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Non-conjugated anthracene derivatives and their mechanofluorochromic properties

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Abstract A series of non-conjugated methylene–anthracene Schiff base derivatives (DNCAs) were designed and synthesized. Photoluminescence emission spectra indicated that DNCA-4 and DNCA-12 showed obviously mechanofluorochromic properties, and distinctive 26- and 37-nm hypochromic shifts were observed, respectively. The experiment results revealed that there is no specific relationship between alkoxy chain lengths and their stimuli–response behavior. The PXRD profiles demonstrated a transformation from crystalline to amorphous state upon grinding.

Keywords Anthracene · Luminescence · Stimuli–response

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Introduction

Mechanofluorochromic (MFC) materials are a kind of smart materials which exhibit fluorescence color changes in response to external pressure [1–6]. In 2001, Tang reported the first kind of solid-state MFC materials [7]. Since then, a number of MFC materials have been successfully developed [8–12], among which 9,10-bisvinylanthracene derivatives (DSA) have become the focus of organic MFC materials [13–19]. These materials emit weak fluorescence in solution but intense fluorescence in the aggregated state. Based on current research, the MFC nature of the above templates could be significantly affected by the peripheral aryl units connected to the 9,10-anthylene core. In addition, the alkyl lengths can significantly influence their MFC properties [20]. However, while many researchers have focused on the MFC properties of conjugated 9,10-bisvinylanthracene derivatives [5, 21–25], research on non-conjugated derivatives has seldom been reported. Therefore, based on the structure of DSA, we modified the molecular structure and further explored the fluorescent and MFC properties of non-conjugated 9,10-bisvinylanthracene derivatives.

In this work, three non-conjugated methylene–anthracene Schiff base molecules (DNCAs) were designed and synthesized. Furthermore, the relationships between the lengths of alkoxy chains and MFC properties were discussed. The optical and MFC properties were determined by UV–Vis absorption spectra and liquid/solid-state photoluminescence (PL) emission spectra. The MFC mechanism was investigated by powder wide-angle X-ray diffraction (PXRD). This work has laid the preliminary foundation for research on solid-state fluorescence materials.

Experimental

Materials and characterization

All the raw materials were obtained commercially and used without further purification. ^{1}H NMR were recorded by using a Bruker Avance 400 MHz spectrometer with $CDCl_3$ as solvent. High-resolution mass spectra were measured on a Bruker Paltonicsmicro TOF-Q II instrument. UV–Vis spectra were performed on an Evolution 300 UV–Vis spectrophotometer. Photoluminescence spectra of solids were obtained with a Horiba Jobin–Yvon Fluorolog-3 spectrophotometer. PWXD measurements were recorded on a Miniflex 600 Powder X-ray Diffractometer of Rigaku, with the following instrument parameters: 35 V, 15 A, and $5°\mathrm{min}^{-1}$.

Synthesis of compound 1 [26]

To a round-bottom flask containing anthracene (1.00 g, 5.60 mmol), paraformaldehyde (0.17 g, 5.6 mmol), CTAB (22.4 mg, 0.06 mmol) and acetic acid (1.4 mL), 4.12 mL HBr aqueous solution (concentration 40%) were added dropwise. The flask was placed under N_2 at 80 °C for 5 h. The mixture was cooled to room temperature and filtered, washed with 100 mL distilled water, dried under vacuum and recrystallized from toluene to give yellow needle-shaped crystals, 0.43 g, 21% yield. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 7.57–7.59 (m, 4H), 7.36–7.33 (m, 4H), 4.46 (s, 4H).

Synthesis of compound 2 [27]

A mixture of compound 1 (0.24 g, 0.66 mmol) and methenamine (0.28 g, 2.00 mmol) was refluxed in 35 mL chloroform for 24 h. The mixture was cooled to room temperature and the yellow solid was isolated by filtration and washed with 30 mL chloroform. The solid was refluxed in 30 mL ethanol and 10 mL hydrochloric acid (37.5%) for 48 h and then cooled to 0 °C. After filtration, the crude product was washed with 50 mL cold ethanol to give the hydrochloride of compound 2. The above compound was dissolved in distilled water. After the pH was adjusted to 8, the solution was extracted three times with chloroform (3×30 mL). The combined organic phases were dried over anhydrous $MgSO_4$ and concentrated to give a yellow solid, 0.11 g, 73% yield.

General procedures for the synthesis of compounds 3 [28]

To a flask containing of 2-hydroxybenzaldehyde (3.00 g, 24 mmol), K_2CO_3 (3.18 g, 30 mmol), 30 mL *N*,*N*-dimethylformamide and KI (catalytic amount), 1-bromobutane (2.40 mL, 27 mmol) were added dropwise. After stirring at 80 °C for 8 h, the mixture was cooled to room temperature and 50 mL of distilled water was added. The mixture was extracted three times with dichloromethane (3×30 mL). The organic phase was washed with 10% NaOH solution (3×30 mL) and distilled water (3×30 mL), respectively, dried over anhydrous $MgSO_4$ and concentrated to give a brown liquid, 3.30 g, 73% yield. Compounds 3–8 and 3–12 were prepared in the same manner.

General procedures for the synthesis of compounds DNCAs

To a flask containing compound 2 (1.27 g, 5.38 mmol) and 3–4 (2.84 g, 16 mmol), anhydrous $MgSO_4$ (2.02 g, 21 mmol) and 20 mL anhydrous dichloromethane were added. After stirring at 35 °C under N_2 for 12 h, the mixture was concentrated, filtered, recrystallized from dichloromethane/methanol (1/2, v/v), and filtered to give a pale yellow solid, 1.27 g, 42% yield. M.p.: 160.1–160.2 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.72 (s, 2H), 8.45–8.42 (m, 4H), 7.95–7.93 (m, 2H), 7.56–7.54 (m, 4H), 6.92 (t, $J = 7.60$ Hz, 2H), 6.80 (d, $J = 8.40$ Hz, 2H), 3.82 (t, $J = 6.40$ Hz, 4H), 1.51–1.44 (m, 4H), 1.15–1.05 (m, 4H), 0.77 (t, $J = 7.60$ Hz, 6H); HRMS (ESI): calcd. for $C_{38}H_{40}N_2O_2$ 556.3084 $[M + H]^+$; found 557.3165.

DNCA-8: white solid, 1.44 g, 40% yield. M.p.: 110.2–110.3 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.77 (s, 2H), 8.46–8.44 (m, 4H), 7.93–7.92 (m, 2H), 7.56–7.54 (m, 4H), 6.91 (t, $J = 7.60$ Hz, 2H), 6.81 (d, $J = 8.40$ Hz, 2H), 3.83 (t,

$J = 6.40$ Hz, 4H), 1.54–1.51 (m, 4H), 1.35–1.19 (m, 21H), 0.93 (t, $J = 7.60$ Hz, 6H); HRMS (ESI): calcd. for $C_{46}H_{56}N_2O_2$ 668.4436 $[M + H]^+$; found 669.4415.

DNCA-12: yellow solid, 1.38 g, 33% yield. M.p.: 81.9–82 °C. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): 8.78 (s, 2H), 8.46–8.44 (m, 4H), 7.94–7.91 (m, 2H), 7.56–7.53 (m, 4H), 6.91 (t, $J = 7.60$ Hz, 2H), 6.81 (d, $J = 8.40$ Hz, 2H), 3.83 (t, $J = 6.40$ Hz, 4H), 1.54–1.51 (m, 4H), 1.30–1.19 (m, 40H), 0.91 (t, $J = 7.60$ Hz, 6H); HRMS (ESI): calcd. for $C_{54}H_{72}N_2O_2$ 780.5588 $[M + H]^+$; found 781.5665 (Scheme 1).

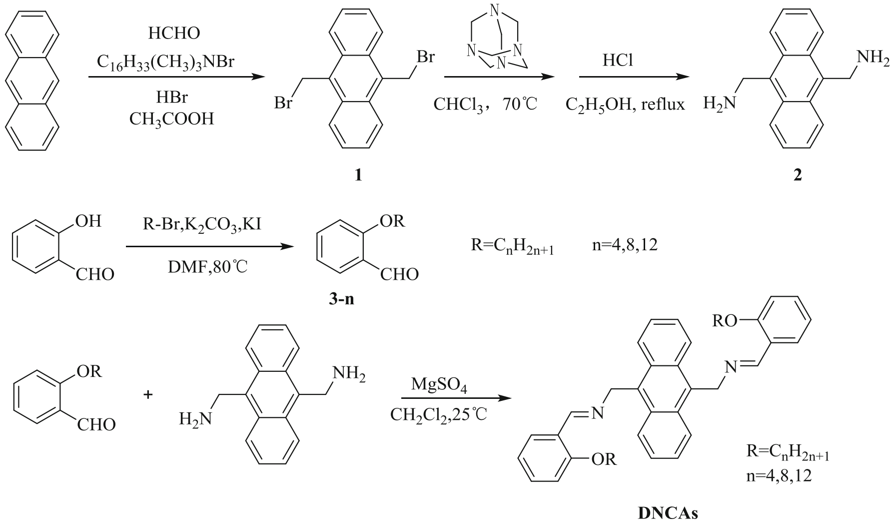
Results and discussion

UV–Vis spectra

UV–Vis absorption spectra of three DNCAs (DNCA-4, DNCA-8 and DNCA-12) were examined. As shown in Fig. 1, the UV–Vis absorption spectra of all three compounds are quite similar ($\lambda_{max} = 254$ nm). The peaks centered at 250 nm can be attributed to π–π* transitions, and the absorption bands located at 380 and 400 nm can be assigned to the weak ICT transition [29].

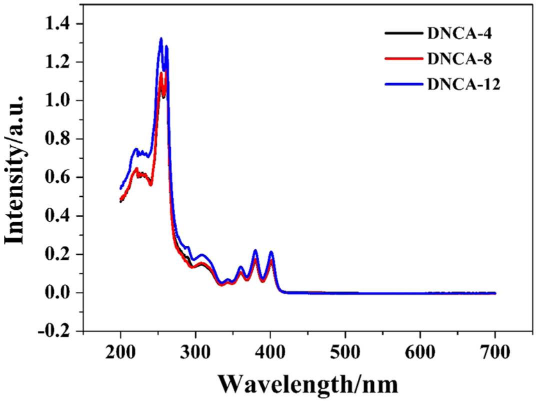
Mechanofluorochromic properties

Mechanofluorochromic properties were examined to explore the optical properties of DNCAs. As shown in Fig. 2, it can be seen that DNCA-4, DNCA-8 and DNCA-12 presented pale yellow, light white and yellow under natural light, respectively. Upon mechanical stimuli, all of them displayed obvious color changes, into faint



Scheme 1 Synthesis and structures of DNCAs

Fig. 1 UV–Vis absorption spectra of DNCAs in THF solution; concentration: 10 μM



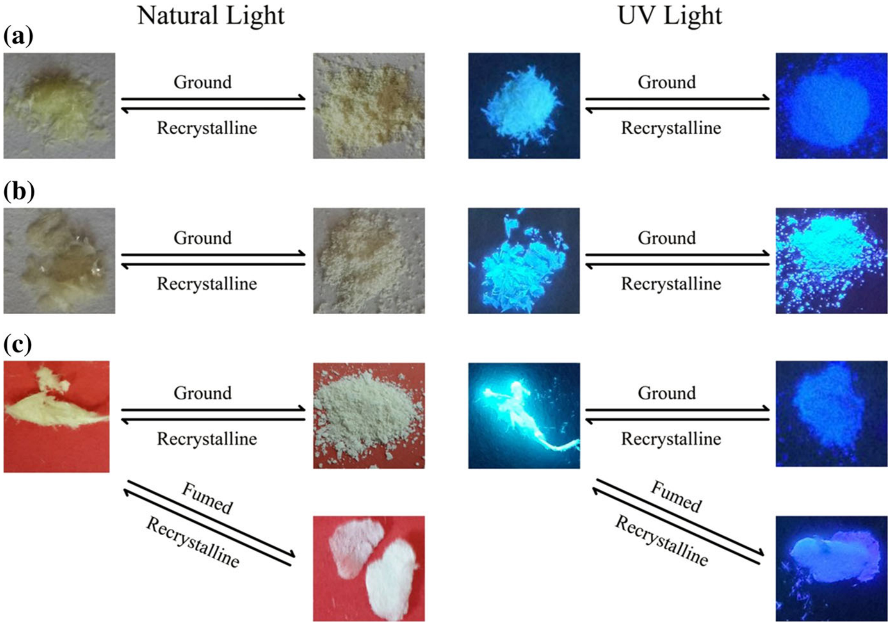


Fig. 2 Emission images of DNCAs before and after grinding under natural light and a 365-nm UV lamp. **a** DNCA-4, **b** DNCA-8 and **c** DNCA-12

yellow, milk white and white, respectively, under natural light. The fluorescence of the ground DNCA-4 and DNCA-12 were changed from cyan to purple, while DNCA-8 still emitted cyan fluorescence under a 365-nm UV lamp, indicating the obvious MFC properties of DNCA-4 and DNCA-12. Furthermore, DNCA-12 was found to be rather special as its fluorescent color could be changed by fuming with DCM. All these samples returned to their original states on recrystallization from DCM/methanol (1/2, v/v). This process indicated the unchanged chemical structures of these compounds despite the changed fluorescence upon grinding or fuming.

To quantify the optical properties of the DNCAs under pressure and fumigation, fluorescence emission spectra of each sample were investigated: (1) the original samples (original); (2) the mixed samples of original samples and KBr under pressure of 2400 psi for 3 min (pressed); (3) the samples annealed under certain temperature for 5 min (annealed); (4) the samples fumigated with dichloromethane (fumed); (5) the original crystals fumigated with dichloromethane (original-fumed); (6) the ground samples (ground); and (7) the ground samples fumigated with dichloromethane (ground-fumed). All these solid fluorescence emission spectra are shown in Fig. 3, and their fluorescence spectra data are listed in Table 1.

It can be seen from Table 1 and Fig. 3 that the DNCAs had different performances in response to grinding and fuming stimulation. The original sample of DNCA-4 exhibited a maximum fluorescence emission peak at 460 nm with two shoulder peaks at 434 and 487 nm. After grinding, the maximum fluorescence emission wavelength shifted to 434 nm along with a shoulder peak at 460 nm, and a 26-nm PL spectrum hypsochromic shift could be seen. For the original sample of DNCA-8, there was a fluorescence emission peak at 442 nm and a shoulder at 464 nm. Both of the ground samples before and after fuming had exhibited a maximum fluorescence emission wavelength at 440 nm with almost no wavelength change. For DNCA-12, the maximum fluorescence emission wavelength exhibited a 37-nm blue-shift after grinding. The fluorescence emission peak of the ground

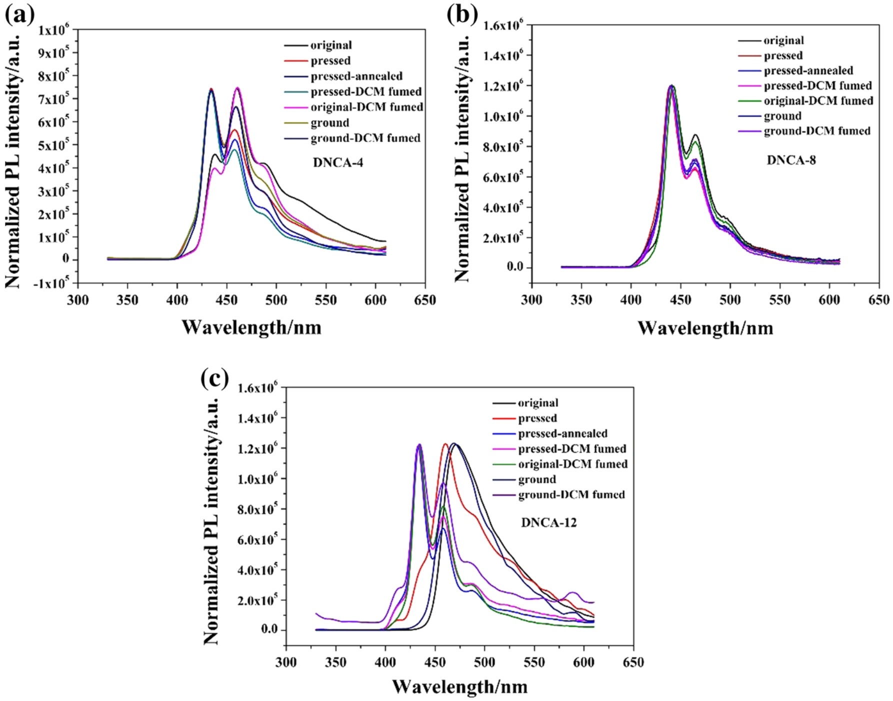


Fig. 3 The PL spectra of DNCAs under original, pressed, pressed-annealed, pressed-DCM fumed, original-DCM fumed, ground, and ground-DCM fumed states

Table 1 Peak emission wavelengths (λ/nm) of DNCAs under various external stimuli

Samples	$\lambda_{Original}$	λ_{Ground}	$\lambda_{Original\text{-}fumed}$	$\lambda_{Ground\text{-}fumed}$	$\lambda_{Pressed}$	$\lambda_{Annealed}$	λ_{Fumed}	$\lambda_{Recrystal}$
DNCA-4	460	434	460	460	434	434	434	459
DNCA-8	442	440	442	440	439	439	439	442
DNCA-12	471	434	434	434	460	432	432	466

$\Delta\lambda$	DNCA-4	DNCA-8	DNCA-12
$\Delta\lambda_1$	26	2	37
$\Delta\lambda_2$	26	3	11
$\Delta\lambda_3$	0	0	37

Ground-induced spectral shift, $\Delta\lambda_1 = \lambda_{Original} - \lambda_{Ground}$

Pressing-induced spectral shift, $\Delta\lambda_2 = \lambda_{Original} - \lambda_{Pressed}$

Fuming-induced spectral shift, $\Delta\lambda_3 = \lambda_{Original} - \lambda_{Original\ fumed}$

sample showed no significant change after fumigating. In conclusion, the maximum fluorescence emission peak of the DNCAs showed blue-shifted mechanofluorochromic properties. However, there was no general regularity between the MFC properties and the changes in alkoxy chain lengths.

As we can see from Fig. 3, the fluorescence spectra of DNCA-4 and DNCA-8 show no difference after fumigation ($\Delta\lambda = 0$ nm), while the maximum fluorescence emission wavelength of DNCA-12 blue-shifted to 434 nm ($\Delta\lambda = 37$ nm). We speculate that the original states of the DNCAs are microcrystalline structures. After grinding, the crystalline structures of these compounds were changed or destroyed, which led to blue-shifts of their fluorescence spectra. When the ground samples were fumigated, these compounds did not recover their original crystalline states. On account of the solvatochromic properties of the DNCAs, we consider that only the original sample of DNCA-12 underwent microcrystalline change during solvent fumigation.

On the other hand, for DNCA-4 and DNCA-8, no fluorescence change upon grinding, annealing or fuming was observed. The PL spectra of DNCA-12 exhibited a blue-shifted tendency upon external pressure. After annealing and fuming, the fluorescence exhibited a further blue-shifted PL spectrum. According to the above results, we believe that the crystals of DNCA-12 could not be effectively changed or damaged upon mechanical stimuli, but could be changed upon annealing or fuming.

PXRD experiments

In order to explore the mechanochromism of DNCAs, PXRD was performed. As shown in Fig. 4, the diffraction patterns of the three original DNCAs exhibited multiple sharp and intense reflections, indicating regular micro-crystalline structures. Upon grinding, the intensity of the diffraction peaks of DNCA-4 decreased and even disappeared, which can be ascribed to the transformation from the crystalline phase to the disorder amorphous state. However, the ground DNCA-12

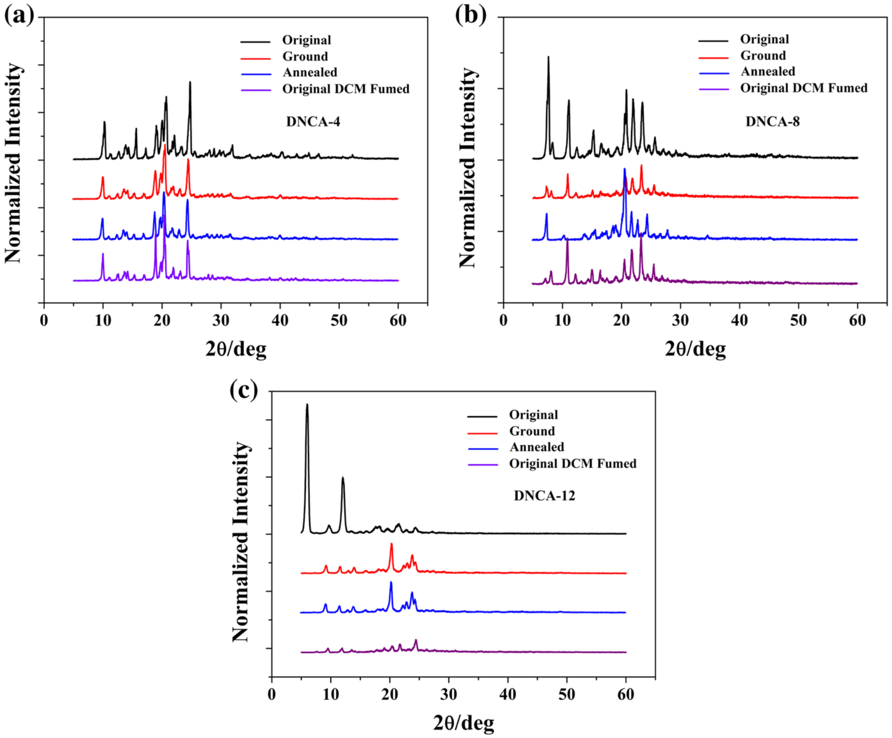


Fig. 4 Powder X-ray diffraction patterns of DNCAs solids

exhibited stronger reflections accompanied by some new peaks, which can be attributed to the transformation between two different crystalline states [30, 31]. As a result, a 26-nm spectral shift ($\Delta\lambda_1$) was obtained. No change could be seen when the ground DNCA-4 compound was annealed. This result illustrated that the disorder amorphous state was not able to return to the crystalline state by annealing. Moreover, for the DCM fumigated form, no spectral shift can be seen from DNCA-4, although the intensity of diffraction patterns distinctly declined. As shown in Fig. 4, DNCA-8 displayed almost no diffraction pattern change. Therefore, there is little relationship between the alkoxy lengths and fluorescence emissions, but molecular stacking plays a leading role in the chromism of the DNCAs.

Conclusion

Three non-conjugated methylene–anthracene Schiff molecules (DNCAs) were designed and synthesized. All these compounds exhibited MFC properties, but there was no specific relationship between the changes of the alkoxy chain lengths and the MFC properties. Among them, DNCA-4 and DNCA-12 obviously showed mechanofluorochromic properties with $\Delta\lambda_1$ ($\lambda_{\text{original}} - \lambda_{\text{ground}}$) of 26 and 37 nm, respectively. However, only a shift of 2 nm was obtained from DNCA-8. PXRD profiles indicated a transformation between two different crystalline states, which might account for the mechanochromism of the DNCAs. We hope our work provide a new way to develop novel MFC materials.

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