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### Fluorescence-enhanced organogelators with mesomorphic and piezofluorochromic properties based on tetraphenylethylene and gallic acid derivatives

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#### 1. Introduction

In recent years, low-molecular mass organogelators (LMOGs) have drawn immense interest because of their potential applications in cosmetics, catalysis, drug delivery systems, sensors, switches and other related fields [1,2]. LMOGs can self-assemble into fibers, rods, ribbons or other aggregates in suitable solvents via a combination of noncovalent interactions, such as hydrogen bonding,  $\pi - \pi$  stacking, electrostatic forces, donor-acceptor interactions, metal coordination, solvophobic forces and van der Waals forces, to form entangled networks and gel solvents [3,4]. Most LMOGs, called "smart" or "intelligent" gels, show reversible changes in morphology and/or physical properties in response to various external stimuli, such as temperature, electrical pulse and light [5,6]. But most of chromophores exhibit aggregation-induced quenching in the gel states or in the solid states [7].

#### ABSTRACT

Two novel aggregation-induced emission compounds derived from tetraphenylethylene and gallic acid were synthesized and characterized. Both of the emission compounds possessed mesomorphic properties and exhibited mesomorphic phases over a wide temperature range and the thermal-induced mesomorphic transition from metastable to stable phases accompanied by a change of the luminescent color. The mesomorphic transition may be ascribed to liquid crystalline phase transition. The emission compounds possess different gelation behavior in organic solvents. The emission intensities of the emission compounds can be reversibly changed with the gel–solution transition by alternate cooling and heating. Moreover, the color and emission of these organogelators can be repeatedly switched by various external stimuli including pressing, heating and solvent-fuming. These new compounds may offer potential as external stimuli-responsive materials.

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Recently, aggregation-induced emission (AIE) organogelators have attracted considerable research attention because of their strong gel emission [8]. For example, an AIE organogelator, 1cyano-*trans*-1,2-bis-(3',5-bis-trifluoromethylbiphenyl) ethylene (CN-TFMBE) (Scheme 1), was practically nonfluorescent in the solution state, but highly fluorescent in the gel state, with a more than 100-fold enhancement in the fluorescence intensity [9,10]. In 2008, Chen et al. [11] reported a thermochromic gel generated from a cholesterol-containing salen-based organogelator, which exhibited obvious AIE properties in the gel state. The fluorescence quantum yield of the gel was approximately 600 times greater than that in solution.

Mechano- or piezo-fluorochromic materials have also drawn a great deal of attention because of their fundamental research and practical applications in sensors, optical recording and strain- or pressure-sensing systems [12–29]. These materials generate a fluorescent color in response to external force stimuli, such as grinding, smearing and pressing, and then revert to the original color by heating, recrystallization or exposure to solvent vapor. To date, only a few liquid crystalline materials displaying piezo-fluorochromic property have been reported [30–32]. LMOGs that





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Scheme 1. Synthetic routes for P4 and P5; the chemical structure of CN-TFMBE.

exhibit piezofluorochromic properties are exceedingly rare [33]. In 2012, Ren et al. reported several phosphole-lipids which formed highly fluorescent ionic organogels and their donor and acceptor doped systems exhibited piezofluorochromism. However, organic LMOGs with multimorphic and piezochromic luminescent properties have not been reported thus far to the best of our knowledge. In this article we report our recent results of two organogelators (**P4** and **P5**, Scheme 1) with AIE, multimorphic and piezo-fluorochromic properties, synthesized from tetraphenylethylene and gallic acid derivatives.

#### 2. Experimental

#### 2.1. Materials and measurements

4-Aminophenylboronic acid, 4-bromophenyl phenylmethanone, 2-bromo-1,1,2-triphenylethylene, 4-toluenesulfonic acid, diphenylmethane, 1-bromododecane, methyl 3,4,5-trihydroxybenzoate, 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC-HCl), 4-dimethylamiopryidine (DMAP), *n*-butyllithium, tetrabutyl ammonium bromide (TBAB) and tetrakis(triphenylphosphine) palladium (0) were purchased from Alfa-Aesar company and used as received. Ultra-pure water (18 M $\Omega$ .cm) was used in the experiments. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. All other reagents and solvents were purchased as analytical grade from Guangzhou Dongzheng Company (China) and used without further purification. Methyl 3,4,5tris(dodecyloxy)benzoate (2) [7], 3,4,5-tris(dodecyloxy) benzoic acid (**3**) [34] and 1-bromo-4-(1,2,2-triphenylvinyl)benzene (**TPE-Br**) [35,36] were prepared according to the literature methods.

Proton and carbon nuclear magnetic resonance (<sup>1</sup>H NMR and <sup>13</sup>C NMR) spectra were measured on a Mercury-Plus 300 spectrometer [CDCl<sub>3</sub>, tetramethylsilane (TMS) as the internal standard. For **P<sub>5</sub>NH<sub>2</sub>**, using DMSO-d<sub>6</sub> as solvent]. Mass spectra (MS) were measured on a Thermo DSQ EI-mass spectrometer. Elemental analyses were performed with an Elementar Vario EL elemental analyzer. Photoluminescence spectra (PL) were measured on a Shimadzu RF-5301pc spectrometer with 1.5 nm and 3.0 nm slit widths for excitation and emission, respectively. Ultraviolet-visible absorption spectra (UV-vis) were recorded on a Hitachi UV-vis spectrophotometer (U-3900). Wide-angle X-ray diffraction (WAXD) and small-angle X-ray diffraction (SAXD) measurements were performed by using a Bruker X-ray diffractometer (D8 ADVANCE, Germany) with an X-ray source of Cu Ka  $(\lambda = 0.15406 \text{ nm})$  at 40 kV and 40 mA, at scan rates of 4° and 0.6° per 1 min for WAXD and SAXD, respectively. Time-resolved emission decay behavior was measured on an Edinburgh Instruments Ltd. spectrometer (FLSP920). Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analyzer (DSC 204 F1) at a heating rate of 10 °C/min under N<sub>2</sub> atmosphere. Transition temperatures and textures were determined using a Leitz Orthoplan Pol polarizing optical microscope (POM) equipped with a Likam heating stage system. The THF/water mixtures with different water fractions were prepared by slowly adding distilled water into the THF solution of samples under ultrasound at room temperature. Pressed samples were prepared by pressing in an IR



**Fig. 1.** (a) PL spectra of **P5** in THF/water mixtures with different water fractions (inset: the images of **P5** were taken at room temperature under 365 nm UV light in THF and 90% water); (b) Change in PL peak intensities of **P4** and **P5** with different water fractions in THF/water mixtures (concentration 10  $\mu$ M, excitation wavelength 365 nm).

pellet at 1500 psi for 5 min. Annealing experiments were done on a hot-stage with automatic temperature control system for 5 min, the annealing temperature was 70 °C. The experiment of solvent vapor fuming treatment was performed by filling the pressed sample on a grooved glass slide, which was then placed in a large beaker saturated with  $CH_2Cl_2$  vapor for 5 min at room temperature.

#### 2.2. Synthesis of 4-(1, 2, 2-triphenylvinyl)benzenamine (P<sub>4</sub>NH<sub>2</sub>)

To 2-bromo-1,1,2-triphenylethylene (3.35 g, 10 mmol) and 4aminophenylboronic acid 1.65 g (12 mmol) in THF (50 mL), 2 M K<sub>2</sub>CO<sub>3</sub> aqueous solution (9 mL) and TBAB (0.01 g) were added. The mixture was stirred for 30 min under an argon atmosphere at room temperature. Then the Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst was added and the reaction mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the product was concentrated and purified by silica gel column chromatography with CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane mixed solvent (1:2 by volume) to afford a pale yellow powder **P**<sub>4</sub>**NH**<sub>2</sub> (3.16 g, yield 91.2%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ (ppm): 6.41–6.46 (d, *J* = 7.8 Hz, 2 H); 6.76–6.83 (d, *J* = 7.8 Hz, 2 H); 6.94–7.18 (m, 17 H). MS (EI) calcd for C<sub>26</sub>H<sub>21</sub>N 347, found 347. Anal. calcd for C<sub>26</sub>H<sub>21</sub>N: C 89.88, H 6.09, N 4.03; Found: C 89.84, H 6.05, N 4.07.

## 2.3. Synthesis of 3,4,5-tris(dodecyloxy)-N-(4-(1,2,2-triphenylvinyl) phenyl)benzamide (**P4**)

To P<sub>4</sub>NH<sub>2</sub> (0.18 g, 0.52 mmol) and 3 (0.42 g, 6 mmol) in THF (50 mL), DMAP (0.01 g) and EDC-HCl (0.01 g) were added. The mixture was stirred for 3 days under an argon atmosphere at room temperature. Excess ethanol was added and the resulting precipitate was collected. Then crystallized from THF and ethanol mixture for 3 times to obtain P4 as a white solid (0.48 g, yield 92.8%). Melting point: ~78 °C (DSC). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 0.89 (t, I = 6.3 Hz, 9 H), 1.20–1.48 (m, 52 H), 1.68–1.93 (m, 8 H), 3.96-4.07 (m, 6 H), 6.96-7.17 (m, 19 H), 7.36 (d, J = 8.4 Hz, 2 H), 7.59 (s, 1 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  (ppm): 165.6, 153.3, 143.8, 141.5, 141.0, 140.4, 140.1, 136.4, 131.5, 130.1, 127.8, 126.7, 126.6, 119.3, 105.8, 73.8, 69.7, 32.3, 30.1, 29.7, 26.5, 23.1, 14.5. FT-IR (KBr) v (cm<sup>-1</sup>): 3306, 2921, 2849, 1640, 1580, 1527, 1497, 1467, 1335, 1233, 1113, 748, 699. MS (EI), m/z: 1004 ([M]<sup>+</sup>, calcd for C<sub>69</sub>H<sub>97</sub>NO<sub>4</sub>, 1004). Anal. calcd for C<sub>69</sub>H<sub>97</sub>NO<sub>4</sub>: C 82.50, H 9.73, N 1.39; Found: C 82.44, H 9.81, N 1.32.

#### 2.4. Synthesis of P<sub>5</sub>NH<sub>2</sub>

**TPE-Br** (2.50 g, 6.08 mmol) and 4-aminophenylboronic acid (1.65 g, 12 mmol) were dissolved in the pure THF (50 mL), then TBAB (0.01 g) and K<sub>2</sub>CO<sub>3</sub> (2 M, aq. soln., 9 mL) were added. The mixture was stirred at room temperature for 0.5 h under argon gas followed by addition of the Pd(PPh<sub>3</sub>)<sub>4</sub> catalyst and then heated to 80 °C for 24 h. The reaction mixture was concentrated and purified by column chromatography on a silica gel column with CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane (1:1 by volume) as eluent to give light yellow crystalline powder **P<sub>5</sub>NH<sub>2</sub>** (2.35 g, 92.5% yield). <sup>1</sup>H NMR (300 MHz, DMSO-d<sub>6</sub>)  $\delta$ (ppm): 5.14–5.24 (s, 2 H); 6.54–6.62 (d, *J* = 8.4 Hz, 2 H); 6.88–7.36 (m, 21 H). MS (EI) calcd for C<sub>32</sub>H<sub>25</sub>N 423, found 423. Anal. calcd for C<sub>32</sub>H<sub>25</sub>N: C 90.74, H 5.95, N 3.31; Found: C 90.71, H 5.92, N 3.35.



Fig. 2. (A) SEM images of THF/water (10/90, v/v) mixture of P5, (B) SEM image of xerogel formed with P5 in ethanol.

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Gelation properties of P4 and P5 in various solver	its.

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Solvent	P4	P5	Solvent	P4	P5
THF	S	S	Dichloromethane	S	S
DMSO	Р	Р	Methanol	Ι	Ι
DMF	S	S	n-Hexane	Р	G (41 °C, 10)
Ethyl acetate	S	S	Cyclohexane	S	G (40 °C, 22)
Tetrachloromethane	S	S	Petroleum ether	Р	G (46 °C, 14)
Chloroform	S	S	Ethanol	G (41 °C, 14)	G (42 °C, 20)

G: stable gel formed at room temperature; S: soluble; I: insoluble; P: precipitate. ( $T_{gel}$ ; CGC, mg/mL, measured at 25 °C).

# 2.5. Synthesis of 3,4,5-tris(dodecyloxy)-N-(4-(1,1,2,2-tetraphenylvinyl)phenyl) benzamide (**P5**)

P<sub>5</sub>NH<sub>2</sub> (0.30 g, 1.01 mmol) and **3** (0.98 g, 14.2 mmol) were dissolved in THF (50 mL), and then EDC-HCl (0.01 g) and DMAP (0.01 g) were added. The solution was stirred at room temperature for 3 days. After removing the solvent under reduced pressure, the residue was crystallized from ethanol to give white crystalline powder **P5** (0.62 g, 81.6% yield). Melting point: 127–129 °C (DSC). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm): 0.89 (t, J = 5.1 Hz, 9 H), 1.16– 1.47 (m, 54 H), 1.70-1.90 (m, 6 H), 3.98-4.09 (m, 6 H), 7.10-7.16 (m, 18 H), 7.31–7.38 (d, J = 8.4 Hz, 2 H), 7.53–7.58 (d, J = 8.7 Hz, 2 H), 7.62–7.57 (d, J = 6.9 Hz, 2 H) 7.72–7.76 (s, 1 H); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz) δ (ppm): 165.7, 153.4, 143.8, 142.8, 141.8, 140.7, 138.2, 137.4, 136.9, 132.0, 131.5, 130.1, 126.7, 126.1, 120.4, 106.1, 73.9, 69.8, 32.3, 30.4, 29.7, 26.4, 23.0, 14.5. FT-IR (KBr) v(cm<sup>-1</sup>): 3306, 2921, 2849, 1640, 1580, 1527, 1497, 1467, 1335, 1233, 1113, 748, 699. MS (EI) calcd for C75H101NO4 1081, found 1081. Anal. calcd for C75H101NO4: C 83.36, H 9.42, N 1.30; Found: C 83.41, H 9.57, N 1.24.

#### 3. Results and discussion

#### 3.1. Synthesis

The target compounds were synthesized according to the routes depicted in Scheme 1. The molecular structure of the target compounds consisted of two parts: the tetraphenylethylene and the 3,4,5-tris(dodecyloxy)benzoic acid moieties. For **P5**, the two moieties were linked by a phenylene unit. The design strategy of the



**Fig. 3.** Temperature-dependent fluorescence spectra of **P5** in ethanol (20 mg/mL, excitation wavelength 365 nm), the insets depict changes in PL peak intensity and emission images of the compound in solution state and gel state under 365 nm UV illumination.



**Fig. 4.** (a) Fluorescence spectra of **P5** in gel state and solution state in *n*-hexane with the same concentration (20 mg/mL); (b) Fluorescence images of **P5** for various temperatures; (c) Repeated switching of photoluminescence between the gel and solution states. Excitation wavelength 365 nm.

amide-substituted 3,4,5-tris(dodecyloxy)benzoic acid molecule, including a hydrogen bonding site and a fluorescent tetraphenylethylene core, is expected to make the molecule display piezofluorochromism. One of the major objectives of this study is to examine the influence of the linker on the properties of the compounds. Their molecular structures were confirmed by <sup>1</sup>H- and <sup>13</sup>C NMR spectroscopy, mass spectrometry, Fourier-transform infrared spectroscopy and elemental analysis.



Fig. 5. Calculated spatial electron distributions of LUMO and HOMO (left), and the optimized structures of the compounds (right).

#### 3.2. AIE properties

The UV-vis absorption and PL emission spectra of the diluted mixtures of these compounds were studied in a mixture of THF/ water with different water fractions to determine whether the compounds possess AIE properties. The compounds are soluble in THF and insoluble in water; thus increasing the water fraction in the mixed solvents changes their existing forms from solution state in the pure THF to aggregated particles in the mixtures with higher water content, leading to changes in their UV-vis and PL spectra [36]. The PL spectra of 10 µM P5 in THF/water mixtures with different water contents are shown in Fig. 1 (the PL spectra for P4 are provided in Supporting Information, SI, Fig. S1). The figure shows that the PL intensity was very weak and essentially did not change as the water fraction of the THF/water mixture increased from 0% to 50%. When the water fraction was >60%, the PL intensity slightly increased with the increase in water fraction up to 80%. A dramatic enhancement in luminescence was observed when the water fraction reached 90%, which was approximately 44 times (P4) and 101 times (P5) higher than that in the pure THF. This result indicated that both compounds exhibited strong AIE activity. The AIE activity may be attributed to its twisted structure, in which multiple phenyl peripheries linked to an ethylene core via Cphenyl-Cethenyl single bonds which enable their free rotation. The molecular size and effect of steric hindrance influence their rotation; a larger molecule should have lower freedom of rotation [37]. The results of their molecular structure analysis showed that when one phenyl ring was induced for P5, the molecular size and steric hindrance were expected to be increased.

The UV-vis absorption spectra of **P4** and **P5** in the THF/water mixtures (10  $\mu$ M) are shown in Fig. S2. The spectra displayed absorption tails extending well into the long wavelength region, indicating that the molecules aggregated into nanoparticles in

the mixtures. The Mie effect of the nanoparticles has been considered to cause such leveling-off of tails in the absorption spectra [36–38]. Therefore, the increase in PL intensity can be attributed to an AIE effect caused by the formation of molecular aggregates, in which the restriction of intramolecular rotations increased the fluorescent emission. The SEM image of **P5** particles obtained from the mixed solution containing 90% volume fractions of water are shown in Fig. 2A (A, prepared by dropping the mixture on the quartz slide and slowly evaporating the solvents), which shows that **P5** forms particles of a few hundred nanometers in size.

#### 3.3. Gelation properties

The gelation behavior of compounds **P4** and **P5** were tested in different solvents, with 2.5% (w/v) as a standard concentration. The results are summarized in Table 1. It can be seen that the gelation ability of compound **P4** was generally weak, since it only gelled in ethanol. By contrast, **P5** can be gelated in several solvents such as ethanol, *n*-hexane, cyclohexane and petroleum ether. The critical gelator concentrations (CGC) of these compounds were tested using the "stable to inversion of a test tube" method [11]. The values of gel—sol transition temperature ( $T_{gel}$ ) were determined by the "falling drop" method [6,39]. The CGC and  $T_{gel}$  data for different solvents of the two compounds are also listed in Table 1. The CGC values were between 10 and 22 mg/mL, whereas the  $T_{gel}$  ranged from 40 °C to 46 °C.

The SEM image of **P5** xerogels obtained from the organogels is shown in Fig. 2B. The xerogels generated the formation of entangled networks consisting of porous aggregates on mica, which facilitate the immobilization of large volumes of solvents within and between the networks, resulting in gelation (Fig. 2B, xerogels prepared by slow evaporation of ethanol from the corresponding organogels).



Fig. 6. DSC curves of compounds P4 and P5.

#### 3.4. Gelation-induced fluorescence-enhanced emission

Gelation-induced fluorescence enhancement was observed for both **P4** and **P5**. The fluorescence properties of **P5** in the gel state and in solution are shown in Fig. 3 as an example (the PL spectra for **P4** are provided in SI, Fig. S3). It was found that **P5** was nonfluorescent under illumination with UV irradiation when heated in the solution state, but the fluorescence intensity increased with

Table 2

Phase-transition temperatures  $T(^{\circ}C)$  and associated enthalpy values  $\Delta$  H (KJ/mol) for compounds P4 and P5.

Compound	Transition temperatures (°C) [ $\Delta H$ (kJ/mol)]				$\Delta T (^{\circ}C)$
	РОМ		DSC		
	$T_{S-LC}^{a}$	T <sub>i</sub> <sup>a</sup>	T <sub>S-LC</sub> <sup>b</sup>	T <sub>i</sub> <sup>b</sup>	
P4	86	130	85 (4.24)	122 (8.37)	44
P5	95	132	99 (2.24)	128 (6.23)	37

 $T_{S-LC}$ : crystalline solid phase to liquid crystalline phase;  $T_i$ : liquid crystalline phase to isotropic phase.

 $\Delta T$ : temperature range of transition from the  $T_{S-LC}$  phase to the isotropic phase by POM.

<sup>a</sup> Obtained from POM.

<sup>b</sup> The peak value of the first heating DSC curve.

the decrease in temperature. In addition, when **P5** forms a gel, its fluorescence intensity is very strong.

The fluorescence of both gel and solution in *n*-hexane with the same concentration was also examined to compare the fluorescence intensity of P5 in the gel state and in the solution (Fig. 4a). The solution of **P5** exhibited rather weak fluorescence: however, its fluorescence intensity increased by almost 120 times after gel formation. The remarkable fluorescence enhancement from the gels was possibly due to the formation of self-assembly aggregates. The organogels were completely thermo-reversible in organic solvents. From the thermoreversible gelation process of P5 gel in *n*-hexane (Fig. 4b), the solution became clear after gentle heating to the higher temperature (to >60 °C). Upon cooling to room temperature, the formation of immobile gels was observed. The fluorescence intensity of the gel can be reversibly modulated with the gel-solution transition through alternate cooling and heating (Fig. 4c). These switchable fluorescent organogels may have potential applications in information storage and optical devices [40–42].

Quantum mechanical computations were conducted using the Gaussian 03 software to study the lowest energy spatial conformation of the compounds [43]. The highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) of these compounds were obtained (Fig. 5) according to the density functional method at the B3LYP/6-31G level after structural optimization. P4 and P5 showed similar electron cloud distributions in either their HOMO or LUMO orbital, which illustrates why P4 and P5 exhibited very close UV and PL spectra. As shown by their optimized structures, the three long alkyl chains expanded freely in space, resulting in relatively larger free volume in the aggregates of the compounds, which facilitates the immobilization of large volumes of solvents that result in gelation. The tetraphenylethylene moiety adopted a twisted spatial conformation, which made the formation of close  $\pi - \pi$  packing difficult for the molecule. Due to the twisted conformation and weaker interactions, the interfaces between the molecules are relatively loose and there exist some defects, which may explain the following piezofluorochromic behavior of these compounds.

#### 3.5. Mesomorphic behavior

The mesomorphic behavior of P4 and P5 were evaluated using differential scanning calorimetry (DSC), hot-stage polarized light microscopy (POM), small-angle X-ray diffraction (SAXD) and wideangle X-ray diffraction (WAXD) equipped with a temperature controller. Fig. 6 shows the first heating, cooling and second heating DSC curves of P4 and P5. Their phase-transition temperatures and associated enthalpy values are given in Table 2. For the first heating curve of **P4**, the lower peak temperature at 85 °C was the transition between crystalline solid phase and liquid crystalline (LC) phase, which was confirmed by POM observation. By being heated above the temperature, the sample exhibited fluidity and color birefringence. The other transition at 122 °C belonged to liquid crystalline phase to isotropic phase transition, whereas the transition at 116 °C was possibly one liquid crystalline phase to the other crystalline phase transition. For P5, the transition between the crystalline solid phase and LC phase was found at 99 °C and the other transition from the LC phase to the isotropic phase at 128 °C. During the cooling process, P4 had three exothermic peaks, namely, peaks at 20, 25 and 74 °C. The second heating curve of P4 showed complicated phase transitions, with peak temperatures at 27, 80, 116 and 122 °C. Thus, the transition at 122 °C was considered as  $T_i$ , indicating that the transition temperatures below 122 °C may exhibit the different LC phase and polycrystalline phase transitions. The second heating curve of P5 showed a significant cold crystallization peak at 85 °C and  $T_i$  at 130 °C.



Fig. 7. Optical micrographs of compounds P4 and P5 between crossed polarizers: liquid crystalline texture for P4 at 100 °C (a) and at 120 °C (b); liquid crystalline texture for P5 at 96 °C (c) and at 128 °C (d).

By being heated above temperature of the solid crystalline phase to the liquid crystalline phase transition, the sample began to flow with color birefringence, suggestive of a liquid, indicating the sample really turned into the liquid crystalline state. The POM observations showed that both P4 and P5 exhibited stable LC phases over a relatively wide temperature range (Table 2). According to the textures obtained during cooling from the isotropic melt and observed by POM (Fig. 7), the mesophases formed from P4 and P5 may belong to the frozen smectic LC phases. It should also be noted that the photomicrographs from POM look unlike those of typical smectic liquid crystals, perhaps they may be disordered crystals formed during cooling of the isotropic melt. The results of DSC and POM studies showed that the characteristics of the phase transitions observed in the DSC curves for both P4 and P5 are consistent with those found by POM observations.

SAXD and variable temperature WAXD measurements provided complementary information on the phase transition and the type of mesophase. The diffraction patterns are shown in Fig. 8. The SAXD patterns (Fig. 8a) showed two diffraction peaks at the  $2\theta$  ranging from 1° to 5°. The WAXD patterns exhibited higher-order reflections at 30 °C, as shown in Fig. 8b. The diffraction peaks decreased and some peaks disappeared with the increase in temperature. When the temperature reached 120 °C, **P4** remained at the LC phase. Two obvious sharp peaks were observed at 5.3° and 10.5°, as well as a diffused broad peak with maximum of about 20°. This observation suggests that the mesophase was probably smectic LC [44].

**P5** exhibited multiple diffraction peaks before the temperature increased to 70 °C, indicating that the compound maintained the LC state below that temperature, as shown in Fig. 8c. When the temperature was increased to 88 °C, which corresponded to the phase transition temperature from the solid phase to the LC phase, the diffraction peak became narrow. The sample transformed from the

LC phase to the amorphous state as the temperature was further increased. The diffraction peak completely disappeared when the temperature reached 100 °C, indicating that **P5** dominated the isotropic state at this temperature.

#### 3.6. Piezofluorochromic properties

The three long alkyl chains in the molecules of **P4** and **P5** expanded freely in space, leading to relatively large volume requirement. In addition, the tetraphenylethylene moiety possesses a twisted spatial conformation. The twisted conformation and the weak  $\pi$ – $\pi$  interactions make the molecular packing relatively loose, resulting in lower lattice energy, which rendered the crystals to be easily destroyed by the planarization of the molecular conformation or slip deformation under external pressure. The release of twist stress and the planarization of molecular conformation may result in increased molecular conjugation, thereby facilitating a red-shift of the PL spectrum, exhibiting piezo-fluorochromic phenomena.

The images of the two compounds taken at room temperature under UV light at different conditions are shown in Fig. 9 (left top). **P4** did not exhibit distinct piezofluorochromic properties. However, with only one more phenyl ring in the linkage than that of **P4**, the luminescence color of **P5** changed from blue to blue-green upon pressing in an IR pellet at 1500 psi for 5 min, and then reverted to blue again upon heating at approximately 70 °C for 0.5 h or exposing to dichloromethane vapor for 5 min, showing clear piezochromic luminescence. When the original and the pressed samples of compounds **P4** and **P5** were heated at the temperatures of their LC state then naturally cooled to room temperature, they all converted into strong blue-green luminescence. To date only a few photofunctional LCs were reported to exhibit an LC phase transition associated with a dynamic change of photoluminescent color during heating [30].



**Fig. 8.** (a) SAXD patterns for **P4** and **P5**; (b) variable-temperature WAXD patterns for **P4**; (c) variable-temperature WAXD patterns for **P5**.

The PL spectra of the samples obtained under different treatment conditions are shown in Fig. 9 (right top). The maximum emission wavelengths of **P4** remained almost unchanged after pressing, with only a 1 nm change. Thus, **P4** had no piezofluorochromic property. However, a significant red shift of about 20 nm was observed in **P5** after pressing. After the pressed samples were annealed and fumed, the initial PL wavelengths were partially





**Fig. 9.** WAXD curves, images under UV light (left top) and normalized PL curves (right top) of **P4** under the different conditions: (a) origin, (b) pressed sample (a), (c) heated sample (b) at 116 °C for 0.5 h, (d) heated sample (a) at 116 °C for 0.5 h. WAXD curves, images under UV light (left top) and normalized PL curves (right top) of **P5** under the different conditions: (A) Original; (B) Pressed sample (A); (C) Annealed sample (B) at 70 °C for 0.5 h; (D) Fumed sample (B) in CH<sub>2</sub>Cl<sub>2</sub> vapor for 5 min; (E) heated sample (A) at 100 °C for 0.5 h.

recovered (shown in Table S1). When the original and pressed samples of **P4** and **P5** were heated at 116 °C (**P4** for 0.5 h) and 100 °C (**P5** for 0.5 h), respectively, and then naturally cooled at room temperature, they exhibited a different degree of red-shift. For **P4**, the original sample showed a 13-nm red shift, whereas the pressed one exhibited a 15-nm red shift. For **P5**, the original sample showed a 32-nm red shift, whereas the pressed one exhibited a 22-nm red shift.

WAXD and DSC measurements were conducted to determine the piezofluorochromism mechanism. The WAXD curves of **P4** and **P5** (Fig. 9) exhibited different structures of molecular aggregation before and after pressing. The diffraction patterns of **P4** before and after pressing displayed sharp and intense reflections, which are indicative of crystalline order. However, when the original and pressed samples were heated at 116 °C for 0.5 h and quenched to room temperature [Fig. 9c for pressed sample and (d) for original sample] it can been found that some of the diffused peaks



Fig. 10. The first heating DSC curves of P4 under the different conditions.

disappeared, and the diffraction peaks almost disappeared [Fig. 9d], indicating an amorphous structure.

Compared with **P4**, the original sample of **P5** showed fewer diffused peaks that indicated low crystalline order. After pressing, **P5** showed a weak, broad and diffused peak that indicated an amorphous structure. However, the diffraction curves of the annealed and fumed samples revealed numerous sharp and intense reflections, indicating the recovery of the crystalline order. Moreover, the diffraction peaks of the original and pressed samples heated at 100 °C for 0.5 h and quenched to room temperature almost disappeared, indicating an amorphous structure. The absence of piezofluorochromic properties of **P4** may be due to the high crystalline order that was difficult to disrupt. These results also suggest that the structural changes in molecular aggregation from the crystalline to the amorphous state can induce significant piezofluorochromic properties and photofunctional liquid crystal properties.

The thermal properties of **P4** and **P5** were then examined by DSC. In the first heating process (Fig. 10), both original and pressed samples of **P4** have three endothermic peaks at 86.2, 116.8 and 122.6 °C, respectively. Compared with the original sample, the high temperature peak (at 122.6 °C) of the pressed sample almost unchanged, however, the two low temperature peaks significantly



**Fig. 11.** (a) The PL spectra of the pressed **P5** sample on different temperature in first heating; (b) the dependence of PL wavelength of the pressed **P5** sample on different temperature.

became smaller. Upon heating the original and pressed samples of **P4** at 116 °C, the peaks at 116 °C and 122 °C changed into one sharp peak, and the lower temperature peak decreased and almost disappeared. For **P5**, after pressing (B) and annealing (C), the low endothermic peak changed from 99 °C to 95 °C. By contrast, the fumed sample (D) exhibited an endothermic peak (at 101 °C,  $T_{m1}$ ) and re-crystallization (at 105 °C,  $T_c$ ) before the isotropic temperature was reached (130 °C,  $T_i$ ). When the original and pressed samples of **P5** were heated at 100 °C, the lower endothermic peak disappeared. These results show that the thermally-induced LC transition from metastable to stable phases was accompanied by a change of the luminescent color.

Temperature-dependent fluorescence spectroscopy was conducted to further explore the PL wavelengths and the intensities of the pressed samples for **P5** at variable temperatures (Fig. 11). From the first heating process, the PL wavelengths and intensities decreased with the increase in temperature (T > 90 °C). When the temperature reached 105 °C, the sample remained in the LC state and exhibited a significant red shift at 504 nm. From 115 °C to 130 °C, the PL wavelengths and intensities again decreased, and then increased with the decrease of temperature. Below 100 °C, the pressed samples exhibited a blue shift similar to that in annealing condition with the increase in temperature. From 100 °C to 105 °C, the pressed sample transformed into the LC state, resulting in an instant red shift, and then the PL wavelengths slightly changed. At



Fig. 12. Time-resolved emission decay curves of P4 and P5 samples under different treatment conditions.

the temperature above 130 °C, the pressed sample went into the isotropic phase with a red shift. During the cooling process and the second heating process, the pressed samples exhibited a blue shift and a red shift with the decrease and increase in temperature, respectively.

The time-resolved emission-decay behavior of these compounds under different conditions was also studied. The timeresolved fluorescence curves and the lifetime data are illustrated

#### Table 3

Solid-state fluorescence lifetime data of  $\mathbf{P4}$  and  $\mathbf{P5}$  samples under different conditions.

	Туре	$\tau_1 (ns)^a$	$\tau_2 (ns)^a$	$A_1^{b}$	$A_2^{b}$	$< \tau > (ns)^{c}$
P4	Original	1.01	2.27	77.79	22.21	1.29
	Pressed	0.99	2.28	70.71	29.29	1.37
	Original-116 °C <sup>d</sup>	1.25	4.81	41.34	58.66	3.34
	Pressed-116 °C <sup>d</sup>	1.21	4.86	34.69	65.31	3.59
P5	Original	0.88	1.99	76.76	23.24	1.13
	Pressed	1.03	2.55	72.90	27.10	1.44
	Annealed	0.98	2.42	72.29	27.71	1.38
	Fumed	0.94	2.17	79.93	20.07	1.19
	Original-100 °C <sup>d</sup>	0.97	3.47	19.68	80.32	2.98
	Pressed-100 °C <sup>d</sup>	1.11	3.44	13.81	86.19	3.12

<sup>a</sup> Fluorescence lifetime.

<sup>b</sup> Fractional contribution.

<sup>c</sup> Weighted mean lifetime.

<sup>d</sup> Annealing at corresponding temperature.

in Fig. 12 and Table 3. In all cases, the emission can fit the double exponential decay. The lifetimes may be correlated to the various ground state aggregates, excimers and charge-transfer dimer emissions [45]. The weighted mean lifetimes  $\langle \tau \rangle$  of the original and pressed samples for P4 were similar, and the time-resolved fluorescence curves were almost coincidental with each other. However, the  $\langle \tau \rangle$  values of the original, pressed, annealed and fumed **P5** samples were significantly different. The pressed samples showed longer lifetimes, and after annealing and fuming, their lifetimes were found to be nearly identical to that of the original sample. When heated to LC phase temperature, the original and pressed samples of P4 and P5 showed longer lifetimes with a significant red shift. Thus, pressing and heating may disrupt the ordered assemblies, generating amorphous regions with increasing the formation probability of excimer or intermolecular chargetransfer state, corresponding to the red shift emission [45].

#### 4. Conclusions

Two new gelation-induced enhanced emission compounds, P4 and P5 based on tetraphenylethylene and gallic acid derivatives, have been designed and synthesized. These compounds exhibit AIE behavior, as indicated by the significant fluorescence enhancement in the aggregated states. Moreover, their fluorescence intensities can be reversibly changed with gel-solution transition by alternate cooling and heating. The POM and DSC studies revealed that both P4 and P5 exhibit mesomorphic properties over a relatively wide temperature range. Furthermore, P5 has significant piezofluorochromic properties due to the crystalline-amorphous phase transformation. To the best of our knowledge, a fluorescenceenhanced organogel with both mesomorphic and piezochromic luminescent properties has not yet been reported in the literature. As the compounds show thermally-induced LC transition from metastable to stable phases accompanied by changes in the luminescent color, they may be potential candidates for external stimuli-responsive materials.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2013.08.026.

#### References

- George S, Ajayaghosh A. Self-assembled nanotapes of oligo(p-phenylene vinylene)s: sol-gel-controlled optical properties in fluorescent p-electronic gels. Chem Eur J 2005;11:3217–27.
- [2] Chung J, An B, Park S. A thermoreversible and proton-induced gel-sol phase transition with remarkable fluorescence variation. Chem Mater 2008;20: 6750–5.
- [3] Shen Y, Li C, Chang K, Chin S, Lin H, Liu Y, et al. Synthesis, optical, and mesomorphic properties of self-assembled organogels featuring phenylethynyl framework with elaborated long-chain pyridine-2,6-dicarboxamides. Langmuir 2009;25:8714–22.

- [4] Yan N, He G, Zhang H, Ding L, Fang Y. Glucose-based fluorescent lowmolecular mass compounds: creation of simple and versatile supramolecular gelators. Langmuir 2010;26:5909–17.
- [5] Chung J, Yoon S, Lim S, An B, Park S. Dual-mode switching in highly fluorescent organogels: binary logic gates with optical/thermal inputs. Angew Chem Int Ed 2009;48:7030–4.
- [6] Zhang P, Wang H, Liu H, Li M. Fluorescence-enhanced organogels and mesomorphic superstructure based on hydrazine derivatives. Langmuir 2010;26:10183–90.
- [7] Wan J, Mao L, Li Y, Li Z, Qiu H, Wang C, et al. Self-assembly of novel fluorescent silole derivatives into different supramolecular aggregates: fibre, liquid crystal and monolayer. Soft Matter 2010;6:3195–201.
- [8] Zhao Z, Lam JWY, Tang B. Self-assembly of organic luminophores with gelation-enhanced emission characteristics. Soft Matter 2013;9:4564–79.
  [9] An B, Lee D, Lee J, Park S, Song H, Park S. Strongly fluorescent organogel
- [9] An B, Lee D, Lee J, Park S, Song H, Park S. Strongly fluorescent organogel system comprising fibrillar self-assembly of a trifluoromethyl-based cyanostilbene derivative. J Am Chem Soc 2004;126:10232–3.
- [10] Tong X, Zhao Y, An B, Park S. Fluorescent liquid-crystal gels with electrically switchable photoluminescence. Adv Funct Mater 2006;16:1799–804.
- [11] Chen P, Lu R, Xue P, Xu T, Chen G, Zhao Y. Emission enhancement and chromism in a salen-based gel system. Langmuir 2009;25:8395–9.
- [12] Zhang X, Chi Z, Li H, Xu B, Li X, Zhou W, et al. Piezofluorochromism of an aggregation-induced emission compound derived from tetraphenylethylene. Chem Asian J 2011;6:808–11.
- [13] Zhang X, Chi Z, Zhou X, Liu S, Zhang Y, Xu J. Influence of carbazolyl groups on properties of piezofluorochromic aggregation-enhanced emission compounds containing distyrylanthracene. J Phys Chem C 2012;116: 23629–38.
- [14] Li H, Zhang X, Chi Z, Xu B, Zhou W, Liu S, et al. New thermally stable piezofluorochromic aggregation-induced emission compounds. Org Lett 2011;13: 556–9.
- [15] Li H, Chi Z, Xu B, Zhang X, Li X, Liu S, et al. Aggregation-induced emission enhancement compounds containing triphenylamine-anthrylenevinylene and tetraphenylethene moieties. J Mater Chem 2011;21:3760–7.
- [16] Zhang X, Chi Z, Zhang J, Li H, Xu B, Li X, et al. Piezofluorochromic properties and mechanism of an aggregation-induced emission enhancement compound containing N-hexyl-phenothiazine and anthracene moieties. J Phys Chem B 2011;115:7606–11.
- [17] Zhou X, Li H, Chi Z, Zhang X, Zhang J, Xu B, et al. Piezofluorochromism and morphology of a new aggregation-induced emission compound derived from tetraphenylethylene and carbazole. New J Chem 2012;36:685–93.
- [18] Xu B, Chi Z, Zhang X, Li H, Chen C, Liu S, et al. A new ligand and its complex with multi-stimuli-responsive and aggregation-induced emission effects. Chem Commun 2011;47:11080–2.
- [19] Zhang X, Chi Z, Xu B, Chen C, Zhou X, Zhang Y, et al. End-group effects of piezofluorochromic aggregation-induced enhanced emission compounds containing distyrylanthracene. J Mater Chem 2012;22:18505–13.
- [20] Chi Z, Zhang X, Xu B, Zhou X, Ma C, Zhang Y, et al. Recent advances in organic mechanofluorochromic materials. Chem Soc Rev 2012;41:3878–96.
- [21] Dong Y, Xu B, Zhang J, Tan X, Wang L, Chen J, et al. Piezochromic luminescence based on the molecular aggregation of 9,10-bis((E)-2-(pyrid-2-yl)vinyl) anthracene. Angew Chem Int Ed 2012;51:10782–5.
- [22] Luo X, Li J, Li C, Heng L, Dong Y, Liu Z, et al. Reversible switching of the emission of diphenyldibenzofulvenes by thermal and mechanical stimuli. Adv Mater 2011;23:3261–5.
- [23] Wang J, Mei J, Hu R, Sun J, Qin A, Tang B. Click synthesis, aggregation-induced emission, *E/Z* isomerization, self-organization, and multiple chromisms of pure stereoisomers of a tetraphenylethene-cored luminogen. J Am Chem Soc 2012;134:9956–66.
- [24] Zhang X, Chi Z, Xu B, Jiang L, Zhou X, Zhang Y, et al. Multifunctional organic fluorescent materials derived from 9,10-distyrylanthracene with alkoxyl endgroups of various lengths. Chem Commun 2012;48:10895–7.

- [25] Chi Z, He K, Li H, Zhang X, Xu B, Liu S, et al. Synthesis and properties of a dicarbazolyl tetraphenylethylene multi-functional luminophor. Chem J Chin Univ 2012;33:725–31.
- [26] Liu T, Chien A, Lu J, Zhang G, Fraser C. Arene effects on difluoroboron βdiketonate mechanochromic luminescence. J Mater Chem 2011;21:8401–8.
- [27] Sagara Y, Mutai T, Yoshikawa I, Araki K. Material design for piezochromic luminescence: hydrogen-bond-directed assemblies of a pyrene derivative. J Am Chem Soc 2007;129:1520–1.
- [28] Nguyen N, Zhang G, Lu J, Shermana A, Fraser C. Alkyl chain length effects on solid-state difluoroboron β-diketonate mechanochromic luminescence. [ Mater Chem 2011;21:8409–15.
- [29] Ooyama Y, Kagawa Y, Fukuoka H, Ito G, Harima Y. Mechanofluorochromism of a series of benzofuro[2,3-c]oxazolo[4,5-a]-carbazole-type fluorescent dyes. Eur J Org Chem 2009:5321-6.
- [30] Sagara Y, Yamane S, Mutai T, Araki K, Kato T. A stimuli-responsive, photoluminescent, anthracene-based liquid crystal: emission color determined by thermal and mechanical processes. Adv Funct Mater 2009;19:1869–75.
- [31] Sagara Y, Kato T. Stimuli-responsive luminescent liquid crystals: change of photoluminescent colors triggered by a shear-induced phase transition. Angew Chem Int Ed 2008;47:5175–8.
- [32] Yamane S, Sagara Y, Kato T. A thermoresponsive photoluminescent smectic liquid crystal: change of photoluminescent color on the smectic-smectic phase transition. Chem Commun 2009:3597–9.
- [33] Shi J, Chang N, Li C, Mei J, Deng C, Luo X, et al. Locking the phenyl rings of tetraphenylethene step by step: understanding the mechanism of aggregation-induced emission. Chem Commun 2012;48:10675–7.
- [34] Luo X, Zhao W, Shi J, Li C, Liu Z, Bo Z, et al. Reversible switching emissions of tetraphenylethene derivatives among multiple colors with solvent vapor, mechanical, and thermal stimuli. J Phys Chem C 2012;116:21967–72.
- [35] Dou C, Chen D, Iqbal J, Yuan Y, Zhang H, Wang Y. Multistimuli-responsive benzothiadiazole-cored phenylene vinylene derivative with nanoassembly properties. Langmuir 2011;27:6323–9.
- [36] Seo S, Tew G, Chang J. Lyotropic columnar liquid crystals based on polycatenar 1H-imidazole amphiphiles and their assembly into bundles at the surface of silicon. Soft Matter 2006;2:886–91.
- [37] Zhang X, Chi Z, Xu B, Li H, Yang Z, Li X, et al. Synthesis of blue light emitting bis(triphenylethylene) derivatives: a case of aggregation-induced emission enhancement. Dyes Pigm 2011;89:56–62.
- [38] Xu B, Chi Z, Zhang J, Zhang X, Li H, Li X, et al. Piezofluorochromic and aggregation-induced-emission compounds containing triphenylethylene and tetraphenylethylene moieties. Chem Asian J 2011;6:1470–8.
- [39] Zhang X, Chi Z, Li H, Xu B, Li X, Liu S, et al. Synthesis and properties of novel aggregation-induced emission compounds with combined tetraphenylethylene and dicarbazolyl triphenylethylene moieties. J Mater Chem 2011;21: 1788–96.
- [40] Tang B, Geng Y, Lam J, Li B, Jing X, Wang X, et al. Processible nanostructured materials with electrical conductivity and magnetic susceptibility: preparation and properties of maghemite/polyaniline nanocomposite films. Chem Mater 1999;11:1581–9.
- [41] Abdallah D, Weiss R. n-Alkanes gel n-alkanes and many other organic liquids. Langmuir 2000;16:352–5.
- [42] Wang M, Zhang D, Zhang G, Zhu D. Fluorescence enhancement upon gelation and thermally-driven fluorescence switches based on tetraphenylsilole-based organic gelators. Chem Phys Lett 2009;475:64–7.
- [43] Frisch M, Trucks G, Schlegel H. Gaussian 03. Revision D.01. Wallingford CT: Gaussian, Inc; 2004.
- [44] Yao D, Zhang B, Zhang W, Tian M. A new class of star-shaped cholesteric liquid crystal containing a 1,3,5-trihydroxybenzene unit as a core. J Mol Struct 2008;881:83–9.
- [45] Zhang G, Singer J, Kooi S, Evans R, Thomas E, Fraser C. Reversible solid-state mechanochromic fluorescence from a boron lipid dye. J Mater Chem 2011;21:8295–9.