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Cruciform 9,10-distyryl-2,6-bis(*p*-dialkylamino-styryl)anthracene homologues exhibiting alkyl length-tunable piezochromic luminescence and heat-recovery temperature of ground states

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A series of 2,6-bis(*p*-dialkylaminostyryl)-9,10-distyrylanthracene (**FC*n***) cruciforms with *N*-alkyl chains of different lengths have been synthesized, and their aggregation-enhanced fluorescence and piezochromic luminescence (PFC) behaviours are investigated. These 9,10-distyrylanthracene-containing cruciforms exhibit relatively low fluorescence quantum yields (Φ) in THF solution ($\Phi \approx 10\%$) and moderate aggregation-enhanced emission in aqueous media ($\Phi \approx 25\%$), but strong and chain length-dependent solid-state fluorescence emission. Grinding and pressing experiments indicate that they are all effective PFC materials in terms of mechanical stress-induced spectral shifts ($\Delta\lambda_{\mathrm{PFC}} = 23$–$54$ nm), moreover, the longer alkyl-containing **FC*n*** shows a larger $\Delta\lambda_{\mathrm{PFC}}$. Powder X-ray diffraction and differential scanning calorimetry measurements reveal that the transformation between the crystalline and amorphous states upon external stimuli is responsible for the reversible PFC behaviour. It is found that increasing the *N*-alkyl length could effectively decrease the cold-crystallization temperature of the ground states to render the PFC states with a tunable heat-recovering temperature, and ground **FC10** and **FC12** solids can recover spontaneously to their original states at room temperature.

Introduction

Tuning and switching solid-state luminescence by an external mechanical stimuli (such as grinding, compressing, shearing, deformation, *etc.* named piezo- or mechano-fluorochromism (PFC)), instead of the chemical alteration of molecular structures not only has potential applications in chemo- and mechano-sensors, data storage, security inks and optoelectronic devices, but also in gaining understanding of solid-state photophysical properties.[1–6] Up to now, there has been an increasing interest in the design, synthesis and characterization of PFC materials, and some pyrene-, anthracene-, dibenzofulvene-, tetraphenylethene-, carbazole-, and cyanostilbene-based derivatives, *etc.* which have been shown to be promising PFC materials, and their structure–property relationship has been investigated.[7–12] The results of these studies reveal that the PFC behaviour is closely related to the changes of the molecular aggregation morphology, such as the packing mode of the crystal molecules or the phase transition from the crystalline to amorphous state. However, PFC materials are still at the initial state of investigation, and their numbers and the understanding of the phenomenon are limited. Moreover, most PFC compounds identified are still an isolated event. Therefore, there is a great demand for the exploitation of new PFC materials and the accumulation of relative structure–property knowledge. In this context, the systematically comparable molecular design and tunable recovery behaviour of PFC materials are extremely desirable to both the investigation of the structure–property relationship and various applications.

We have been interested in the optical and optoelectronic properties of linear- and two-dimensional (2-D) cross-conjugated anthracene-based oligomers and polymers.[11*a*,13–26] In principle, an anthracene ring could be linked in two different ways, 9,10- or 2,6-linkages, to form two conjugation pathways with different backbone conformations and quinoid characters. As a sequence, the electronic and photonic properties of anthracene-based conjugated molecules are highly dependent on both the nature of building blocks and the way in which they are linked. For example, most 9,10-bis(arylvinyl)anthracene derivatives exhibit unique aggregation-induced emission (AIE) and PFC behaviour related to the strongly twisted backbone conformations.[8*d*,10*c*,11,25–30] Contrarily, planar 2,6-bis(arylvinyl)-anthracene derivatives show aggregation-quenched emission and non-PFC behaviour. Therefore, it is very interesting to know whether the center-crossed chromophores integrated by 2,6- and 9,10-bis(arylvinyl)anthracenes are AIE- and PFC-active since 2-D cross-conjugated cruciforms have many unique and interesting optical and optoelectronic properties.[31] To the best of our

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knowledge, there are no reports on the construction of cruciforms with AIE and/or PFC behaviour at present, and organic materials exhibiting chain length-dependent PFC behaviour are also scarce, although a number of organic fluorophores with chain length-dependent solid-state fluorescence have been reported in the past few years.[7,11a,25,30,32,33] In the current work, we have designed and synthesized a series of 2,6-bis(*p*-dialkylaminostyryl)-9,10-distyrylanthracenes (**FC*n***, Scheme 1) to examine emphatically the PFC behaviour and the effect of the *N*-alkyl length. We now report that these cruciform homologues are not only effective PFC materials, but also that their heat-recovering temperature of ground states can be effectively tuned by changing the *N*-alkyl lengths.

Experimental section

Synthesis

The synthesis and structure of **FC*n*** is depicted in Scheme 1. The general route to **FC*n*** started from 2,6-bis(diethylphosphoryl-methyl)-9,10-dibromoanthracene (**1**). Intermediate **1** was first subjected to a Heck coupling with styrene to afford the intermediate **2**. The Wittig–Horner reaction of **2** and each 4-dialkylaminobenzaldehyde with different lengths of alkyl chain gave the desirable cruciforms **FC*n*** in good yields and purity after purification by column chromatography on silica gel.

Regents and solvents

Tetrahydrofuran (THF) was distilled over metallic sodium and *N*,*N*-dimethylformamide (DMF) over calcium hydride before use. Styrene, 4-dimethylaminobenzaldehyde, aniline, 1-alkylbromides and others were all commercially available analytical-grade chemicals and were used as received, unless otherwise claimed. 2,6-Bis(diethylphosphorylmethyl)-9,10-dibromo-anthracene was from a previous work.[16]

Measurement

^{1}H (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker-AC500 spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard, and are expressed in ppm (δ). Elemental analysis was performed on a Perkin-Elmer 2400. UV-vis absorption spectra were recorded on a Hitachi U-4100 spectrophotometer. Fluorescence measurements were carried out with a Hitachi F-4600 spectrophotometer. The peak wavelength of the lowest energy absorption band was used as the excitation wavelength for PL measurement. The fluorescence quantum yield (Φ) was determined at room temperature by the dilution method using fluorescein in water (pH = 11) as the reference in which the absolute values of maximal absorption are less than 0.1.[34] Powder wide-angle X-ray diffraction (PWXD) experiments were performed on a powder X-ray diffractometer (INCA Energy, Oxford Instruments) operating at 3 kW. Differential scanning calorimetry (DSC) curves were determined on a Netzsch DSC 204F1 at a heating rate of 10 °C min^{-1}.

Synthetic procedure for the various 4-dialkylaminobenzaldehydes

A mixture of aniline (0.26 g, 2.8 mmol), 1-alkylbromide (7.5 mmol), and K_2CO_3 (1.38 g, 10 mmol) in DMF (20 mL) was stirred for 24 h at 80 °C and then cooled to room temperature and poured into water and extracted with ether. After the solvent was removed by a rotatory evaporator, the crude product was dried *in vacuo* and then added to a stirring solution of phosphoryl trichloride (5 mL) and DMF (20 mL) at room temperature and stirred for 6 h. The resulting mixture was poured into ice-water and extracted with ether. The solvent was evaporated and the crude product was separated by column chromatography on silica gel using hexane–ethyl acetate (15/1) as the eluent. Colourless or a slight yellow oil was obtained in high yields of 80–90%. These compounds were characterized by ^{1}H NMR and the relative data was as follows.

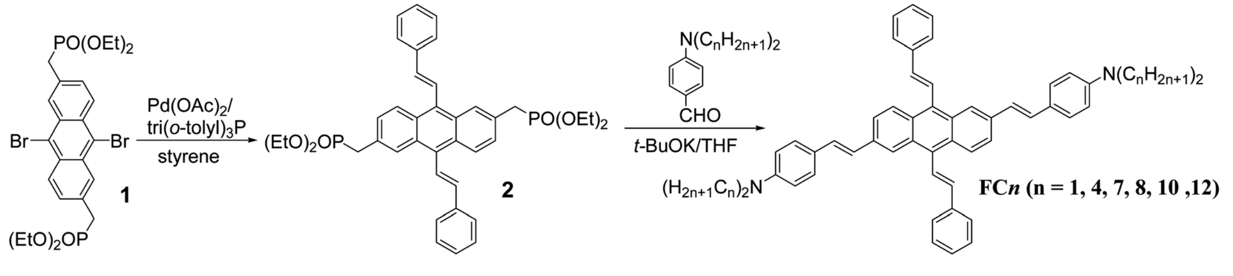
4-Dibutylaminobenzaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.67 (s, 1H), 7.66 (d, $J = 8.5$ Hz, 2H), 6.61 (d, $J = 9$ Hz, 2H), 3.32 (t, 4H), 1.41 (m, 8H), 0.84 (t, 6H).

4-Diheptylaminobenzaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.67 (s, 1H), 7.67 (d, $J = 8.5$ Hz, 2H), 6.61 (d, 2H), 3.32 (t, 4H), 1.60 (m, 4H), 1.31 (m, 16H), 0.86 (t, 6H).

4-Dioctylaminobenzaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.71 (s, 1H), 7.71 (d, $J = 7.5$ Hz, 2H), 6.67 (d, 2H), 3.31 (t, 4H), 1.61 (m, 4H), 1.32 (m, 20H), 0.91 (s, 6H).

4-Didecylaminobenzaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.68 (s, 1H), 7.68 (d, $J = 8.5$ Hz, 2H), 6.62 (d, $J = 9$ Hz, 2H), 3.32 (t, 4H), 1.55 (m, 4H), 1.26 (t, 28H), 0.87 (t, 6H).

4-Didodecylaminobenzaldehyde. ^{1}H NMR (500 MHz, $CDCl_3$, δ): 9.67 (s, 1H), 7.69 (d, $J = 9$ Hz, 2H), 6.63 (d, $J = 9$ Hz, 2H), 3.32 (t, 4H), 1.57 (m, 4H), 1.28 (t, 36H), 0.85 (t, 6H).



Scheme 1 Synthesis and structure of the cruciforms FC*n*.

Synthesis of 2,6-bis(diethylphosphorylmethyl)-9,10-distyrylanthracene

A pressure tube containing styrene (1.11 g, 10.1 mmol), 2,6-bis(diethylphosphorylmethyl)-9,10-dibromoanthracene (1.35 g, 2.13 mmol), $Pd(OAc)_2$ (52 mg, 0.21 mmol), tri(*o*-tolyl) phosphine (0.38 g, 1.21 mmol), $N(C_2H_5)_3$ (7 mL) and THF (7 mL) was sealed with a helix teflon cap under nitrogen and then refluxed at 80 °C for 24 h. After cooling, the solvents were evaporated and the residue was separated by column chromatography on silica gel using ethyl acetate–hexane (3/1) as the eluent. Yield: 1.16 g (80.6%). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.35 (d, $J = 9$ Hz, 2H), 8.21 (s, 2H), 7.89 (d, $J = 11.5$ Hz, 2H), 7.69 (d, $J = 7.5$ Hz, 4H), 7.48 (m, 6H), 7.39 (m, 2H), 6.92 (d, $J = 17$ Hz, 2H), 4.03 (m, 8H), 3.33 (d, 4H), 1.23 (m, 12H). Anal. calcd for $C_{40}H_{44}O_6P_2$: C, 70.37; H, 6.50; O, 14.06; P, 9.07. Found: C, 70.46; H, 6.44.

General synthetic procedure for various 2,6-bis(*p*-dialkylaminostyryl)-9,10-distyrylanthracenes (FC*n*)

Potassium *tert*-butoxide (0.16 g, 1.43 mmol) was added to the mixture of 2,6-bis(diethylphosphorylmethyl)-9,10-distyrylanthracene (0.13 g, 0.19 mmol) and 4-dialkylamino benzaldehyde (0.56 mmol) in anhydrous THF (15 mL) at room temperature under N_2 protection. The mixture was stirred overnight and then 100 mL of methanol was added. The precipitate was collected and purified by column chromatography on silica gel using hexane–CH_2Cl_2 (3/1) as the eluent. The green to orange solids were obtained in 57–73% yields, and their ^{1}H and ^{13}C NMR data and element analysis were as follows.

2,6-Bis(4-dimethylaminostyryl)-9,10-distyrylanthracenes (F1). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.32 (d, $J = 9$ Hz, 2H), 8.18 (s, 2H), 7.92 (d, $J = 16.5$ Hz, 2H), 7.73 (m, 6H), 7.50 (m, 6H), 7.45 (m, 4H), 7.13 (m, 4H), 6.96 (d, $J = 16.5$ Hz, 2H), 6.70 (d, $J = 8$ Hz, 4H), 2.98 (m, 12H). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 147.9, 137.3, 134.8, 134.5, 132.2, 130.6, 129.3, 128.9, 128.2, 128.0, 127.9, 127.0, 126.7, 125.4, 124.4, 124.1, 122.6, 118.5, 111.7, 50.2. Anal. calcd for $C_{50}H_{44}N_2$: C, 89.25; H, 6.59; N, 4.16. Found: C, 89.36; H, 6.53; N, 4.13.

2,6-Bis(4-dibutylaminostyryl)-9,10-distyrylanthracenes (F4). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.33 (d, $J = 9$ Hz, 2H), 8.23 (s, 2H), 7.90 (d, $J = 16.5$ Hz, 2H), 7.75 (m, 6H), 7.51 (m, 4H), 7.42 (m, 6H), 7.11 (m, 4H), 6.98 (d, $J = 16.5$ Hz, 2H), 6.63 (d, $J = 8$ Hz, 4H), 3.30 (t, 8H), 1.59 (m, 8H), 1.37 (m, 8H), 0.97 (m, 12H). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 147.9, 137.3, 134.9, 134.5, 132.2, 130.8, 129.3, 128.9, 128.2, 128.0, 127.9, 127.0, 126.7, 125.4, 124.4, 124.1, 122.6, 118.6, 111.7, 50.8, 29.5, 20.4, 14.1. Anal. calcd for $C_{62}H_{68}N_2$: C, 88.52; H, 8.15; N, 3.33. Found: C, 88.41; H, 8.19; N, 3.37.

2,6-Bis(4-diheptylaminostyryl)-9,10-distyrylanthracenes (F7). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.31 (s, 2H), 8.16 (s, 2H), 7.90 (d, $J = 16.5$ Hz, 2H), 7.74 (m, 6H), 7.50 (m, 4H), 7.41 (m, 6H), 7.10 (m, 4H), 6.96 (d, $J = 16.5$ Hz, 2H), 6.59 (d, 4H), 3.26 (d, 8H), 1.57 (m, 16H), 1.30 (m, 24H), 0.90 (m, 12H). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 147.9, 137.4, 134.9, 134.5, 132.1, 130.0, 129.2, 128.9, 128.2, 128.0, 127.9, 127.0, 126.7, 125.4, 124.5, 124.1, 122.6, 111.7, 109.9, 51.1, 31.9, 29.6, 28.4, 27.3, 22.7, 14.1. Anal. calcd for $C_{74}H_{92}N_2$: C, 88.04; H, 9.19; N, 2.77. Found: C, 88.11; H, 9.14; N, 2.74.

2,6-Bis(4-dioctylaminostyryl)-9,10-distyrylanthracenes (F8). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.30 (d, $J = 9.5$ Hz, 2H), 8.15 (s, 2H), 7.90 (d, $J = 16.5$ Hz, 2H), 7.75 (m, 6H), 7.48 (m, 4H), 7.39 (m, 6H), 7.11 (m, 4H), 6.96 (d, $J = 16.5$ Hz, 2H), 6.59 (d, $J = 8.5$ Hz, 4H), 3.25 (t, 8H), 1.55 (m, 16H), 1.26 (m, 32H), 0.87 (m, 12H). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 147.9, 137.4, 134.9, 134.5, 132.1, 130.0, 129.2, 128.9, 128.4, 128.1, 127.7, 127.0, 126.7, 125.4, 124.5, 124.1, 122.6, 111.7, 109.9, 51.1, 31.9, 29.7, 29.4, 28.4, 27.3, 22.7, 14.1. Anal. calcd for $C_{78}H_{100}N_2$: C, 87.91; H, 9.46; N, 2.63. Found: C, 88.01; H, 9.44; N, 2.60.

2,6-Bis(4-didecylaminostyryl)-9,10-distyrylanthracenes (F10). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.30 (d, $J = 9$ Hz, 2H), 8.15 (s, 2H), 7.90 (d, $J = 16.5$ Hz, 2H), 7.74 (m, 6H), 7.46 (m, 4H), 7.40 (m, 6H), 7.11 (m, 4H), 6.96 (d, $J = 16$ Hz, 2H), 6.60 (d, $J = 8.5$ Hz, 4H), 3.26 (d, 8H), 1.56 (m, 32H), 1.30 (m, 32H), 0.86 (m, 12H). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 147.9, 137.4, 134.9, 134.5, 132.1, 130.0, 129.2, 128.9, 128.2, 128.0, 127.7, 127.0, 126.7, 125.4, 124.4, 124.1, 122.6, 111.7, 110.2, 51.2, 31.9, 30.2, 29.7, 29.4, 28.0, 27.4, 27.1, 22.8, 14.2. Anal. calcd for $C_{86}H_{116}N_2$: C, 87.70; H, 9.93; N, 2.38. Found: C, 87.82; H, 9.88; N, 2.35.

2,6-Bis(4-didodecylaminostyryl)-9,10-distyrylanthracenes (F12). ^{1}H NMR (500 MHz, $CDCl_3$, δ): 8.31 (d, $J = 8$ Hz, 2H), 8.15 (s, 2H), 7.92 (d, $J = 16.5$ Hz, 2H), 7.73 (m, 6H), 7.49 (m, 4H), 7.39 (m, 6H), 7.11 (m, 4H), 6.97 (d, $J = 16.5$ Hz, 2H), 6.60 (d, $J = 8.5$ Hz, 4H), 3.27, 3.26, 3.24 (t, 8H), 1.54 (m, 48H), 1.30 (m, 32H), 0.87 (m, 12H). ^{13}C NMR (500 MHz, $CDCl_3$, δ): 148.0, 137.5, 134.9, 134.5, 132.1, 130.0, 129.2, 128.9, 128.2, 128.0, 127.7, 126.9, 126.7, 125.5, 124.4, 124.1, 122.6, 111.7, 110.2, 51.3, 32.1, 31.9, 30.5, 30.2, 29.7, 29.4, 28.0, 27.4, 27.1, 22.8, 14.2. Anal. calcd for $C_{94}H_{132}N_2$: C, 87.52; H, 10.31; N, 2.17. Found: C, 87.61; H, 10.25; N, 2.13.

Piezochromic and stimulus-recovering experiments

Grinding experiment. Pristine **FC*n*** solid was put on a glass plate and ground with a metal spatula at room temperature. *Pressing experiment*: 5–7 mg of **FC*n*** solid and *ca.* 250 mg of KBr powder were simply mixed in a mortar (for the sake of minimizing the amount of fluorophore), and then pressed with an IR pellet press under the pressure of 1500 psi for 30 seconds at room temperature. *Annealing experiment*: the ground or pressed **FC1**–**FC8** samples were placed into an oven with a temperature 20 °C above the respective cold-crystallization temperature and stood for 3 minutes, and the ground or pressed **F10** and **FC12** samples were stood at room temperature. *Solvent-fuming experiment*: in a sealed CH_2Cl_2-containing beaker, the sample was suspended above the solvent level and exposed for 30 seconds at room temperature. After external stimuli, the fluorescence images and emission spectra were recorded at room temperature.

Results and discussion

General photophysical properties

As expected, these cruciforms show the same absorption and emission spectra (Fig. 1a) and fluorescence quantum yields

(Φ = 10–12%) in THF solution because of their identical conjugated skeletons, indicating the *N*-alkyl chain lengths do not substantially affect their solution photophysical properties.

However, it is noted that the Φ values of **FC*n*** in THF solution are obviously higher than those of the linear 9,10-distyrylanthracene derivatives whose solutions are weak or non-fluorescent. This implies that the non-radiative decay caused by the free intramolecular torsion of the two styryl moieties at the 9,10-positions of the anthracene core has been depressed in the cruciform configuration. As a result, **FC*n*** may show a weak AIE effect in aqueous media. This is evidenced by the emission spectra and fluorescence images of **FC4** in THF solution and a THF–water (1/9) mixture (Fig. 1b). The emission spectrum in aqueous media is slightly blue-shifted relative to that in THF solution, and the Φ value in the aqueous dispersion is only about twice that in THF solution (inset in Fig. 1b).

Nevertheless, **FC*n*** are still AIE-active molecules and exhibit strong solid-state fluorescence. This is probably due to the highly distorted 9,10-distyryl moieties caused by the strongly steric hindrance of the 1,8-positions of the anthracene core, even after stacking, disturb the intermolecular close packing, to diminish the intermolecular quenching effects. In addition, it is noted that the fluorescence emission of the pristine **FC*n*** solids depends on the *N*-alkyl length (left column in Fig. 2 and Table 1). Alkyl chain length-dependent solid-state fluorescence emission is an interesting phenomenon and has been reported in other organic fluorophores. However, there are few reports on the cruciform fluorophores exhibiting chain length-dependent solid-state fluorescence, which will be further investigated elsewhere.

Piezofluorochromic and recovering behaviour

Most linear and branched 9,10-diarylvinylanthracene derivatives have been found to show PFC behaviour. However, two branches of **FC*n***, 2,6-bis(*p*-dialkylaminostyryl)anthracenes and 9,10-distyrylanthracene, do not show PFC behaviour. To investigate whether cruciforms **FC*n*** exhibit mechanochromic luminescence, we first simply ground the pure **FC*n*** solids on the glass plate using a metal spatula. It is observed that all the **FC*n*** solids showed changed fluorescence colors upon grinding (Fig. 2). Interestingly, the fluorescence colors of the ground **FC1–FC8** solids are stable and remain unchanged over 24 hours at room temperature, but ground **FC10** and **FC12** can spontaneously change back to original colors within seconds at room temperature (bottom, Fig. 2). Considering that the difference among these cruciforms is only the *N*-alkyl length, it is concluded that the alkyl chains play a crucial role in determining the solid-state optical properties and the heat-recovering behaviour of the ground states. To further understand the recovering properties of the ground **FC1–FC8** solids, the ground solids are thermally annealed or exposed to solvent vapor (fuming on dichloromethane at room temperature). The results show that the fluorescence colors of the ground states are almost converted to the original colors, and regrinding the annealed or fumed samples affords the same fluorescence color changes as the first grinding. This process is reproducible, indicating a reversible PFC phenomenon.

Meanwhile, we have also carried out the pressing experiment of the **FC*n*** samples (5–7 mg of **FC*n*** solid was mixed with KBr to minimize the amount of fluorophores) with an IR pellet press (30 seconds at 1500 psi) at room temperature. Since **FC*n*** are organic and non-polar and KBr is an inorganic salt, **FC*n*** should

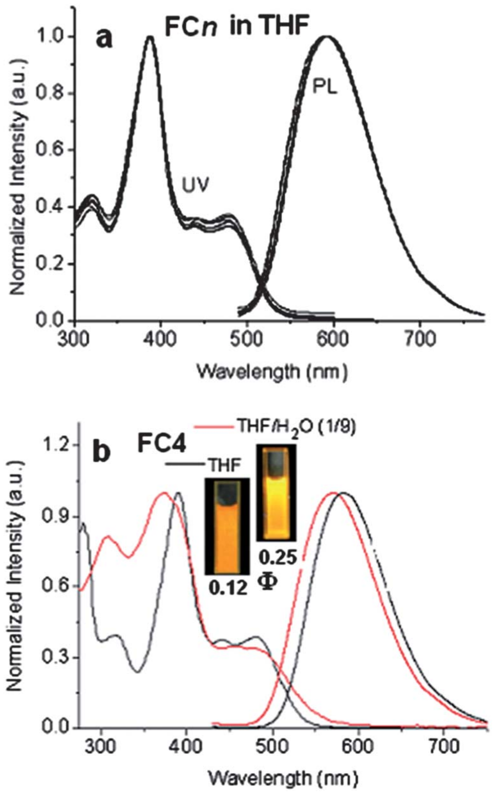


Fig. 1 Absorption and emission spectra at 1.0×10^{-5} M: (a) **FC*n*** in THF solutions; (b) **FC4** in THF and THF–H_2O (1/9) mixture (the inset is the corresponding fluorescence images and Φ).

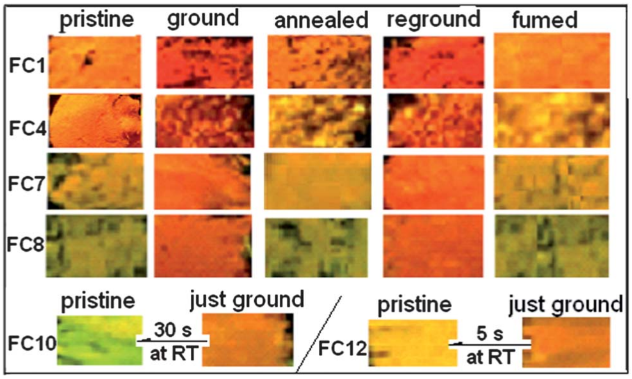


Fig. 2 Fluorescence images of pure **FC*n*** solids under as-prepared (pristine) and various external stimuli states illuminated by a UV lamp of 365 nm. Piezofluorochromic and recovering behaviour.

Table 1 Peak emission wavelengths (λ, in nm) and thermal transition data of **FC*n*** solids under various external stimuli

Cpds	$\lambda_{\text{pristine}}$[a]	λ_{pressed}	$\lambda_{\text{annealed}}$	$\lambda_{\text{re-pressed}}$	λ_{fumed}	$\Delta\lambda_{\text{PFC}}$[b]	T_m[c]/°C	T_{cc}[d]/°C
FC1	591	616	593	615	593	23	>300	138
FC4	597	613	588	613	588	25	245	95
FC7	563	595	565	593	563	30	143	72
FC8	541	598	544	597	547	54	136	50
FC10	538	597	552	597	554	45	nd[e]	≤RT
FC12	551	596	547	597	555	49	nd[e]	<RT

[a] Peak emission wavelengths of as-prepared solids. [b] Pressing-induced spectral shift, $\Delta\lambda_{\text{PFC}} = \lambda_{\text{pressed}} - \lambda_{\text{annealed}}$. [c] Isomeric melt transition temperature. [d] Cold-crystallization temperature of ground solids. [e] Not determined.

disperse in KBr non-molecularly and show solid-state properties. Overall, the pressing gives the same effectiveness as the grinding, and the fluorescence colours can be changed reversibly by thermal annealing, solvent-fuming, and repressing (Fig. 3). Interestingly, the fluorescence colours of the pressed **FC10** and **FC12** samples can remain almost unchanged over 5 min at room temperature, which allows the spectral measurement. The phenomena that piezochromic luminescence can retain a relatively longer time using the KBr-diluted sample than the pure solid was observed by us in the previous long alkyl-containing PFC materials.[25] This implies that the KBr matrix could decrease the molecular motion of the dispersed fluorophores and delay the recovery process. These observations suggest that we have not only obtained a new class of PFC materials with cruciform configuration, but also realized the tunable thermal-recovering behaviour by changing the *N*-alkyl lengths.

In addition to the above visual fluorescence images, the fluorescence emission spectra in the pressing experiment were recorded on a luminescence spectrophotometer (Fig. 4), and the corresponding spectroscopic data is summarized in Table 1. All the ground **FC*n*** samples show similar emission spectra whose peak wavelengths are in a relatively narrow range of 616–595 nm, although their peak emission wavelengths in pristine solids are very different (597–538 nm) (Table 1). Moreover, most pressed samples can revert back to the fluorescence emission similar to the pristine solids upon annealing or solvent-fuming. In terms of pressing-induced spectral shift ($\Delta\lambda_{\text{PFC}} = \lambda_{\text{pressed}} - \lambda_{\text{annealed}}$), **FC*n*** with longer *N*-alkyl chains show a more remarkable PFC behaviour ($\Delta\lambda_{\text{PFC}} = 45$–$54$ nm), and those with shorter *N*-alkyl chains have $\Delta\lambda_{\text{PFC}}$ of 23–30 nm (Table 1). These $\Delta\lambda_{\text{PFC}}$ values are qualitatively consistent with the corresponding fluorescence images observed (Fig. 3). Overall, **FC*n*** solids are a class of effective and chain length-dependent PFC materials, and their alkyl length-dependency is similar to those of 9,10-bis(*p*-alkoxystyryl)anthracenes,[27,30] β-cyano-substituted bis(*p*-alkoxystyryl)benzenes,[32b] and 9,10-bis[(9,9-dialkylfluorene-2-yl)vinyl]anthracenes,[25] but thoroughly different from that of 9,10-bis[(*N*-alkylcarbazol-3-yl)vinyl]anthracenes.[11a] These dichotomous alkyl length-dependent PFC behaviours underline the complexity of the structure–property relationship and also provide new material systems for further comparable investigation.

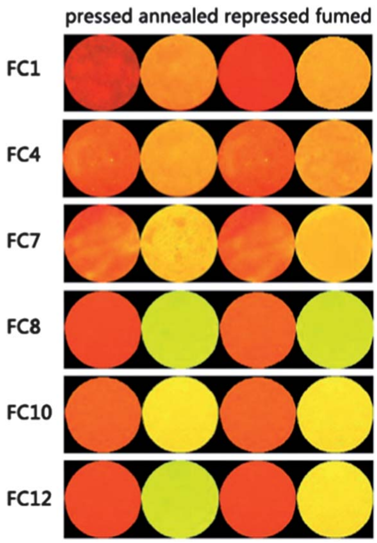


Fig. 3 Fluorescence images of the **FC*n*** samples mixed with KBr under various external stimuli illuminated by a UV lamp of 365 nm.

X-ray diffraction and DSC analysis

To understand the PFC mechanism and the effect of *N*-alkyl chains on the thermal-recovering behaviour of cruciform **FC*n*** solids, powder wide-angle X-ray diffraction and differential scanning calorimetry (DSC) experiments on pristine and ground **FC1–FC8** solids were conducted. The X-ray diffraction patterns of the pristine **FC1–FC8** solids show sharp and intense reflections indicative of a well-ordered microcrystalline structure (Fig. 5a). In contrast, the diffractograms of the ground samples display broad and featureless reflections along with a series of overlapped peaks, reflecting notable amorphous features. The formation of amorphous states upon grinding was further confirmed by DSC experiment. As shown in Fig. 5b, there are no thermal transitions for the pristine solids before isotropic melt transition (T_m); however, each ground solid shows the respective cold-crystallization transition.

Furthermore, **FC4** and **FC8** solids are molten and then rapidly put into liquid N_2, which should afford real amorphous states. It is shown that the quenched solids have the

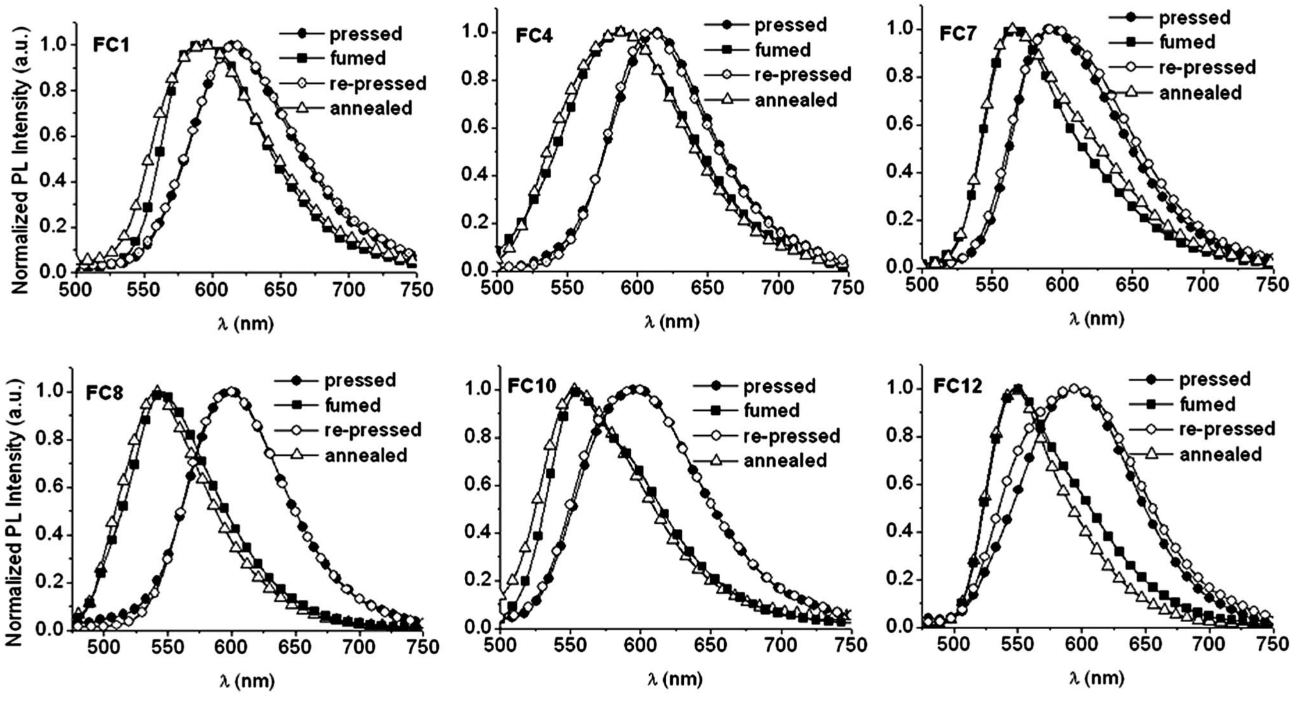


Fig. 4 Fluorescence emission spectra of the **FC*n*** samples mixed with KBr after various external stimuli. The spectra were recorded at room temperature.

same emission spectra as the ground or pressed samples (Fig. 6). These findings indicate that the transformation between the amorphous and crystalline states under various external stimuli is responsible for the reversible PFC behaviour. Further inspection of the DSC curves of the ground solids reveals that the cold-crystallization temperatures (T_{cc}) of the ground **FC*n*** solids decreases gradually with the length of *N*-alkyl chains (Fig. 5b and Table 1). Based on the decreased rate of T_{cc} from **FC1** to **FC8**, the T_{cc} values of the ground **FC10** and **FC12** should be at or below room temperature. This implies that changing the length of the *N*-alkyl chains can significantly affect the T_{cc} of amorphous **FC*n*** solids. We have observed that the fluorescence colors of the ground samples are stable below respective T_{cc} (T_{cc} − 20 °C), but recover rapidly upon annealing above respective T_{cc} (T_{cc} + 10 °C). Thus T_{cc} can be regarded as the critical thermal recovering temperature of ground **FC*n***. The spontaneous recovery behaviour of ground **FC10** and **FC12** at room temperature could be ascribed to the low T_{cc}. It could be thought that long alkyl chain should not be in favor of molecular close packing and endow the materials with a low thermal transition temperature and easily-destroyed packing structure. Unfortunately, the single crystals of **FC*n*** are still unobtainable at present, and this impedes the discovery of the real reason. Overall, we can endow these PFC cruciforms with a tunable heat-recovering temperature, which could better satisfy various applications.

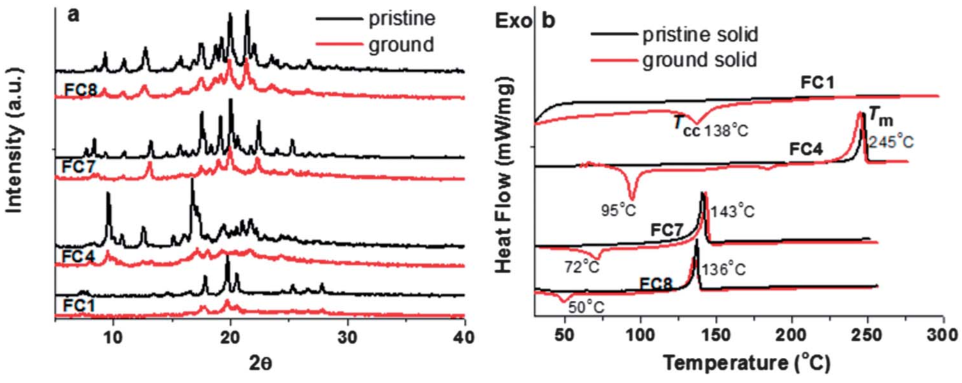


Fig. 5 Powder X-ray diffraction patterns at room temperature (a) and DSC curves upon the heating procedure (b) of **FC*n*** solids before and after grinding.

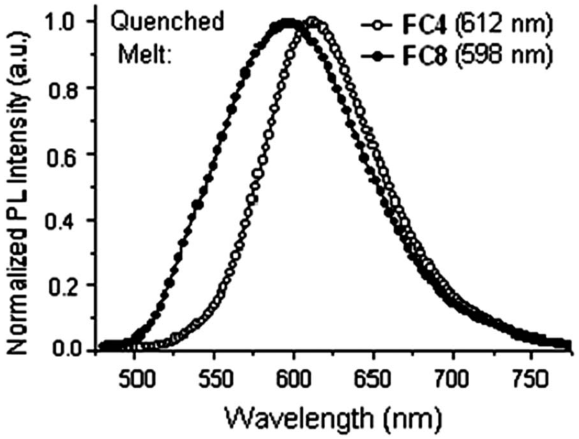


Fig. 6 Emission spectra of quenched **FC4** and **FC8** melts recorded at room temperature.

Conclusions

We have demonstrated that anthracene-centered cruciforms (**FC*n***) integrated by the aggregation-induced emission (AIE) 9,10-distyrylanthtracene and the aggregation-quenched emission 2,6-bis(*p*-dialkylaminostyryl)anthracenes are still AIE-active dyes and exhibit remarkable piezochromic luminescence with mechanical stress-induced spectral shifts ($\Delta\lambda_{\mathrm{PFC}}$) of 23–54 nm. Increasing the *N*-alkyl length can not only enlarge the $\Delta\lambda_{\mathrm{PFC}}$ but also change the cold-crystallization temperature of ground states to render the PFC states with tunable heat-recovering temperature. We have confirmed that the transformation between the crystalline and amorphous states is responsible for the reversible PFC behaviour upon external stimuli, and the spontaneously self-recovering emission of ground **FC10** and **FC12** solids at room temperature is due to the low cold-crystallization temperature. Cruciform dyes with structure-dependent fluorescence properties and tunable heat-recovering PFC behaviour should be promising material systems for the investigation of structure–property relationships and various potential applications.

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Notes and references

1 Y. Sagara and T. Kato, *Nat. Chem.*, 2009, **1**, 605.

2 Editorial, Mechanoresponsive Materials, *J. Mater. Chem.*, 2011, **21**, 8235–8236.

3 Z. Chi, X. Zhang, B. Xu, X. Zhou, C. Ma, Y. Zhang, S. Liu and J. Xu, *Chem. Soc. Rev.*, 2012, **41**, 3878.

4 J. Luo, L. Li, Y. Song and J. Pei, *Chem.–Eur. J.*, 2011, **17**, 10515.

5 B. Crenshaw, M. Burnworth, D. Khariwala, A. Hiltner, P. Mather, R. Simha and C. Weder, *Macromolecules*, 2007, **40**, 2400.

6 X. Zhang, Z. Chi, Y. Zhang, S. Liu and J. Xu, *J. Mater. Chem. C*, 2013, **1**, 3376.

7 Y. Sagara, T. Mutai, I. Yoshikawa and K. Araki, *J. Am. Chem. Soc.*, 2007, **129**, 1520.

8 (*a*) Y. Sagara, S. Yamane, T. Mutai, K. Araki and T. Kato, *Adv. Funct. Mater.*, 2009, **19**, 1869; (*b*) Z. Zhang, D. Yao, T. Zhou, H. Zhang and Y. Wang, *Chem. Commun.*, 2011, **47**, 7782; (*c*) H. Li, Z. Chi, B. Xu, X. Zhang, X. Li, S. Liu, Y. Zhang and J. Xu, *J. Mater. Chem.*, 2011, **21**, 3760; (*d*) Y. Dong, B. Xu, J. Zhang, X. Tan, L. Wang, J. Chen, H. Lv, S. Wen, B. Li, L. Ye, B. Zou and W. Tian, *Angew. Chem., Int. Ed.*, 2012, **51**, 10782.

9 X. Luo, J. Li, C. Li, L. Heng, Y. Dong, Z. Liu, Z. Bo and B. Tang, *Adv. Mater.*, 2011, **23**, 3261.

10 (*a*) B. Xu, Z. Chi, X. Zhang, H. Li, C. Chen, S. Liu, Y. Zhang and J. Xu, *Chem. Commun.*, 2011, **47**, 11080; (*b*) B. Xu, Z. Chi, H. Li, X. Zhang, X. Li, S. Liu, Y. Zhang and J. Xu, *J. Phys. Chem. C*, 2011, **115**, 17574; (*c*) Z. Yang, Z. Chi, B. Xu, H. Li, X. Zhang, X. Li, S. Liu, Y. Zhang and J. Xu, *J. Mater. Chem.*, 2010, **20**, 7352; (*d*) C. Dou, L. Han, S. Zhao, H. Zhang and Y. Wang, *J. Phys. Chem. Lett.*, 2011, **2**, 666; (*e*) S. Varghese and S. Das, *J. Phys. Chem. Lett.*, 2011, **2**, 863.

11 (*a*) Y. Wang, W. Liu, L. Bu, J. Li, M. Zheng, D. Zhang, M. Sun, Y. Tao, S. Xue and W. Yang, *J. Mater. Chem. C*, 2013, **1**, 856; (*b*) Z. Yang, Z. Chi, T. Yu, X. Zhang, M. Chen, B. Xu, S. Liu, Y. Zhang and J. Xu, *J. Mater. Chem.*, 2009, **19**, 5541.

12 S. Yoon and S. Park, *J. Mater. Chem.*, 2011, **21**, 8338.

13 W. Yang, D. Kim, M. Jeong, H. Kim, S. Jeon and B. Cho, *Chem. Commun.*, 2003, 2618.

14 H. Kim, W. Yang, C. Kim, W. Park, S. Jeon and B. Cho, *Chem.–Eur. J.*, 2005, **11**, 6386.

15 J. Xu, Y. Fang, P. Ren, H. Zhang, E. Guo and W. Yang, *Macromol. Rapid Commun.*, 2008, **29**, 1415.

16 H. Zhang, E. Guo, Y. Zhang, P. Ren and W. Yang, *Chem. Mater.*, 2009, **21**, 5125.

17 H. Zhang, X. Zhang, B. Zhang and W. Yang, *Mater. Lett.*, 2009, **63**, 2503.

18 P. Ren, Y. Zhang, H. Zhang, X. Zhang, W. Li and W. Yang, *Polymer*, 2009, **50**, 4801.

19 H. Zhang, E. Guo, X. Zhang and W. Yang, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 463.

20 X. Zhang, W. Li, X. Li, T. Liu, Z. Fan and W. Yang, *J. Polym. Sci., Part A: Polym. Chem.*, 2010, **48**, 5704.

21 Y. Zhang, P. Ren, H. Zhang, E. Guo and W. Yang, *J. Lumin.*, 2010, **130**, 527.

22 X. Li, X. Zhang, W. Li, Y. Wang, T. Liu, B. Zhang and W. Yang, *J. Mater. Chem.*, 2011, **21**, 3916.

23 T. Liu, C. Yang, J. Li, L. Bu, M. Zheng, W. Liu and W. Yang, *J. Lumin.*, 2013, **134**, 459.

24 Y. Wang, T. Liu, L. Bu, J. Li, C. Yang, X. Li, Y. Tao and W. Yang, *J. Phys. Chem. C*, 2012, **116**, 15576.

25 L. Bu, M. Sun, D. Zhang, W. Liu, Y. Wang, M. Zheng, S. Xue and W. Yang, *J. Mater. Chem. C*, 2013, **1**, 2028.

26 W. Liu, Y. Wang, L. Bu, J. Li, M. Sun, D. Zhang, M. Zheng, C. Yang, S. Xue and W. Yang, *J. Lumin.*, 2013, **143**, 50.

27 T. Schwaebel, O. Trapp and U. Bunz, *Chem. Sci.*, 2013, **4**, 273.

28 S. Kim, Q. Zheng, G. He, D. Bharali, H. Pudavar, A. Baev and P. Prasad, *Adv. Funct. Mater.*, 2006, **16**, 2317.

29 J. He, B. Xu, F. Chen, H. Xia, K. Li, L. Ye and W. Tian, *J. Phys. Chem. C*, 2009, **113**, 9892.

30 X. Zhang, Z. Chi, B. Xu, L. Jiang, X. Zhou, Y. Zhang, S. Liu and J. Xu, *Chem. Commun.*, 2012, **48**, 10895.

31 (*a*) M. Gholami and R. Tykwinski, *Chem. Rev.*, 2006, **106**, 4997; (*b*) T. Saragi, T. Spehr, A. Siebert, T. Lieker and J. Salbeck, *Chem. Rev.*, 2007, **107**, 1011; (*c*) A. Zucchero, P. McGrier and U. Bunz, *Acc. Chem. Res.*, 2010, **43**, 397; (*d*) G. Bartholomew, M. Rumi, S. Pond, J. Perry, S. Tretiak and G. Bazan, *J. Am. Chem. Soc.*, 2004, **126**, 11529; (*e*) J. Klare, G. Tulevski, K. Sugo, A. Depicciotto, K. White and C. Nuckolls, *J. Am. Chem. Soc.*, 2003, **125**, 6030.

32 (*a*) M. Sase, S. Yamaguchi, Y. Sagara, I. Yoshikawa, T. Mutai and K. Araki, *J. Mater. Chem.*, 2011, **21**, 8347; (*b*) J. Kunzelman, M. Kinami, B. Crenshaw, J. Protasiewicz and C. Weder, *Adv. Mater.*, 2008, **20**, 119; (*c*) N. Nguyen, G. Zhang, J. Lu, A. Sherman and C. Fraser, *J. Mater. Chem.*, 2011, **21**, 8409.

33 (*a*) R. Davis, N. Kumar, S. Abraham, C. Suresh, N. Rath, N. Tamaoki and S. Das, *J. Phys. Chem. C*, 2008, **112**, 2137; (*b*) N. Kumar, S. Varghese, N. Rath and S. Das, *J. Phys. Chem. C*, 2008, **112**, 8429; (*c*) N. Kumar, S. Varghese, C. Suresh, N. Rath and S. Das, *J. Phys. Chem. C*, 2009, **113**, 11927; (*d*) R. Thomas, S. Varghese and G. Kulkarni, *J. Mater. Chem.*, 2009, **19**, 4401; (*e*) Q. Liu, W. Liu, B. Yao, H. Tian, Z. Xie, Y. Geng and F. Wang, *Macromolecules*, 2007, **40**, 1851.

34 J. Demas and G. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.