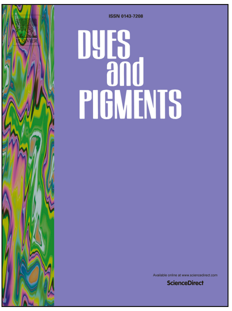

Novel fluorescent perylene liquid crystal with diphenylacrylonitrile groups: Observation of a large pseudo stokes shift based on AIE and FRET effects

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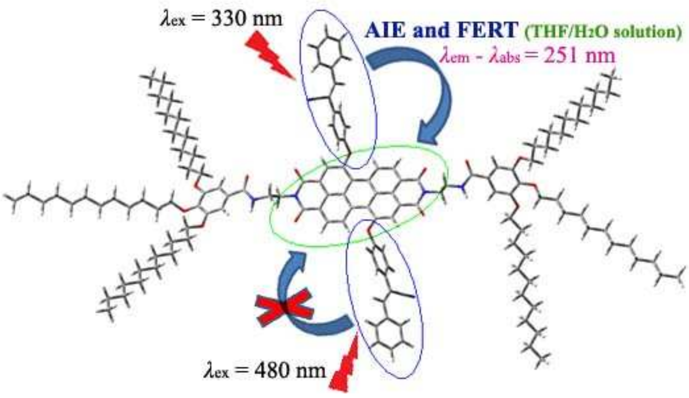

The novel *perylene liquid crystal bearing diphenylacrylonitrile groups exhibited the hexagonal columnar mesophase and good fluorescence in THF/*H_2O *mixtures based on AIE and FRET effect.*

Novel fluorescent perylene liquid crystal with diphenylacrylonitrile groups: Observation of a large pseudo Stokes shift based on AIE and FRET effects

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A novel perylene liquid crystal with diphenylacrylonitrile groups on 1,7-bay positions was synthesized in high yield. This highly decorated perylene bisimide showed the ordered hexagonal columnar liquid crystalline behaviour between 124.9 and 189.5 °C. Upon excitation of 480 nm, an attenuation of fluorescent intensity was observed with the increase of water fraction in THF/H_2O mixtures. However, the fluorescence intensity enhanced dramatically and attained a maximum value at water fraction of 40% in THF/H_2O systems when excited at 330 nm. The fluorescence intensity increased by 10 times and the pseudo Stokes shift achieved 251 nm. These phenomena were well elucidated by the AIE and FRET effect, which were supported by the investigation of fluorescence quantum yield and fluorescence lifetime.

Keywords: Perylene; Diphenylacrylonitrile; Fluorescence resonance energy transfer; Aggregation-induced emission; Mesophase

1. Introduction

Perylene bisimides (PBIs) are important organic dyes with excellent photoluminescence, which exhibit promising applications in fluorescent emitters and biosensors, organic light harvesting systems, organic electronic devices and self-assembling nanostructures [1-5]. In order to prepare the high ordered PBI materials [6, 7], the thermotropic PBI liquid crystals (LC) were paid much attention due to their excellent supramolecular self-assembling abilities [8, 9]. Up to now, various PBI liquid crystals, of which the imide groups were modified by siloxane [10, 11], organosilica [12, 13], dendritic peptides [14], alkoxyl or alkyl groups [15, 16, 17, 18, 19, 20], ester-bridging chains [21], cholesterol groups [22, 23], and triphenylene groups [24-28], were synthesized and exhibited interesting mesomorphic properties. However, these studies implied that, although the mesomorphic properties were tuned effectively by the structures of the substituents on imide positions, the fluorescent properties were difficult to be improved due to their same perylene skeleton. Moreover, their small Stokes shifts (20-30nm) and the strong π-π interaction in the polar solvents usually resulted in re-absorption, self-quenching or aggregation-caused quenching (ACQ) effect [29, 30]. Thus, the study on perylene liquid crystal with both good liquid crystalline property and unique photophysical property is still challenging task.

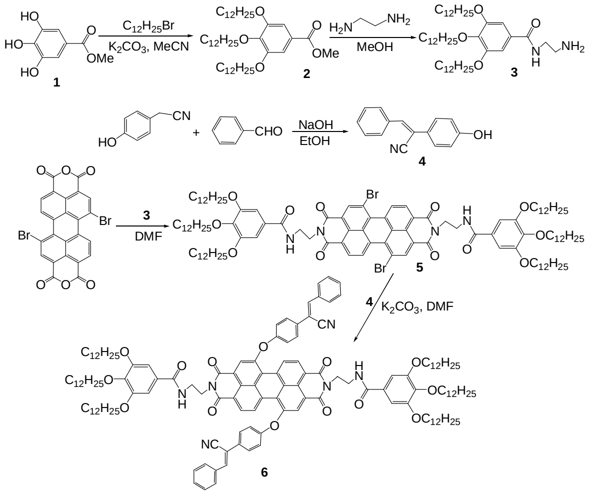
In order to avoid the re-absorption of small Stokes shift, some perylene derivatives with large Stokes shifts were prepared by enlarging the perylene conjugated system. But the syntheses were complicated in most cases [31-33]. Recently, the technique of fluorescence resonance energy transfer (FRET) provided an effective solution by the formation of a large Stokes shift based on the substantial overlap between emission of donor and absorption of acceptor [34-37]. But this strategy has not been applied for preparing perylene liquid crystal with large Stokes shifts. On the other hand, Tang's group reported the aggregation-induced emission (AIE) effect recently [30, 38, 39]. Based on this strategy, the ACQ effect of perylene bisimides was avoided successfully by introducing tetraphenylethene onto bay positions of perylene [41, 42]. This strategy had been also applied in preparing the liquid crystalline molecules by using AIE-active units such as tetraphenylethene and diphenylacrylonitrile as rigid cores [43-50]. However, as to perylene liquid crystal, no AIE-active perylene liquid crystal with good fluorescence was reported. Therefore, the design and synthesis of perylene liquid crystal with large Stokes shift based on AIE and FRET effect remains unknown. In this paper, by introducing two AIE-active diphenylacrylonitrile groups onto the 1,7-bay positions of perylene bisimides, the first AIE-active diphenylacrylonitrile-modified perylene liquid crystal was conveniently obtained. This perylene derivative not only exhibited stable columnar liquid crystalline behavior but also showed strong fluorescence with large pseudo Stokes shift in polar solution. The FRET phenomenon and AIE effect were observed for perylene liquid crystal for the first time, indicating that AIE and the FRET effect are good strategy for design and synthesis of novel perylene liquid crystal with unique photophysical property.

2. Experimental

2.1 General

All chemical reagents were purchased from Aladdin Co. Ltd and used directly. The other organic solvents were treated with purification according to standard process before use. Column chromatography was done by using silica gel (200-300 mesh) as adsorbent. NMR spectra were obtained in $CDCl_3$ on a Bruker-ARX 400 instrument at 26^{o}C. Chemical shifts were recorded in ppm with tetramethylsilane (TMS) as internal standard. MS spectra were carried out on Bruker mass spectrometer. UV-Vis spectra were performed on Varian spectrometer. Fluorescence spectra were obtained in a conventional quartz cell (10×10×45 mm) at 25^{o}C on a Hitachi F-4500 spectrophotometer. The excitation and emission slits were 10 nm wide. The fluorescence absolute Φ_F values and fluorescence lifetime were investigated on FLS920 Fluorescence Spectrometer with a 6-inch integrating sphere.

POM (Leica DMRX) was done on a hot stage (Linkam THMSE 600) to confirm phase transitions. Thermal analysis of the materials was performed by DSC (Thermal Analysis Q100) with the scanning rate of 10^{o}C/min under N_2 atmosphere. XRD experiments were done on SEIFERT-FPM (XRD7). Compounds **2** and **3** were prepared according to the literature method [20]. Compound **4** was synthesized by the reported procedure [49]. Compound **5** was obtained according to the published method [17].



Scheme 1 The synthetic route of perylene liquid crystal **6** with diphenylacrylonitrile group on bay-positions

*2.2. Synthesis of target compound **6***

Under N_2 atmosphere, the mixture of compound **5** (0.195g, 0.1 mmol), compound **4** (0.066g, 0.3 mmol) and anhydrous K_2CO_3 (0.050g, 0.036mmol) were stirred in DMF solution (30 mL) at 100^{o}C for 24 h. This reaction was monitored by TLC, indicating the disappearance of compound **5** in 24 h. After reaction completion, HCl solution (1M, 60 mL) was poured in reaction system, and the solution was extracted of $CHCl_3$ (50 mL). The organic layer was separated, washed by brine solution and dried over anhydrous $MgSO_4$, and filtrated and concentrated. The residue was purified by column chromatography (DCM/ethyl acetate (6/1, v/v) as eluent). The compound **6** was then collected as red purple solid in the yield of 70%. Compound **6**: FT-IR(KBr), v/cm^{-1}: 2923. 2852, 1697, 1660, 1594, 1500, 1340, 1262, 1227, 1116; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 9.50 (d, J = 8.0 Hz, 2H, ArH), 8.61(d, J = 8.0 Hz, 2H, ArH), 8.34(s, 2H, ArH), 8.03 (bs, 2H, NH), 7.93(d, J = 8.0 Hz, 4H, ArH), 7.78(d, J = 8.0 Hz, 4H, ArH), 7.59(s, 2H, C=CH), 7.45-7.52 (m, 6H, ArH), 7.21(d, J = 8.0 Hz, 4H, ArH), 6.93(s, 4H, ArH), 4.50 (bs, 4H, NCH_2), 3.80-3.99(m, 16H, OCH_2 and NCH_2), 1.18-1.85(m, 120H, CH_2), 0.87(t, J = 8.0Hz, 18H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$) δppm: 167.55, 164.02, 163.10, 155.66, 154.30, 152.81, 142.46, 140.62, 133.55, 133.33, 131.63, 130.78, 129.90, 129.20, 129.02, 128.94, 125.38, 124.73, 124.36, 123.76, 122.00, 119.45, 117.62, 116.81, 110.27, 105.27, 73.42, 69.05, 39.43, 35.43, 30.32, 29.74, 29.69, 29.45, 29.39, 29.34, 26.08, 22.71, 14.14; MALDI-TOF-MS Calcd.for m/z = 2268.4, found: m/z = 2269.9 (MK^+). HR-MS (ESI) ($C_{144}H_{190}N_6O_{14}$) $[M]^+$: Calcd.: 2228.4368. found: 2228.4368.

3. Results and discussion

3.1. Synthesis and characterization

The previous literatures has shown that the multiple alkyl chains (6 chains usually) on imides positions of perylene were favourable for columnar perylene liqud crystals [17-20]. And the introduction of functional groups on bay-positions improved the photophysical properties based on the conjugated and sterically hindered effect for perylene skeleton [47-49]. On the other hand, the diphenylacrylonitrile moiety had shown a strong AIE effect [30, 38, 39], and its emission band is overlapped with the absorption band of perylene, which is favourable for FRET effect. Thus, the target molecule was designed as compound **6**, in which the six chains located at the amide positions ensured the columnar mesophase and the two diphenylacrylonitrile units on bay positions would produce novel photophysical properties based on AIE and FRET effect. The synthetic route to the new molecules **6** is depicted in Scheme 1. According to the published procedure [20], gallic ether derivative **2** with three alkyl chains was synthesized by treating methyl gallate **1** with bromodecane in yield of 80%. Subsequently, compound **2** was converted to compound **3** by reacting compound **2** with excess ethylenediamine in yield of 86%. By refluxing compound **3** with 1,7-dibrominated perylene bisanhydride in formdimethylamide (DMF) at 110^{0}C for 12 h, the perylene bisimides **5** was collected after column chromatography in 50% yield [17]. On the other hand, the diphenylacrylonitrile derivative **4** was prepared by condensating 4-hydroxyphenylacetonitrile with benzaldehyde. As reactants **4** and **5** were prepared, compound **6** was prepared by further treating **4** and **5** in K_2CO_3/DMF system at 100^{o}C for 24 h. The yield was 70% after column chromatography. The structure of new perylene derivative **6** was confirmed by IR spectrum, NMR spectrum, and high-resolution mass spectral analysis. The molecular ion peak appeared at 2228.4368 in HR-MS spectrum, which was exactly in accordance with the molecular weight of compound **6**. In the ^{1}H NMR spectrum of compound **6**, the proton NMR signals agreed well with the proposed structure (see SI). The signals in ^{13}C NMR spectrum also supported the structure of compound **6**. This novel perylene derivative possesses good solubility in a wide range of organic solvents (such as $CHCl_3$, toluene, CH_2Cl_2, DMSO, THF, DMF).

3.2. Mesomorphic properties

As target compound **6** was prepared, its mesomorphic property was studied by DSC, polarising optical microscopy (POM) and XRD. The DSC curve was illustrated in Figure 1 and the phase transition temperatures and enthalpy changes were summarized in Table 1. The corresponding DSC data of its precursor **5** were quoted for the purpose of comparison, showing the influence of two diphenylacrylonitrile groups on liquid crystalline behaviour. It can be seen that compound **6** exhibited good reversible phase transition behaviours with two obvious phase transition temperatures on cooling and second heating. The two endothermic peaks at 124.9 and 189.5 ^{o}C on heating, and two exothermic peaks at 120.1 and 180.2 ^{o}C on cooling were observed. These results certainly supported the phase transition process of the crystal phase-mesophase-isotropic phase for compound **6**. The slight hysteresis phenomenon for phase transition temperatures on cooling was observed, which was normal for this kind of viscous material with a large molecular weight. Comparing with its precursor **5**, the crystal phase-mesophase transition temperature of compound **6** increased from 41.3 ^{o}C to 124.9 ^{o}C but their mesophase-isotropic phase transition temperature were almost same. Correspondingly, the scope of phase transition temperature narrowed from 160 ^{o}C of compound **5** to 65 ^{o}C of compound **6** after calculation. These phenomena were in accordance with the structure of compound **6**, in which the bulky diphenylacrylonitrile units on the bay-positions enlarged the area of rigid perylene core, enhanced the π-π action and resulted in the higher crystal phase-mesophase transition temperature. On the other hand, the bulky diphenylacrylonitrile units on bay-positions were probably oriented near perpendicular to the perylene core and thus the whole unit was no longer planar, which might counteract the enhanced π-π action at mesophase, and leaded to the similar mesophase-isotropic phase transition temperatures finally. These analyses also agreed with the previous reports that the bulky substituents on bay positions increased the phase transition temperatures and destroyed π-π action to a certain degree [17, 51]. Based on these DSC data, it could be concluded that, although the bulky diphenylacrylonitrile units were introduced onto bay positions, compound **6** still possessed stable and reversible mesophase from 124.9 to 189.5 ^{o}C.

The mesomorphic property of compound **6** was further investigated by POM. The phase transitions of Cr-Col and Col-Iso phase were clearly observed. Their phase transition temperatures were consistent with the DSC data approximately. Figure 2 exhibited the mesomorphic texture at 150^{0}C. This type of pseudo-confocal conic texture was typical columnar mesophase, which was also confirmed by XRD.

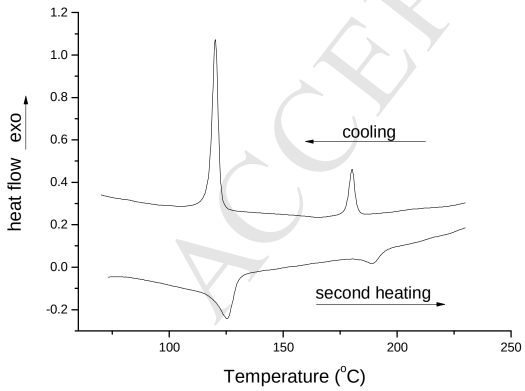


Figure 1 The DSC trace of compound **6** on second heating and cooling (scan rate 10^{o}C min^{-1})

Table 1 Transition temperatures (^{o}C) and enthalpy changes (kJ/mol) of compound **6** and its precursor **5**

compound	Phase transition[a]	Heating scan T(ΔH)	Cooling scan T(ΔH)
6	Cr-Col	124.9(18.36)	120.1(19.98)
	Col-Iso	189.5(4.34)	180.2(5.79)
5[b]	Cr-Col$_h$	41.3(16.86)	35.6(12.74)
	Col$_h$-Col$_d$	190.1(1.44)	171.9(0.24)
	Col$_d$-Iso	202.8(18.75)	188.8(14.08)

[a] Cr=crystalline, Col=columnar mesophase, Col$_h$=hexagonal columnar mesophase, Col$_d$=disordered columnar mesophase, Iso=isotropic; [b] These data were quoted from reference [17].

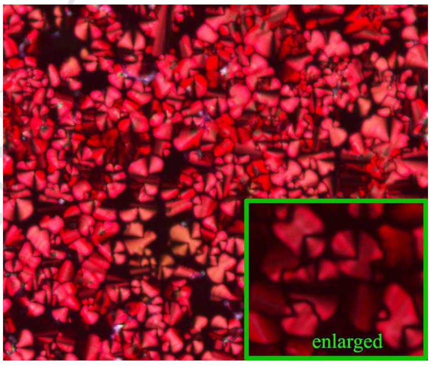


Figure 2 The texture of compound **6** obtained with POM on cooling at 150^{o}C (Zooming in 200 times for big picture and 500 times for small picture)

The XRD analysis of mesophase of compound **6** was investigated at 150^{o}C as shown in Figure 3. In the small-angle region, one strong reflection and two weak reflections were observed at 1.98^{o}, 3.43^{o} and 3.97^{o}, respectively. After calculation according to the Bragg equation, the corresponding distances for these reflections were 44.58 Å, 25.73 Å, and 22.24 Å, which agreed with the ratio of 1:1/√3:1/√4, indicating the [d$_{100}$], [d$_{110}$] and [d$_{200}$] reflections of hexagonal columnar liquid crystal for compound **6**. In the wide-region, the broad halo at 2θ = 15~30^{o} implied the mean distance of 4.4Å and the short correlation length for the molten alkyl chains. A small reflection at 22.51^{o} suggested the distance of 3.95 Å, which was in accordance with the typical values of intracolumnar distance of π-π interaction of the ordered hexagonal columnar liquid crystal. On the other hand, the lattice parameter *a* for compound **6** could be calculated as 51.48 Å, which was smaller than the diameter of compound **6** (~64 Å) obtained by CPK molecular model. This result might suggest that the soft alkyl chains in compound **6** were folding conformation or the possible interdigitation in the neighbouring columns. Thus, the possible molecular stacking for hexagonal columns of compound **6** was proposed in Figure 3 (as shown in inserted box). Combining all the results of DSC, POM and XRD experiments, it could be deduced that, despite of the bulky diphenylacrylonitrile units onto perylene skeleton, compound **6** maintained the ordered hexagonal columnar mesophase between 124.9 and 189.5 ^{o}C.

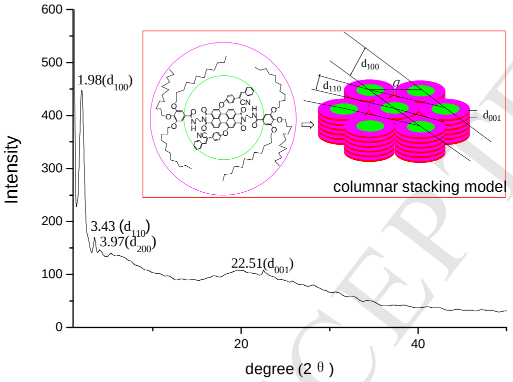


Figure 3 XRD trace of compound **6** measured at 150 ^{0}C and the proposed molecular stacking model for hexagonal column

3.3. photophysical properties

The photophysical property of compound **6** was investigated to study the influence of diphenylacrylonitrile units on luminescence. The UV/Vis spectra of compound **6** and its precursor **5** in THF solution were presented in Figure 4. It can be seen that, compound **5** exhibited strong peak at λ = 450-550 nm for perylene skeleton only, but sample **6** showed the strong absorption at λ = 300-350 nm and 450-600 nm for diphenylacrylonitrile moiety and perylene skeleton, respectively. The results suggested little interaction between the two moieties of perylene and diphenylacrylonitrile. In Figure 5, their fluorescence spectra of **6** presented a strong emission at λ = 525-650 nm. In comparison with compound **5**, the small bathochromic shift in both absorption and emission spectra for sample **6** could be attributed to the introduction of substituents on bay-posiutions leading in the twisting of perylene skeleton and the loss of rigidity and planarity of perylene bisimide chromophore [51-53].

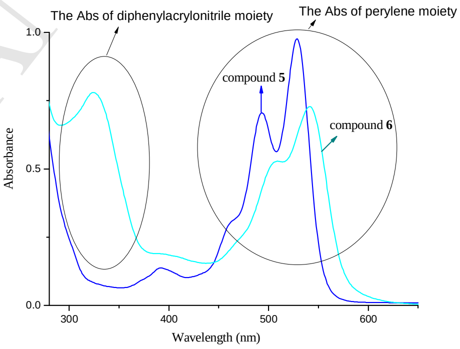


Figure 4 The absorption spectra of compounds **5** and **6** in THF solution (2×10^{-6} M)

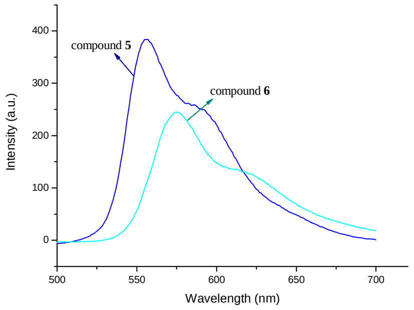


Figure 5 The emission spectra of compounds **5** and **6** in THF solution (2×10^{-6} M) excited at λ= 480 nm for compound **5** and 500 nm for compound **6**.

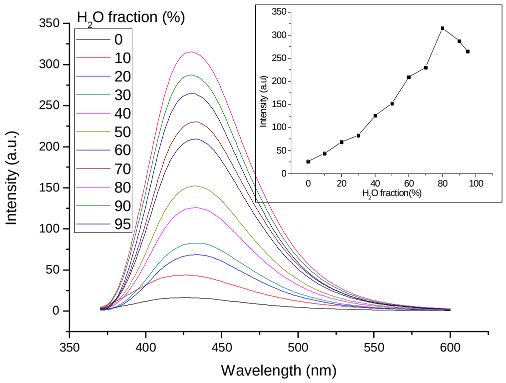


Figure 6 The emission spectra of compound **4** with different fractions of H_2O in THF/H_2O mixtures (4×10^{-6} M) excited at $\lambda = 330$ nm. (The square inserted: Variation in intensity with fractions of H_2O in THF/H_2O mixtures)

Furthermore, the AIE and FRET effect of compound **6** were studied in THF/H_2O mixtures. Firstly, the AIE activity of diphenylacrylonitrile **4** was explored at λ_{ex} = 330 nm as shown in Figure 6. With the increase of water fraction, the fluorescence of compound **4** increased gradually and attained a maximum at the water fraction of 80%. This result suggested compound **4** possessed good AIE effect. Secondly, the AIE activity of precursor **5** was also investigated at either 330 nm or 480 nm, respectively, for the purpose of comparing with the data of compound **6** bearing diphenylacrylonitrile units. The results were illustrated in Figure 7 and Figure 8. One can see that the fluorescence intensity decreased gradually with the increase of water fraction THF/H_2O mixtures when excited at both 330 nm and 480 nm for precursor **5**. Moreover, the strongest fluorescence intensity excited at 330 nm (33 a.u.) was far smaller than that excited at 480 nm (398 a.u.). These phenomena were in accordance with the structure of compound **5** without AIE-active group. With the increase of water fraction, the solubility of compound **5** decreased slowly, resulting in the aggregation of compound **5** gradually and ACQ effect finally.

However, by comparison with precursor **5**, compound **6** with AIE-active diphenylacrylonitrile unit exhibited markedly different changes when excited at 330 nm or 480 nm. As shown in Figure 9 excited at 330nm, the fluorescence intensitybetween 550-650 nm for perylene skeleton of compound **6** was weak (30 a.u.) in pure THF solution, which was similar with that of compound **5** under same condition. With the increase of water fraction, the fluorescence intensity enhanced rapidly and attained a maximum value at a water fraction 40%. The highest intensity at water fraction of 40% was 300 a.u., which was ten times than that in pure THF solution. With the water fraction increased further (> 40%), the fluorescence intensity decreased quickly to 20 a.u. at water fraction of 90%. In addition, although the strong fluorescence intensity appeared at 400-500 nm for diphenylacrylonitrile **4** with the increase of water fraction (Figure 6), no obvious fluorescence emission for sample **6** with diphenylacrylonitrile units was observed at 400-500 nm with the increase of water fraction. On the other hand, when excited at 480 nm, the fluorescence intensity of compound **6** decreased with the increase of water fraction, which was similar to the changes of precursor **5** (Figure 10). Obviously, the different change for compound **6** excited at 330 nm and 480 nm suggested the different fluorescence emission mechanism, which could be explained smoothly by the AIE and FRET effect as following analysis.

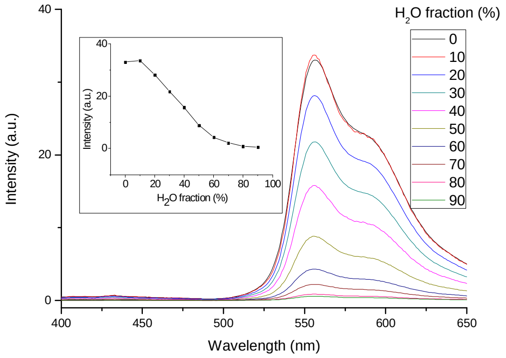


Figure 7 The emission spectra of compound **5** with different fractions of H_2O in THF/H_2O mixtures (2×10^{-6} M) excited at λ = 330 nm. (The square inserted: Variation in intensity with fractions of H_2O in THF/H_2O mixtures)

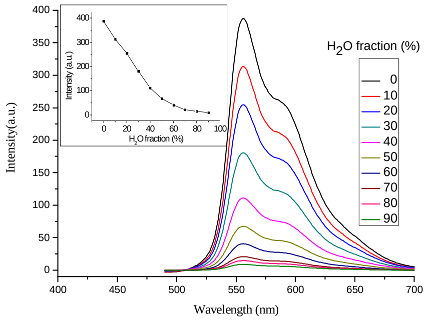


Figure 8 The emission spectra of compound **5** with different fractions of H_2O in THF/H_2O mixtures (2×10^{-6} M) excited at λ = 480 nm. (The square inserted: Variation in intensity with fractions of H_2O in THF/H_2O mixtures)

As compound **6** possessed two absorption peaks for perylene unit and diphenylacrylonitrile unit independently, the strong fluorescence for diphenylacrylonitrile unit should appear based on the AIE effect with the increase of water fraction when excited at 330 nm. Therefore, no fluorescence emission observed at 400-500 nm for sample **6** in THF/H_2O mixture might indicate the FRET effect between diphenylacrylonitrile and perylene moiety. As a result, when the water fraction increased from 0% to 40%, the enhanced AIE effect produced stronger FRET effect, leading to the increase of fluorescence intensity for perylene unit finally. On the other hand, with the increase of the water fraction, the solubility of compound **6** decreased rapidly and the strong aggregation for perylene skeleton appeared, leading to the ACQ effect. When the water fraction was smaller than 40%, the AIE and FRET effect of diphenylacrylonitrile unit were stronger than the ACQ effect, resulting in the enhancement of fluorescence intensity with the increase of water fraction. As the water fraction exceeded 40%, the ACQ effect of perylene skeleton was stronger than the AIE and FRET effect of diphenylacrylonitrile unit, leading to the decrease of fluorescence intensity for perylene skeleton. These results suggested the existence of delicate balance between AIE-FRET effect and ACQ effect. The water fraction of 40% was the balance point with the strongest emission for compound **6**. However, when excited at 480 nm, the perylene skeleton of compound **6** could emitted as compound **5**, but the diphenylacrylonitrile moiety of sample **6** showed little emission at this excited wavelength and produced little AIE effect. Thus, compound **6** when excited at λ = 480 nm showed similar fluorescence change as compound **5**.

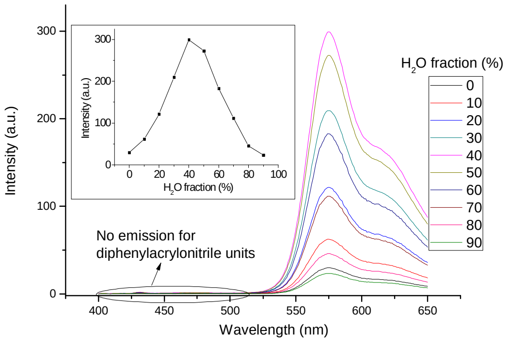


Figure 9 The emission spectra of compound **6** with different

fractions of H_2O in THF/H_2O mixtures (2×10^{-6} M) excited at λ = 330 nm. (The square inserted: Variation in intensity with fractions of H_2O in THF/H_2O mixtures)

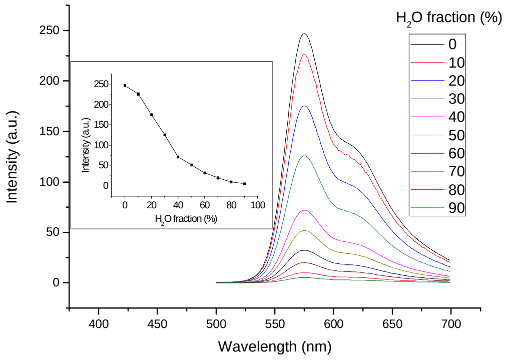


Figure 10 The emission spectra of compound **6** with different fractions of H_2O in THF/H_2O mixtures (2×10^{-6} M) excited at λ = 480 nm. (The square inserted: Variation in intensity with fractions of H_2O in THF/H_2O mixtures)

Table 2 Absorption and fluorescent data of compounds **6** and **5** (2×10^{-6} M).

Comp.	λ_{abs} (nm)	λ_{em} (nm)	τ (ns)	Stokes shift (nm)	Φ_F[e]	Φ_F[f]
6	324[a]	575	4.86[c]	251	0.04[c]	0.36
6	541[b]	575	4.63[d]	34	0.30[d]	0.07
5	/	556	3.94[c]	/	0.03[c]	0.02
5	528[b]	556	3.93[d]	28	0.34[d]	0.06

[a] The absorption maximum of diphenylacrylonitrile unit.

[b] The absorption maximum of perylene unit.

[c] The λ_{ex} = 330 nm.

[d] The λ_{ex} = 480 nm.

[e] The Φ_F values in THF solution.

[f] The Φ_F values in THF/H_2O mixture with water fraction of 40%.

Furthermore, this deduction for mechanism was confirmed by the fluorescence quantum yield and fluorescence lifetime of compound **6** excited at 330nm and 480 nm in pure THF and THF/H_2O with water fraction of 40%, respectively. Table 2 exhibited all these data of photophysical properties of compounds **5** and **6**. The values (τ) of fluorescence lifetime of compound **6** excited at 330 nm and 480 nm was 4.86 ns and 4.63 ns, respectively. The obvious difference for these fluorescence lifetimes indicated the different emission mechanism at 330 nm and 480 nm. The value (Φ_F) of fluorescence quantum yield of compound **6** in THF/H_2O with water fraction of 40% was as high as 0.36, which was far higher than that in pure THF solution. This result was also in accordance with the AIE and FRET effect of compound **6** in THF/H_2O mixture. Combining all these above analysis, it could be concluded that the effective AIE and FRET process existed for compound **6** with diphenylacrylonitrile units when excited at 330 nm in THF/H_2O mixture. The fluorescence intensity at THF/H_2O with water fraction of 40% was 10 times higher than that in pure THF solution. The pseudo Stokes shift was as large as 251 nm for this fluorescence emission. After calculated with the density functional theory (DFT) method at the B3LYP/6-31G(d) level by Gaussian 09 program, the optimized structure of compound **6** with lowest energy was obtained as shown in Figure 11. Based on this optimized structure, the proposed AIE effect and energy-transfer process was exhibited in Figure 11. In a word, perylene derivative **6** bearing diphenylacrylonitrile groups not only was the novel hexagonal columnar perylene liquid crystal, but also exhibited good fluorescence with large pseudo Stokes shift based on AIE and FRET effects.

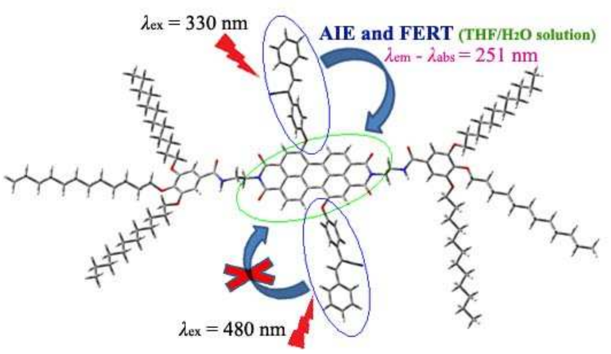


Figure 11 The proposed AIE and FERT mechanism for compound **6**

4. Conclusion

In summary, a novel perylene liquid crystal with diphenylacrylonitrile groups on the 1,7-bay positions was designed and synthesized in 70% yield. Its structure was confirmed by FT-IR, NMR and HR-MS. Its mesomorphic properties were studied by DSC, POM and XRD analysis, indicating that it possessed the ordered hexagonal columnar mesophase between 124.9 and 189.5 ^{o}C. The studies on photophysical properties revealed that the fluorescence intensity of compound **6** excited at 480 nm decreased rapidly with the increase of water fraction in THF/H_2O mixtures. However, when excited at 330 nm, the fluorescence intensity of compound **6** enhanced with the increase of water fraction and attained summit at water fraction of 40%. The fluorescence intensity increased by 10 times and the pseudo Stokes shift was as large as 251 nm. These phenomena could be well explained by the AIE effect of diphenylacrylonitrile units and the FRET process between perylene and diphenylacrylonitrile moiety. The delicate balance between AIE-FRET effect and ACQ effect existed for compound **6** when excited at 330 nm. The deduction of AIE and FRET mechanism was also confirmed by the investigation of fluorescence quantum yield and fluorescence lifetime of compound **6**. This type of AIE and FRET effect was observed for the first time for a perylene liquid crystal, which opens new strategy to design and synthesis of novel perylene liquid crystal possessing unique fluorescence with large Stokes shift.

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