

New Thermally Stable Piezofluorochromic Aggregation-Induced Emission Compounds

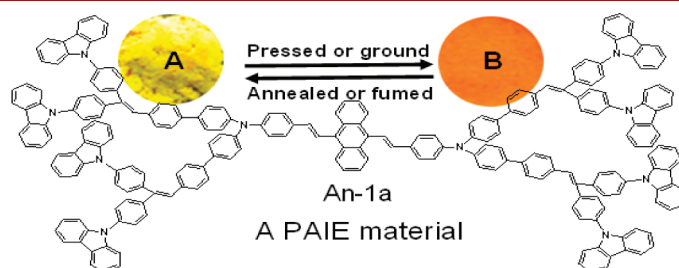
Haiyin Li, Xiqi Zhang, Zhenguo Chi,* Bingjia Xu, Wei Zhou, Siwei Liu, Yi Zhang, and Jiarui Xu*

PCFM Lab and DSAPM Lab, FCM Institute, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-sen University, Guangzhou 510275, China

chizhg@mail.sysu.edu.cn; xjr@mail.sysu.edu.cn

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ABSTRACT



New piezofluorochromic compounds with high thermal stabilities and aggregation-induced emission behavior were developed. The spectroscopic properties and morphological structures of these compounds were reversed upon pressing (or grinding)/annealing (or fuming). The switchable color change feature and aggregation-induced emission make the compounds promising candidates for optical recording, pressure-sensing, and light-emitting systems.

Although modification of molecular structures is the most common approach to controlling fluorescence properties, materials having dynamically reversible fluorescence with high efficiency and speed are quite limited because most chemical reactions in the solid state frequently result in insufficient conversion, irreversible reactions, or loss of fluorescence.¹ To overcome this problem, an attractive approach is to control the solid fluorescence properties dynamically by altering the solid state molecular packing without changing the chemical structure of the

constituent molecules. If a material has a fluorescent color change based on pressure-dependent molecular packing, then it is called a piezochromic fluorescent (PCF) material. Many piezochromic materials based on the change of absorption characteristics under pressure have been reported.² As fluorescence can be detected with high sensitivity, materials exhibiting piezochromic fluorescence have a wide variety of applications, such as optical recording and strain- or pressure-sensing systems. However, PCF materials are exceedingly rare.³ Most of the pure organic

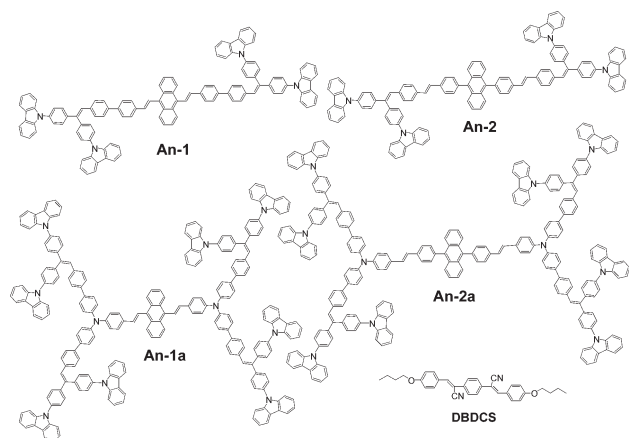
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PCF compounds contain long flexible alkyl or alkyloxy side chains in their molecular structures, which means they should not have good thermal stabilities such as high glass transition temperature and high decomposition temperature. Recently, many fluorescent compounds with high thermal stabilities and aggregation-induced emission (AIE) have been synthesized in our laboratory. Interestingly, most of the AIE compounds are PCF materials and are hereafter labeled by us as PAIE materials. Hence, a relationship in molecular structure between the AIE and the PCF effect is hypothesized. AIE materials are an important class of antiaggregation-caused quenching materials first reported by Tang in 2001.⁴ Since then, a large number of AIE compounds have been developed by various research groups.⁵ Combining the AIE and PCF properties should be very useful in expanding their applications.

Scheme 1. Chemical Structure of the Compounds



However, only one PAIE compound containing two butoxy groups (DBDCS, Scheme 1) has been reported to date in the literature.⁶ In this communication, we report our preliminary investigations on the new PAIE compounds An-1 and An-1a with wholly aromatic structures. For comparison, an isomer of An-1 (i.e., An-2) and an analogue of An-1a (i.e., An-2a) were also investigated. Their chemical structures are also shown in Scheme 1.

An-1 and An-1a are linked by 9,10-anthracene, whereas An-2 and An-2a are linked by 9,10-diphenylanthracene. These differences, however, lead to distinct differences in thermal and photophysical properties (Table S1 in the Supporting Information, SI). All compounds possess very high glass transition temperatures (T_g). The T_g values of

An-1, An-2, An-1a, and An-2a are 196, 201, 223, and 242 °C, respectively. Among them, the T_g of An-2a is the highest. The melting point (T_m) of An-2 is 369 °C, which is ~21 °C higher than that of An-1; the T_m of An-1a is 336 °C, which is lower than those of An-1 and An-2 because of the introduction of triphenylamine and dendritic structures in An-1a. However, the T_m of An-2a cannot be detected, indicating the as-synthesized An-2a is completely amorphous. Their decomposition temperatures (T_d , defined as the temperature at which a minimum of 5% weight loss is observed) were > 491 °C. The results indicate that the compounds have high thermal stabilities. The maximum photoluminescence (PL) emission wavelengths (λ_{em}) of An-2 are blue-shifted relative to An-1 by 53 nm in the solid state and 107 nm in dichloromethane solution. This indicates that the introduction of diphenylanthracene decreases molecular conjugation. A similar effect was observed in the analogues An-1a and An-2a. An obvious blue shift (~32 nm) in the λ_{em} of An-1 is observed by changing the state from solution to solid; An-2, by contrast, shows a 22 nm red shift. An-1a and An-2a exhibit slight red shifts of 6 and 2 nm, respectively. By comparing the emission spectra of An-1 and An-1a, the λ_{em} of An-1a is noticeably longer in the solid state than that of An-1. The reverse is observed in solution.

The PL spectra of 10 μ M An-1a in water/tetrahydrofuran (THF) mixtures with various water content are shown in Figure S1 in the SI. The compound in pure THF exhibits a very weak PL intensity. However, the fluorescence intensity is significantly enhanced when the water fraction exceeds 10%. The PL intensity in pure THF is 5.7, and it increases to ~58.5 in 30% water/THF mixture, a 10-fold enhancement. This indicates that the compound has significant AIE effect. The AIE effect is caused by the formation of molecular aggregates upon adding water to the solution. Similar results were obtained for An-1, An-2, and An-2a (Figures S2–S4, SI), indicating that all of them are AIE compounds. The PL quantum yields were calculated for the compounds in the water/THF mixtures with different water fractions, using quinine sulfate as the reference (Figure S5, SI), which had the similar change tendency with the PL intensity with different water fraction.

The common structural feature of the reported AIE compounds, such as the triphenylethylene,⁷ tetraphenylethylene,⁸ silole,⁹ cyanodistyrylbenzene,¹⁰ and distyrylanthracene¹¹ derivatives, is that multiple peripheral phenyl groups are linked to an olefinic core via rotatable carbon–carbon single bonds to form an AIE moiety. The steric effect between the phenyl rings forces the AIE moieties or the molecules to take a twisted conformation. Due to the

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twisted conformation and the weaker π – π interactions, the molecular packings are relatively loose, leading to defects (cavities). Thus, the crystals are readily destroyed, which may trigger planarization of molecular conformation or slip deformation under external pressure. The collapse of the crystalline structure leads to the planarization of molecular conformation because of the release of twist stress, which is considered as one of the possible reasons for the increased molecular conjugation, thus resulting in a red shift of the PL spectrum and the PAIE behavior. Thus, we propose that if an AIE compound exists in two different pressure-dependent stable or meta-stable states, it will exhibit piezochromic fluorescence.

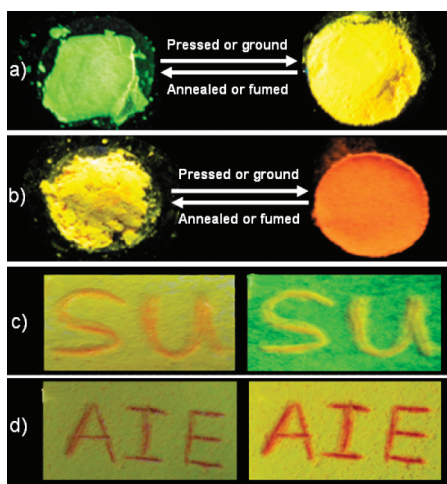


Figure 1. The images of (a) An-1 and (b) An-1a taken at room temperature under 365 nm UV light: (left) as-synthesized samples or annealed samples (at 300 °C, for 5 min); (right) pressed (1500 psi for 5 min) or ground sample. An-1 (c) and An-1a (d) were cast on filter paper and “SU” and “AIE” were written with a metal spatula at room temperature under ambient light (left) and UV light (right).

An-1 and An-1a exhibit significant piezofluorochromic properties. The annealed and fumed (CH_2Cl_2 vapor exposed) samples of An-1 and An-1a show strong green and yellow emissions, respectively, under 365 nm UV light, and after being pressed or ground they show strong yellow and orange-red emissions, respectively (Figure 1a,b). The two emission colors are completely reversible through pressing (or grinding) and annealing (or fuming with a good solvent vapor). When the sample is pressed by streaking a metal spatula across filter paper containing it, a color path was observed (Figure 1c,d). The color change occurred only at the streaked area. Under ambient or UV light, the marked “SU” and “AIE” can be clearly seen on the streaked An-1 and An-1a samples on paper, respectively. The results suggest that these materials have a color-switchable feature that may be a potential for application in optical recording and temperature- or pressure-sensing materials.

However, An-2 and An-2a do not show piezochromic behavior although they possess AIE properties. Opposite behaviors were observed in these compounds (Figures

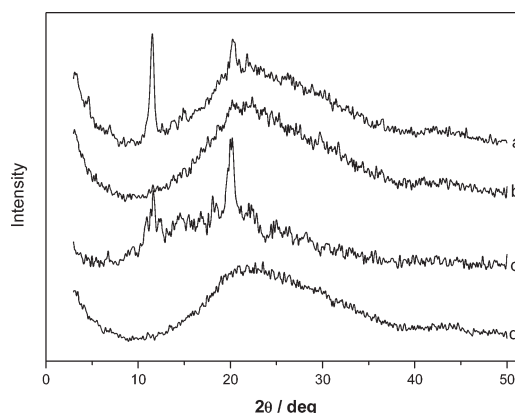


Figure 2. WAXD curves of the sample An-1a: (a) as-synthesized sample; (b) after pressing at 1500 psi for 5 min; (c) after annealing the (b) sample at 300 °C for 5 min; (d) after pressing the (c) sample at 1500 psi for 5 min.

S6–S16, SI). The A and B aryl rings in An-2 and An-2a (Figure S17, SI) are more twisted at $\sim 76^\circ$ dihedral angle, whereas in An-1 and An-1a, this angle was $\sim 60^\circ$. The more twisted bridge structure hinders molecular packing and decreases the degree of crystallization, which was confirmed by wide-angle X-ray diffraction (WAXD). The WAXD results of the as-synthesized An-1 and An-1a samples exhibit sharp and intense reflections at $2\theta < 25^\circ$ (Figure 2a, and Figure S18a in the SI), indicating some crystalline order. However, no such reflections can be observed in the as-synthesized An-2 and An-2a samples (Figures S19a and S20a, SI); hence, these samples may have poor crystallinity or may be amorphous. Given that PAIE behavior depends on the packing change from the crystalline to the amorphous state, the packing structures of initially amorphous An-2 and An-2a do not change under pressure; thus, the two compounds are not PAIE-active. In other words, a relatively stable crystalline state is necessary for PAIE compounds.

Figure 2 shows the WAXD curves of the An-1a samples obtained under different conditions. An-1a exhibits different molecular aggregation structures before and after the pressing treatment. The diffraction curves of the as-synthesized and annealed powders display sharp and intense reflections at $2\theta = 11.6^\circ$ and 20.2° , indicating some crystalline order. The diffraction curves of the pressed or ground sample show a weak, broad, and diffuse peak, indicating an amorphous structure. The amorphous sample obtained by pressing can be reverted to the crystalline state by annealing for a short time (i.e., 5 min) or fuming with a good solvent vapor such as CH_2Cl_2 . Similar results were obtained for An-1 (Figure S18, SI). However, there is almost no difference in WAXD before and after pressing for An-2 and An-2a (Figures S19 and S20, SI). These results indicate that the interchange between crystalline–amorphous packing modes causes the PAIE effect in An-1 and An-1a.

The differential scanning calorimetry (DSC) results of An-1a (Figure 3) have a reproducible cold-crystallization

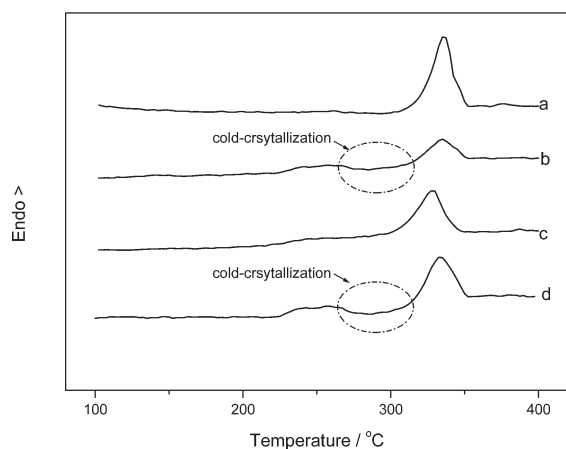


Figure 3. DSC heating curves of the samples: (a) the as-synthesized sample; (b) pressing at 1500 psi for 5 min; (c) annealing the (b) sample at 300 °C for 5 min; (d) pressing the (c) sample at 1500 psi for 5 min.

transition at ~ 290 °C, indicating that the aggregation structure in the pressed sample is a metastable state that transforms into a more stable packing structure through annealing or fuming. The as-synthesized or annealed samples have no such transition. After pressing, the glass transition becomes sharper. The results reveal that the morphological change of the compound induced by pressing is reversible. Similar results were obtained for An-1 (Figure S21, SI). The cold-crystallization transition in the heating DSC curves of the pressed An-2 and An-2a samples is very weak or unnoticeable (Figures S22 and S23, SI). Thus, the cold-crystallization cannot cause a large change in the mode of the packing structure. This finding agrees with the result of WAXD. On the basis of the WAXD results, the annealed samples were crystalline whereas the pressed samples were amorphous. The amorphous pressed samples were converted exothermically to the more stable crystalline state (i.e., annealed samples) after heating beyond the transition temperature. The thermal behaviors are ascribed to an amorphous–crystalline transition, which confirms the mechanism of the stimuli-responsive smart and rewritable natures of An-1 and An-1a.

The PL spectra of the as-synthesized and pressed samples via different excitation wavelengths are shown in Figures S24–S27 in the SI. The spectra of the samples are very different. The emission wavelengths of the pressed samples of An-1 and An-1a significantly red-shifted with the increase in excitation wavelength. The red-shifted emission may be due to the fact that they contain both amorphous and small crystal aggregation states. Two peaks were present in the fluorescence emission spectra.

The peak at the longer wavelength increases and the shorter one decreases with increasing excitation wavelength. However, the emission wavelength of the as-synthesized and annealed samples shows almost no change.

Time-resolved emission decay behaviors of the annealed and pressed samples were studied. The time-resolved fluorescence curves were illustrated in Figures S28–S31 in the SI, and fluorescence decay parameters are summarized in Table S2 in the SI. As can be seen from the table, there are two relaxation pathways in the fluorescence decays. This implies that the time-resolved PL spectra of the compounds include independent emissions from the segments with different π -conjugation lengths because multiple lifetimes have been detected. The two PAIE compounds, An-1 and An-1a, showed significant changes before and after pressing in the weighted mean lifetimes ($\langle \tau \rangle$), from 0.96 to 1.33 ns and from 1.11 to 0.95 ns, respectively. The An-2 and An-2a exhibited little changes in $\langle \tau \rangle$. It is suggested that the changes of $\langle \tau \rangle$ of the PAIE compounds are caused by the changes of their aggregation structures after pressing.

In summary, two new thermally stable piezofluorochromic compounds showing aggregation-induced emission were developed. The T_g is as high as 242 °C for compound An-1a. The spectroscopic properties and morphological structures are reversed upon pressing or annealing. The PL spectra of the two pressed samples depend on the excitation wavelength, and red shift with increase in excitation wavelength. The piezochromic fluorescent nature is generated through a crystalline–amorphous phase transformation. This switchable color feature makes the compounds promising candidates for optical recording, temperature- or pressure-sensing, and light-emitting systems.

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Supporting Information Available. Experimental details and Figures S1–S52 (including PL spectra, PL quantum yields, WAXD curves, heating DSC curves, Time-resolved emission decay curves, and NMR, HRMS, and FT-IR spectra). This material is available free of charge via the Internet at <http://pubs.acs.org>.