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Novel AIE columnar liquid crystals: the influence of the number of diphenylacrylonitrile groups on the mesomorphic and fluorescence properties†

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The novel triphenylene derivatives with one, two or three diphenylacrylonitrile groups on the side chain were prepared in yields of 75–83%. The influence of the number of diphenylacrylonitrile groups on the mesophase and fluorescence properties were investigated. The triphenylene derivatives with one or two diphenylacrylonitrile groups exhibited not only the ordered hexagonal columnar mesophase but also good AIE fluorescence properties in both solution and solid state.

Columnar discotic liquid crystals, possessing the unique cores with π - π stacking structures, have attracted much commercial and academic research interest over the years.¹ They were high ordered columnar mesophases with fast charge carrier mobility, exhibiting application prospects in various fields such as organic field-effect transistors, organic light-emitting diodes, organic photovoltaic cells, gas sensors, and so on.^{2–5} Recently, columnar luminescent liquid crystals have been paid considerable attention due to their effective combination of an intrinsic luminescence capability, the supramolecular organization and self-healing characteristic within a mesophase.^{6,7} For example, by using perylene or Bodipy as aromatic conjugated core,^{8–20} the luminescent liquid crystals could be constructed conveniently. However, although most of reported luminescent liquid crystals showed high fluorescence in solution, they could not emit fluorescence effectively in solid-state due to the aggregation caused quenching (ACQ) effect. Thus, various molecular designs were applied to avoid the ACQ effect,^{21,22} but often enhanced the expense of ordered molecular packing, making the synthesis of light-emitting liquid crystalline material a difficult task.

Recently, Tang's group discovered the aggregation-induced emission (AIE) effect, which implied the aggregation could enhance the light emission.^{23–25} Obviously, introduction of AIE-active dye into liquid crystal is a good strategy to solve the above problem. Thus, some liquid crystalline molecules with AIE effect were designed and synthesized by grafting the long alkyl chains on AIE molecules such as diphenylacrylonitrile and

tetraphenylethene.^{26–37} However, most reported AIE liquid crystals were smectic or nematic mesophases, and only one columnar AIE liquid crystal was obtained by mixing tetraphenylethene–triphenylene oligomer with 2,4,7-trinitrofluorenone.³⁷ These AIE liquid crystals were difficult to form columnar mesophase although they usually possessed highly symmetric structures containing a rigid aromatic core with several soft side-chains. The reason might be attributed to that the conjugated aromatic rings of AIE molecules are not the complete coplanar structures, which are against effective π - π packing in column. Based on this speculation, it could be deduced that the columnar AIE liquid crystal could be prepared by using normal discotic coplanar aromatic structure as core which was favourable for columnar mesophase, and controlling the numbers of AIE groups on side chain to avoid the destruction of columnar mesophase. But no paper concerned on this study up to now. In order to confirm this speculation, in this paper, three novel triphenylene liquid crystals with multiple diphenylacrylonitrile groups were designed and synthesized. Moreover, the influences of the numbers of diphenylacrylonitrile groups on mesomorphic and fluorescence properties were investigated. The experimental results confirmed the above speculation that the mesomorphic and fluorescence properties were influenced greatly by the numbers of AIE groups on side chains. The triphenylene liquid crystals with one or two diphenylacrylonitrile groups exhibited not only good AIE-luminescence property but also ordered hexagonal columnar mesophase.

It is well known that the monohydroxytriphenylene was a convenient platform to construct various triphenylene liquid crystals with good columnar mesophase.^{38–47} On the other hand, the excellent AIE-fluorescence property of diphenylacrylonitrile had been reported extensively.^{23–25} Thus, by using monohydroxytriphenylene and diphenylacrylonitrile as building blocks, the triphenylene derivatives with one, two or three

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Table 1 Transition temperatures (°C) and enthalpy changes (kJ mol⁻¹) of samples **9**, **10** and **11**

Compd.	Phase transition ^a	Heating scan $T(\Delta H)$	Cooling scan $T(\Delta H)$
9	Cr-Col	43.7(10.1)	39.7(13.2)
	Col-Iso	129.2(21.5)	123.1(5.6)
10	Cr-Col	51.7(11.3)	40.2(15.6)
	LC-Iso	117.2(18.6)	113.2(12.8)
11	Cr-Iso	59.8(22.4)	57.2(24.7)

^a Cr = crystalline, Col = columnar mesophase, Iso = isotropic.

sample **10** with two diphenylacrylonitrile group (65.5 °C). Three diphenylacrylonitrile groups on triphenylene derivative **11** destroyed the mesomorphic properties completely. These results suggested that, based on the strong columnar-induced packing capability of triphenylene unit, the triphenylene derivatives with one or two diphenylacrylonitrile groups still possessed the columnar mesophase.

Under the POM observation, sample **11** exhibited the Cr-Iso phase transition upon heating and cooling, and no mesophase was observed. However, compounds **9** and **10** showed the Cr-Col and Col-Iso phase transition at the approximate temperatures of DSC curves. As slowly cooling from isotropic phase, the liquid crystalline textures formed gradually. The corresponding textures for samples **9** and **10** at 70 °C were illustrated in Fig. 2. One can see that these textures were the pseudo-confocal conic ones, indicating the columnar liquid crystals for samples **9** and **10**.

Moreover, the XRD analysis was employed to study the columnar stacking behaviors of mesophase of compounds **9** and **10**. Their corresponding XRD traces at 70 °C were exhibited in Fig. 3. In the small-angle region, both samples **9** and **10** showed the three peaks at 4.77°, 8.27°, 9.55° and 4.72°, 8.18°, 9.45°, respectively. Based on these reflections, the *d*-spacings calculated by formula $d = \lambda/(2 \sin \theta)$ were 18.51 Å, 10.68 Å and 9.25 Å for compound **9** and 18.70 Å, 10.80 Å and 9.35 Å for compound **10**, respectively. These data were in agreement with the ratio of 1 : 1/√3 : 1/√4 for (100), (110) and (200) reflections of hexagonal columnar mesophase. Also, the lattice parameter (α) for compounds **9** and **10** could be calculated as 21.36 Å and 20.60 Å based on the strong [100] reflections of column phase. In their wide-angle regions, the broad halos at 15–25° indicated the distances of 3.6–5.9 Å approximately, which could be

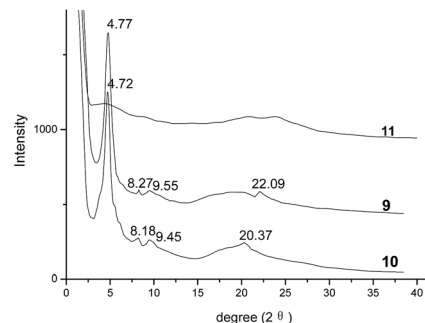


Fig. 3 XRD traces of compounds **9**, **10** and **11** measured at 70 °C.

attributed to the reflections of very short correlation length of the molten alkyl chains. The weak reflections at 22.09° for sample **9** and 20.37° for sample **10**, suggesting the spacings of 4.02 Å and 4.36 Å, could be assigned for the typical characteristic of π - π interaction for the intracolumnar distance of columnar liquid crystals. Thus, all these data in small- and wide-angle region implied the hexagonal columnar mesophase for compounds **9** and **10**. On the other hand, compound **11** showed no obvious peak, indicating it had been melted at 70 °C without mesophase, which were in accordance with the analysis of DSC and POM. All these XRD analyses supported that, although one or two diphenylacrylonitrile groups were introduced on the side-chains of triphenylene derivatives **9** and **10**, they still maintained the ordered hexagonal columnar mesophase based on the strong columnar-induced mesophase of triphenylene unit as expected.

On the other hand, due to one, two or three AIE active groups of diphenylacrylonitrile grafted onto the triphenylene derivatives **9**, **10** and **11**, respectively, it was interesting to investigate the influences of the numbers of diphenylacrylonitrile groups on absorption spectra and fluorescence properties. The absorption spectra of compounds **9**, **10** and **11** were depicted in Fig. 4. All of them showed very similar absorption profiles with three obvious peaks at 235 nm, 277 nm and 320 nm. But the peaks at 320 nm exhibited different absorbance. These results were in accordance with their structures. The similar absorption profiles were attributed to their similar functional structures. The different absorbance at 320 nm were ascribed to the

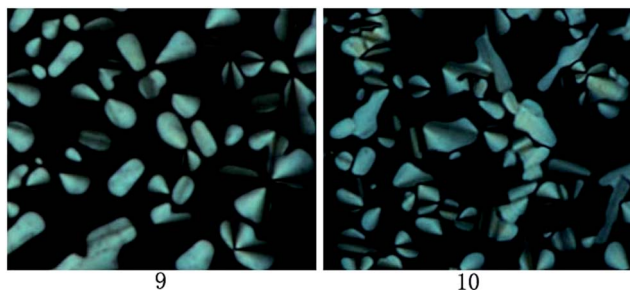


Fig. 2 The textures of compounds **9** and **10** under POM on cooling at 70 °C (×400).

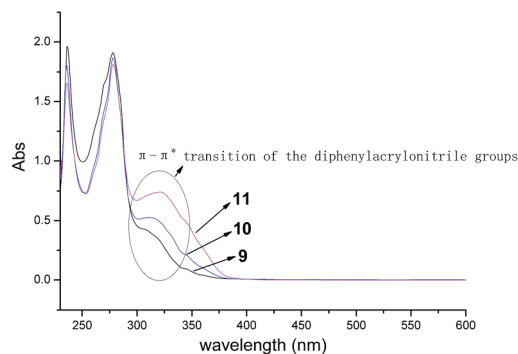


Fig. 4 The UV-vis absorption spectra of samples **9**, **10** and **11** in THF solution.



π - π^* transition of the different numbers of diphenylacrylonitrile groups. The more diphenylacrylonitrile groups resulted in the stronger absorbance at 320 nm.

As diphenylacrylonitrile was a well-known AIE luminogen, the fluorescence (FL) spectra of samples **9**, **10** and **11** in THF solution and THF/H₂O mixture were measured to investigate the influences of the numbers of diphenylacrylonitrile groups on fluorescence properties. The fluorescence spectra of samples **9**, **10** and **11** in THF/H₂O mixture with different fractions of H₂O and their corresponding plot of values (I/I_0) versus the fractions of the aqueous mixtures were exhibited in Fig. 5. It can be seen that, in pure THF solution, all of them showed weak fluorescence emission. With the addition of H₂O in THF solution, however, the fluorescence emission increased gradually. The increases of intensity were slow at low water fractions (<40%) but became very remarkable afterward. The strongest fluorescence emissions were in the solution of THF/H₂O mixtures with 60% of H₂O for **10** and 70% of H₂O for **9** and **11**. These results certainly suggested that compounds **9**, **10** and **11** possessed the AIE fluorescence properties as expected. Due to the low solubility resulting in the precipitation, the fluorescence intensities decreased at high water fractions (>60% for **10** and >70% for **9**

and **11**). This other possibility for these phenomena, such as crystalline-induced emission, could be excluded by the XRD analysis which suggested the amorphous state for the precipitation (Fig. S22[†]). Moreover, by comparing the fluorescence intensities and I/I_0 values of samples **9**, **10** and **11**, it can be seen that the fluorescence intensities in pure THF solution showed the order of **9** < **10** < **11**. But their strongest fluorescence intensities in mixture solutions and their I/I_0 values presented the inverse order of **9** > **10** > **11**. These phenomena might be explained by their structures. Due to samples **9**, **10** and **11** had good solubility and little aggregate in pure THF solution, the more diphenylacrylonitrile groups led to the stronger fluorescence intensity, resulted in the order of **9** < **10** < **11** for the fluorescence intensities of samples **9**, **10** and **11** with one, two and three diphenylacrylonitrile groups, respectively. On the other hand, the literatures had revealed that the J-aggregate for diphenylacrylonitrile derivatives increased the fluorescence intensity but the H-aggregate might decrease the fluorescence intensity due to the strong π - π^* interaction.^{48–51} The sample **9** with one diphenylacrylonitrile group preferred to J-aggregate in mixture solutions, enhancing the fluorescence intensity greatly by 24 times. However, due to the two or three diphenylacrylonitrile groups grafted onto the closed *o*-position of one aromatic ring in samples **10** and **11**, the diphenylacrylonitrile groups might be more easily to form the H-aggregate in mixture solutions than sample **9**, suggesting that samples **10** and **11** might possess not only J-aggregate but also H-aggregate in a certain degree. The existence of some H-aggregate for samples **10** and **11** decreased fluorescence intensity, although the strong J-aggregate for samples **10** and **11** still enhanced their fluorescence intensities. The H-aggregate was also confirmed by some blue shift for UV absorption maximum with the increase of water fractions in the solution of THF/H₂O mixtures (Fig. S23[†]). Thus, although samples **10** and **11** possessed two or three diphenylacrylonitrile groups, their highest fluorescence intensities and maximum I/I_0 values in mixture solutions were smaller than that of sample **9**. Moreover, the fluorescence peaks of samples **9**, **10** and **11** in mixture solutions exhibited obvious red shifts in comparison with that in pure THF solutions. The values for red shift were 45 nm, 51 nm and 70 nm for samples **9**, **10** and **11**, respectively. The fluorescence red-shift order of **9** < **10** < **11** might also suggest the existence of some H-aggregates for samples **10** and **11** because the stronger π - π^* interaction of the H-aggregate led to the larger red shift than that of J-aggregate. On the other hand, the fluorescence quantum yield (Φ_F) of samples **9**, **10** and **11** in solid state were investigated as 15.9%, 7.5% and 5.6%, respectively. These data revealed that compounds **9**, **10** and **11** possessed the middle fluorescence emission in solid state, although some H-aggregate for samples **10** and **11** resulting in the order of **9** < **10** < **11**. Combining all these photophysical analysis, it could be summarized that the triphenylene derivatives **9**, **10** and **11** with one, two or three diphenylacrylonitrile groups had good AIE fluorescence properties. The largest I/I_0 values of fluorescence in THF/H₂O solution attained 24 times and the highest Φ_F in solid state achieved 15.9% for compound **9**. The numbers of diphenylacrylonitrile groups had important influence on the fluorescence properties.

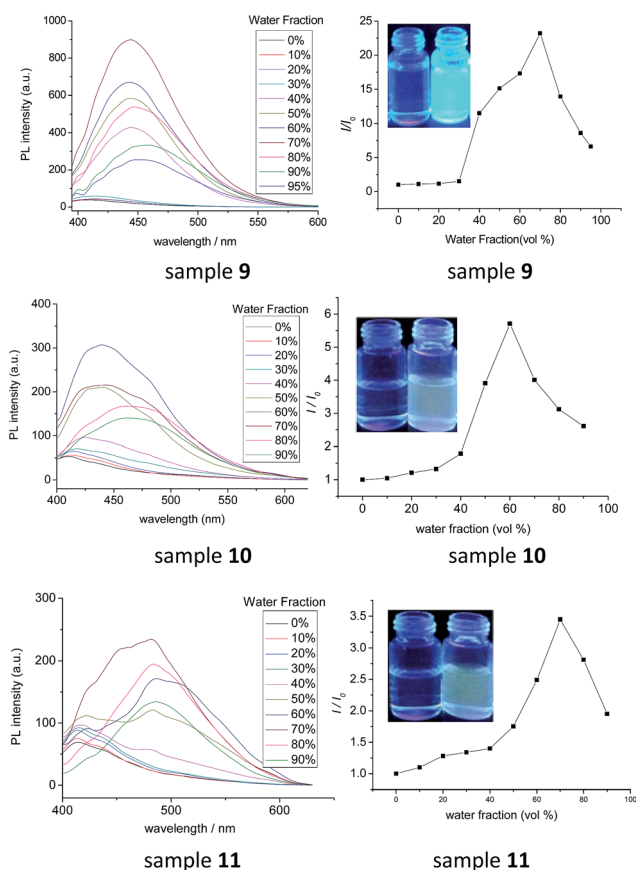


Fig. 5 (left) Fluorescence spectra of samples **9**, **10** and **11** with different fractions of H₂O in THF/H₂O mixtures (1.0×10^{-5} M, $\lambda_{\text{ex}} = 364$ nm). (right) Plot of values (I/I_0) versus the fractions of the aqueous mixtures. I_0 = emission intensity in pure THF solution. The inset graph was fluorescence pictures of samples in THF solution and 10/90 THF/H₂O mixture under UV light.



The multiple diphenylacrylonitrile groups exhibited both the strong AIE fluorescence properties based on the J-aggregate, and weak ACQ effect due to some H-aggregate of multiple diphenylacrylonitrile groups on the closed *o*-position of one aromatic ring. This kind of novel luminescent LC showed both excellent light-emitting property and ordered columnar mesophase, which exhibited potential application as novel fluorescent liquid crystalline functional materials in liquid crystal display and opto-electronic devices, such as novel organic light-emitting diodes and sensors, etc.

Conclusions

In summary, three novel triphenylene derivatives with one, two or three diphenylacrylonitrile groups on the side chain were designed and synthesized by the Schiff-based condensation in yields of 75–83%. The studies on mesomorphic property revealed that triphenylene derivatives with one or two diphenylacrylonitrile groups exhibited the ordered hexagonal columnar mesophase, but the one with three diphenylacrylonitrile groups showed no mesophase. The photophysical experiments suggested that all of them had good AIE fluorescence properties. The largest fluorescence I/I_0 values were 24 times and the highest Φ_F in solid state were 15.9% for triphenylene derivative with one diphenylacrylonitrile group. The AIE properties presented the order of **9** > **10** > **11** due to the multiple diphenylacrylonitrile groups exhibited both the strong AIE fluorescence properties and weak ACQ effect. This research confirmed that the columnar AIE liquid crystal could be prepared by using normal discotic coplanar aromatic structure as core and controlling the number of AIE groups on side chain, which is a new strategy to design and synthesis of the novel AIE columnar liquid crystals.

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