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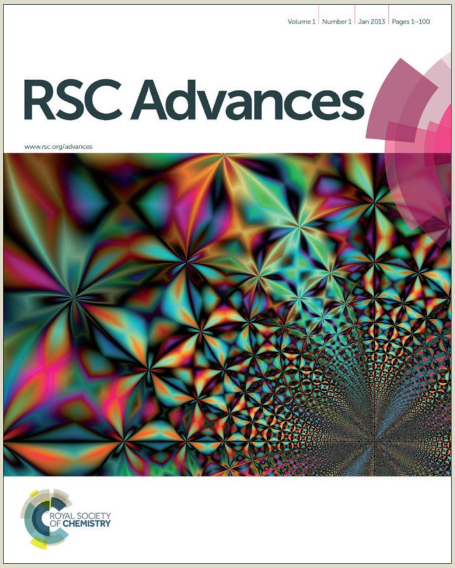

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9,10-Bis(*N*-alkylindole-3-yl-vinyl-2)anthracenes as a new series of alkyl length-dependent piezofluoro-chromic aggregation-induced emission homologues

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The introduction and length-extending of peripheral alkyl chains is usually to improve the solubility of conjugated organic molecules. This article reports the synthesis and optical properties of 9,10-bis(*N*-alkylindole-3-yl-vinyl-2)anthracenes (**IAC*n***) with different alkyl lengths. These homologues exhibit the strong alkyl length-dependent piezofluorochromic (PFC) behaviour, and their PFC spectral shifts are in the range of 27–65 nm. It is found that the shorter the *N*-alkyl length, the larger the spectral shift upon mechanical grinding or pressing. Wide-angle X-ray diffraction evidenced that the mechanical grinding has resulted in destruction of pristine ordered structures, formation of crystal defects, and appearance of some amorphous states, which is responsible for the PFC behaviour.

Introduction

Stimuli-responsive luminescent materials are regarded as a class of "smart" fluorophores whose fluorescence colour and emission change upon external stimuli. Among them, mechano- or piezo-fluorochromic (PFC) materials have recently attracted much attention due to their unique optical properties and potential applications in sensors, data storages, security inks and optical records.[1–3] It is well known that the conjugated organic molecules exhibiting aggregation-induced emission (AIE) are characterized by the strongly twisted conjugation skeleton, which could render them loose inter-molecular stacking and weak π-π interactions in the solid states.[4–7] Such aggregates are usually easy to destroyed upon external stimuli to change the molecular conformations and aggregate morphologies. As a sequence, AIE molecules have become the mainstay of PFC materials reported to date. Moreover the strong solid-state fluorescence of AIE molecules is desirable for observation of PFC phenomenon.[8] In 2010, Chi et al reported first the PFC phenomenon of 9,10-disyryl-anthracene end-capped with other bulky or AIE-active moieties.[9] Since then, a number of simple 9,10-bis(arylvinyl)-anthracene derivatives are also found to show remarkable PFC behaviour,[10–13] and 9,10-bis(arylvinyl)anthracene derivatives have been among the extensively investigated molecules with PFC behaviours at present. We consider that PFC materials with simple and comparable structures, especially those easy-prepared homologues and isomers, are very interesting since they are advantageous to investigation of structure-property relationship. To our knowledge, such molecular design and PFC investigation is still rare although there have been increasing reports on PFC materials. Nevertheless, PFC materials are at the initial state of development, and most identified PFC compounds are isolated facts. Therefore, there is still a great demand on exploitation of new PFC materials with comparable molecular structure and accumulation of relative structure-property knowledge.

Very recently, we and others have found that some alkyl-containing 9,10-bis(arylvinyl)anthracene homologues show different alkyl length-dependent solid-state fluorescence emission and PFC behaviours, for example, 9,10-bis[(*N*-alkyl-carbazol-3-yl)-vinyl-2]anthracenes (**ACZ*n***) with shorter alkyl chains, 9,10-bis[(9,9-dialkylfluorene-2-yl)vinyl-2]anthracenes (**FLA-C*n***) and 9,10-bis(*N*-alkylphenothiazin-3-yl-vinyl-2)-anthracenes (**PT-C*n***) with longer alkyl chains exhibit more remarkable PFC spectral shifts,[12b–d] and 9,10-bis(*p*-alkoxy-styryl)anthracenes (***p*OC*n***) only with sufficient long alkyl chains ($n \geq 10$) are effective PFC materials.[11c,12a,13] These dichotomy PFC behaviours underline the complexity of structure-property relationship and also provide investigation-valuable material systems and stimulate the relative exploitation.[14] To further understand the effect of alkyl lengths on PFC behaviour and develop a new series of PFC materials, in the current work, we have designed and synthesized a series of 9,10-bis(*N*-alkylindole-3-yl)vinyl-2]anthracene homologues (named **IAC*n***, Scheme 1) and their optical properties are investigated. We now report that these compounds are not only effective PFC materials but also exhibit remarkably alkyl length-dependent grinding- or pressing-induced spectral shifts.

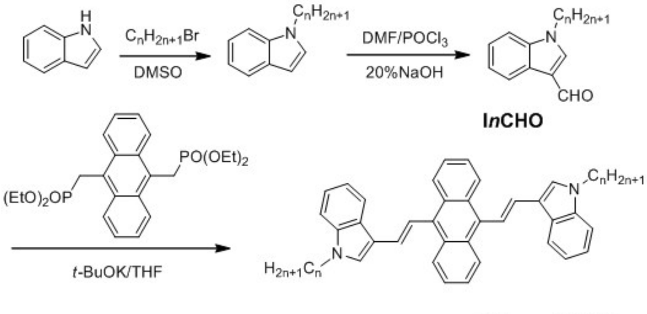
Experimental Section

Regents and solvents

Tetrahydrofuran (THF) was distilled over metallic sodium and *N*,*N*-dimethylformamide (DMF) over calcium hydride before use. Indole, *n*-alkyl bromides, potassium *t*-butoxide, triethyl phosphite, phosphoryl trichloride, paraformaldehyde and others were all commercial available analytical-grade chemicals and were used as received, unless otherwise claimed. 9,10-bis(diethoxylphosphorylmethyl)anthracene was from previous work.[12]

Measurements

^{1}H and ^{13}C NMR spectra were recorded on a Bruker–AC500 (500 MHz) spectrometer with $CDCl_3$ as solvent. The elemental analysis was performed on Perkin–Elmer 2400. Photoluminescence spectra were measured with Hitachi F-4600 spectrophotometer, and the peak wavelength of the lowest energy absorption band was used as the excitation wavelength. Powder wide angle X-ray diffraction (PWXD) measurements were performed on a Powder X-ray Diffractometry (INCA Energy, Oxford Instruments), operating at 3 kW. Differential scanning calorimetry (DSC) experiments were carried out on a Netzsch DSC204F1 at a heating rate of 10 °C/min.



IAC*n*,*n*=2,7,8,12.

Scheme 1. Synthesis and Structure of Cruciform **IAC*n***.

Piezochromic and stimuli-recovering experiments.

Grinding experiment: Pristine **IAC*n*** solid was put on a glass plate and then ground with a metal spatula at room temperature. Pressing experiment: A quantity of **IAC*n*** and KBr powder was simply mixed in a mortar and then pressed with IR pellet press for 1 min at room temperature under the pressure of 1500 psi. Annealing experiment: the ground sample was put into an oven with the temperature 180 °C (**IAC2**) and 90 °C (**IAC7**, **IAC8** and **IAC12**) for 3 min. Solvent-fuming experiment: The ground sample was above the dichloromethane level and was exposed to the vapor for 30 seconds at room temperature. After external stimuli, the fluorescence images and emission spectra were recorded at room temperature.

Synthesis

***N*-ethylindole.** A mixed of NaOH (1.02 g, 25.61 mmol), DMSO (30 mL) and indole (2 g, 17.07 mmol) was slowly added bromoethane (2.23 g, 20.48 mmol) at room temperature overnight. After that, the brine was added to the mixture and the organic phase extracted with dichloromethane was dried over $MgSO_4$. The solvent was removed and residue was purified with column chromatography (silica gel, petroleum ether/dichloro-methane = 10/1, v/v) to give 2.46 g of straw yellow liquid (yield: 99.2 %).

***N*-ethyl-3-formylindole (I2CHO).** A cooled flask in ice bath was added phosphoryl chloride (1.1 mL, 12.12 mmol) and anhydrous DMF (7.6 mL, 99.18 mmol). This mixture was added *N*-ethylindole (1.6 g, 11.02 mmol, in 20 mL sym-dichloroethane). After stirring for 1 h at 35 °C, the reaction temperature was raised to 100 °C and kept for 6 h. The mixture was cooled and poured into ice water and extracted with dichloromethane. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, ethyl acetate/hexane, 1/10, v/v). A solid was obtained (1.89 g, 99.0%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.31 (d, 1H), 7.75 (d, 1H), 7.38 (d, 1H), 7.31 (m, 2H), 4.24 (m, 2H), 1.56 (t, 3H) ppm.

9,10-Bis[(*N*-ethylindole-3-yl)vinyl-2]anthracene (IAC2). 9,10-Bis(diethoxylphosphorylmethyl)anthracene (0.2 g, 0.42 mmol) and *N*-ethyl-2-formylindole (0.16 g, 0.92 mmol) was dissolved in 20 mL of anhydrous THF. Potassium *tert*-butoxide (0.37 g, 3.3 mmol) was added and the suspension was stirred for 3 h at room temperature. Methanol was added into the mixture and a yellow solid was collected by filtration. The crude product was purified by column chromatography (silica gel, petroleum ether/methylene chloride = 4/1, v/v). A yellow solid with a yield of 81.8% (0.18 g) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (m, 4H), 8.14 (d, 2H), 7.90 (d, 2H), 7.44 (m, 8H), 7.34 (t, 2H), 7.27 (t, 2H), 7.12 (d, 2H), 4.25 (m, 4H), 1.56 (t, 6H) ppm. ^{13}C NMR (125MHz, $CDCl_3$) δ 136.90, 133.46, 130.38, 129.80, 127.70, 126.80, 126.31, 124.86, 122.29, 121.02, 120.59, 120.25, 114.42, 109.74, 41.11, 15.42 ppm. Anal. Calcd for $C_{38}H_{32}N_2$: C, 88.34; H, 6.24; N, 5.42. Found: C, 88.30; H, 6.28; N, 5.44.

The other compounds **I*n*CHO** and **IAC*n*** were synthesized as described for **I2CHO** and **IAC2**, respectively. The target compounds were unambiguously characterized by ^{1}H and ^{13}C NMR spectroscopic analysis and the relative data were as follows.

I7CHO: ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.98 (s, 1H), 8.30 (d, 1H), 7.75 (d, 1H), 7.39 (d, 1H), 7.33 (m, 2H), 4.15 (t, 2H), 1.89 (m, 2H), 1.29 (m, 8H), 0.86 (t, 3H) ppm.

I8CHO: ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.99 (s, 1H), 8.31 (d, 1H), 7.77 (d, 1H), 7.38 (d, 1H), 7.29 (m, 2H), 4.14 (t, 2H), 1.86 (m, 2H), 1.25 (m, 10H), 0.86 (t, 3H) ppm.

I12CHO: ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.01 (s, 1H), 8.30 (d, 1H), 7.72 (d, 1H), 7.38 (d, 1H), 7.26 (m, 2H), 4.18 (t, 2H), 1.90 (m, 2H), 1.29 (m, 18H), 0.88 (t, 3H) ppm.

IAC7: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (m, 4H), 8.14 (d, 2H), 7.90 (d, 2H), 7.45 (m, 8H), 7.32 (t, 2H), 7.27 (t, 2H), 7.11 (d, 2H), 4.17 (t, 4H), 1.92 (m, 4H), 1.40 (m, 16H), 0.89 (t, 6H) ppm. ^{13}C NMR (125MHz, $CDCl_3$) δ 137.10, 133.43, 130.39, 129.81, 127.73, 126.82, 126.27, 124.84, 122.27, 121.04, 120.57, 120.20, 114.36, 109.77, 53.39, 46.52, 31.75, 30.20, 29.16, 22.48, 13.88 ppm. Anal. Calcd for $C_{48}H_{52}N_2$: C, 87.76; H, 7.98; N, 4.26. Found: C, 87.69; H, 7.93; N, 4.31.

IAC8: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55 (m, 4H), 8.15 (d, 2H), 7.91 (d, 2H), 7.46 (m, 8H), 7.35 (t, 2H), 7.28 (t, 2H), 7.10 (d, 2H), 4.18 (t, 4H), 1.92 (m, 4H), 1.39 (m, 20H), 0.86 (t, 6H) ppm. ^{13}C NMR (125MHz, $CDCl_3$) δ 137.16, 133.45, 130.41, 129.76, 127.76, 126.79, 126.27, 124.85, 122.23, 120.92, 120.54, 120.18, 114.19, 109.87, 53.41, 46.56, 31.79, 30.24, 29.18, 27.06, 22.45, 14.04 ppm. Anal. Calcd for $C_{50}H_{56}N_2$: C, 87.67; H, 8.24; N, 4.09. Found: C, 87.63; H, 8.27; N, 4.12.

IAC12: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.54 (m, 4H), 8.14 (d, 2H), 7.91 (d, 2H), 7.45 (m, 8H), 7.36 (t, 2H), 7.29 (t, 2H), 7.11 (d, 2H), 4.18 (t, 4H), 1.91 (m, 4H), 1.41 (m, 36H), 0.87 (t, 6H) ppm. ^{13}C NMR (125MHz, $CDCl_3$) δ 137.19, 133.46, 130.42, 129.78, 127.77, 126.80, 126.33, 124.84, 122.23, 120.98, 120.54, 120.18, 114.26, 109.87, 53.41, 46.56, 31.90, 30.25, 29.59, 29.47, 29.39, 29.30, 22.66, 22.44, 22.28, 14.04 ppm. Anal. Calcd for $C_{58}H_{72}N_2$: C, 87.38; H, 9.10; N, 3.51. Found: C, 87.32; H, 9.14; N, 3.54.

Results and Discussion

Synthesis and characterization

Synthetic route and structure of 9,10-bis(*N*-alkylindole-3-yl-vinyl-2)anthracenes (**IAC*n***) are shown in Scheme 1. Alkylation of indole with n-alkyl bromides followed by the treatment with $POCl_3$/DMF afforded *N*-alkyl-3-formylindoles (**I*n*CHO**). **IAC*n*** were facilely prepared by the Wittig-Horner reaction of 9,10-bis(diethoxylphosphorylmethyl)anthracene and **I*n*CHO** in high yields of 80–90 %. Target dyes (**IAC*n***) were unambiguously characterized by ^{1}H and ^{13}C NMR spectroscopic analysis and elemental analysis.

AIE effect

As shown in Fig. 1, all **IAC*n*** derivatives are of aggregation-induced emission (AIE) activity—very weak fluorescence in THF solution but moderately increased fluorescence intensity in THF/water media (1/9 in v/v), indicating the existence of the non-radiative decay induced by relatively free intramolecular torsional motions (ITM) in the molecularly dissolved solution and the restriction of ITM in aqueous aggregation state,[4,9–11] regardless of the length of alkyl chains. However, the fluorescence emissions of **IAC*n*** in THF/water mixtures are not very strong, and the AIE effect is relatively low in terms of the intensity ratio of fluorescence emission in THF/water media and THF solution (α_{AIE}), which are only about 5–11-fold (Fig. 2).

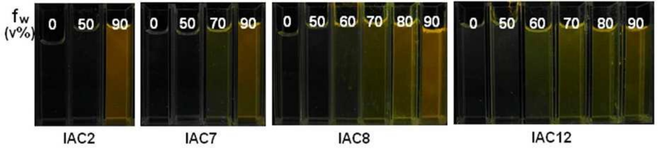


Fig. 1 Fluorescence images of **IAC*n*** at 1.0 × 10^{-5} M in THF and THF/water mixtures under a 365 nm UV lamp (f$_w$ represents the water percent in vol.).

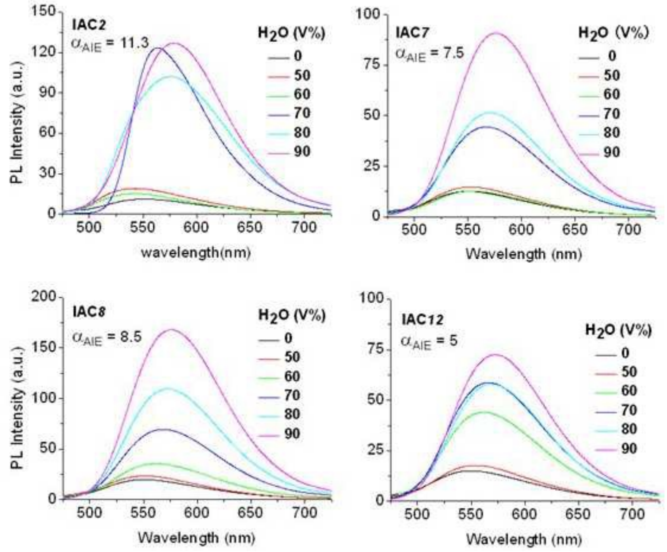


Fig. 2 Emission spectra of **IAC*n*** in THF/water mixtures at 1.0 × 10^{-5} M (excited at 470 nm).

Piezofluorochromic and recovering behaviour

Although AIE activity of **IAC*n*** is unimpressive, their solids emits strong fluorescence. To investigate whether **IAC*n*** exhibit PFC behaviour, the as-prepared solids (pristine) were first simply ground on the glass plate using a metal spatula. It is observed that all the **IAC*n*** solids showed the changed fluorescence colours upon grinding (Fig. 3a). Secondly, the samples mixed with KBr (in order to save fluorophores) were pressed with IR pellet press. Fig. 3b shows the fluorescence images of **IAC*n*** samples upon a cycle of pressing, heat-annealing, repressing and solvent-fuming. All **IAC*n*** samples exhibit changed fluorescence colours upon external stimuli under UV lamp, which are same as grinding experiment in fluorescence colour change. It is noted that, with the decrease of alkyl length, the pressed (ground) states show gradually red-shifted fluorescence colours, and the annealed (pristine or fumed) states exhibit gradually blue-shifted ones. As a sequence, the fluorescence colour contrast between pressed and annealed (or fumed) states becomes more and more striking with the decrease of alkyl length, that is, the shorter the alkyl chain, the more remarkable the PFC behaviour of **IAC*n***. These fluorescence colour changes are reproducible, indicating a reversible PFC behaviour.

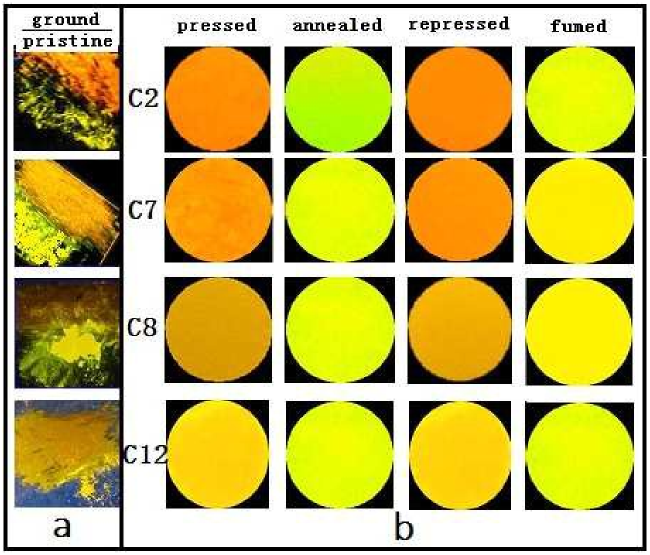


Fig. 3 (a) Fluorescence images of pure **IAC*n*** powder under pristine and ground states. (b) Fluorescence images of **IAC*n*** mixed with KBr under pressed, annealed (3 min, **IAC2** at 180 °C, **IAC7**, **IAC8** and **IAC12** at 90 °C), re-pressed and solvent-fumed states (30 seconds on CH_2Cl_2).

The emission spectra of **IAC*n*** samples upon external stimuli are depicted in Fig. 4, and the corresponding spectroscopic data are summarized in Table 1. The emission spectra are qualitatively consistent with the fluorescence colours observed under UV lamp (Fig. 3 and Fig. 4). The pressing-induced spectral shifts ($\Delta\lambda_{PFC} = \lambda_{pressed} - \lambda_{annealed}$) are in the range of 27–65 nm and increase with the decrease of alkyl lengths. This change tendency in $\Delta\lambda_{PFC}$ for **IAC*n*** is same as that observed in 9,10-bis[(*N*-alkyl-carbazol-3-yl)vinyl-2]anthracenes,[12b] but opposite to that shown in 9,10-bis[(9,9-dialkylfluorene-2-yl)vinyl-2]anthracenes.[12c] To primarily test the optical recording potential of **IAC*n***, the filter papers soaked with **IAC*n*** solution are dried in air and then written using a metal spatula. As an example, **IAC8** only shows the moderate PFC behaviour among **IAC*n***, but a dried filter paper absorbed **IAC8** is drawn a rabbit, a clear pattern with commendable fluorescence contrast is still observed under UV lamp (the inset in Fig. 4). adumbrating the promising potential for mechano-sensing and optical recording.

Table 1. Peak emission wavelengths (λ, in nm) of **IAC*n*** solids under various external stimuli.

Cpds	$\lambda_{pressed}$	$\lambda_{annealed}$	$\lambda_{repressed}$	λ_{fumed}	$\Delta\lambda_{PFC}$[a]
IAC2	592	527	593	535	65
IAC7	581	535	580	546	46
IAC8	576	536	577	548	40
IAC12	564	537	563	539	27

[a] Pressing-induced spectral shift, $\Delta\lambda_{PFC} = \lambda_{pressed} - \lambda_{annealed}$.

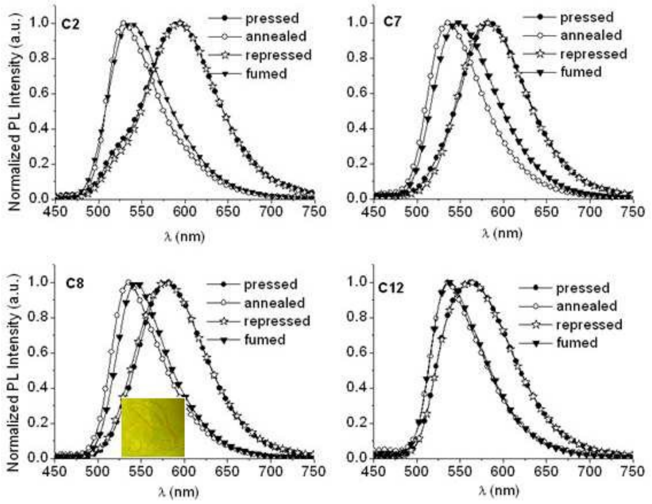


Fig. 4 Normalized emission spectra of **IAC*n*** samples upon external stimuli (excited at 470 nm). Inset: A piece of filter paper soaked with **IAC8** is drawn a rabbit using a metal spatula and illuminated under UV light.

X-ray difraction and DSC analysis

To understand the PFC behaviour of **IAC*n***, we have carried out powder wide-angle X-ray diffraction (PWXD) and differential scanning calorimetry (DSC) measurements on the pristine and ground solids. PWXD measurements reveal these compounds exhibit different structures of molecular aggregation before and after grinding treatment (Fig. 5a). The diffraction patterns of the pristine samples display sharp and intense reflections, indicative of some crystalline order (Fig. 5a). However, the diffraction patterns of the ground samples show broaden and diffuse peaks, indicating destruction of pristine ordered structures, formation of crystal defects, and appearance of some content amorphous states. The existence of residual crystal seeds in the ground states is probably the reason that the ground states could change rapidly back to pristine states upon annealing or solvent-fuming. Fig. 5b shows the DSC curves of pristine and ground **IAC*n*** solids upon heating mode. It is observed that no thermal transition can be detected before the isotropic melt transition, and the melt points decrease with the increase of alkyl length. The decreased melt points could be ascribed to the fact that the long alkyl chains are not advantageous for the close packing of molecules and decrease the intermolecular interactions. Unexpectedly, there is no cold-crystallization phenomenon observed upon heating the ground samples, which is different from those observed in other 9,10-bis(alkylarylvinyl)-anthracene analogues exhibiting alkyl chain length-dependent PFC behaviour, such as **ACZ*n***, **FLA-C*n***, **PT-C*n*** reported previously by our group,[12] indicating that the amorphization does not play an essential role in determining PFC behaviour of **IACn**.

It is noted that the phenomenon that the shorter the N-alkyl chain of **IAC*n***, the more remarkable the PFC behaviour, which is same as that observed in **ACZ*n*** but thoroughly different from those reported in 1,4-bis(4-alkyloxy-α-cyano-styryl)benzenes, **FLA-C*n***, **PT-C*n*** and ***p*OC*n*** in which longer alkyl chains are essential and beneficial for effective piezo-fluorochromism.[12,15] The reason for the contrary dependence of PFC behaviour of these systems on terminal alkyl length is unclear at present. It is only concluded that the different types of π-conjugated backbones and aromatic substituents might involve a different balance between the π-π and aliphatic interactions through the variation of electron density in the central ring and the length of the peripheral aliphatic tails,[15,16] which makes the design of PFC materials and the understanding of the PFC phenomenon at the molecular level more complicated but represent a rich new approach to side chain engineering.

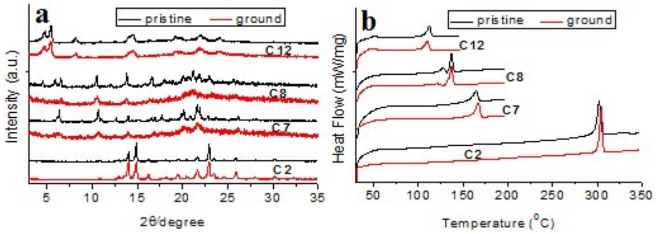


Fig. 5 PWXD (a) and DSC (b) curves of **IAC*n*** under pristine and ground solid states.

Conclusions

We have developed a new series of PFC materials, 9,10-bis(*N*-alkylindole-3-yl-vinyl-2)anthracene (**IAC*n***). Homologous **IAC*n*** can be facilely prepared and exhibit strong and negative alkyl length-dependent spectral shifts of 27–65 nm, i.e. the shorter the *N*-alkyl chain, the more remarkable the grinding- or pressing-induced spectral shifts. The PFC mechanism is ascribed to destruction of pristine ordered structures, formation of crystal defects, and appearance of some content amorphous states upon mechanical grinding evidenced by powder wide-angle X-ray diffraction. The existence of residual crystal seeds in the ground states is probably why the ground states could change rapidly back to pristine states upon annealing or solvent-fuming. This work demonstrates once again that subtle manipulation of end groups of 9,10-divinyl-anthracene derivatives could endow them with unique and tunable solid-state optical properties.

Acknowledgements

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Notes and references

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