPT

Novel tetraphenylethylene acylhydrazone derivatives 11, 12 and 13 were prepared.

Compounds 11, 12 and 13 possess hexagonal columnar mesophases.

Compounds 11, 12 and 13 presented excellent AIE effect.

The number of alkyl chains influences the mesophase and fluorescence emission.

Sample 12 displayed the electroluminescence performance on OLED device.

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