Piezofluorochromic Properties and Mechanism of an Aggregation-Induced Emission Enhancement Compound Containing N-Hexyl-phenothiazine and Anthracene Moieties

Xiqi Zhang, Zhenguoh Chi,* Jianyong Zhang, Haiyin Li, Bingjia Xu, Xiaofang Li, Siwei Liu, Yi Zhang, and Jiarui Xu*

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

Supporting Information

ABSTRACT: A fluorescent compound, 9,10-bis(2-(10-hexyl-10H-phenothiazin-3-yl)vinyl)anthracene, has been synthesized and studied. The results show that the compound possesses piezofluorochromic properties as well as aggregation-induced emission enhancement effect. The spectroscopic properties and morphological structures are reversibly exhibited upon pressing (or grinding) or annealing (or fuming). The piezofluorochromatic nature is generated through phase transformation under the stimulus of external pressure. The reason for the phase transformation caused by external pressure is ascribed to the twisted conformation of the molecule which leads to poor solid molecular packing and weak interactions in the interfaces of lamellar layers confirmed by its single-crystal X-ray diffraction analysis.

INTRODUCTION

Piezofluorochromic or piezochromic fluorescent material is a “smart” material whose fluorescent properties can be changed in response to external pressure stimuli. Although modification or alteration of molecular chemical structures is the most common approach to control their fluorescence properties, however, for dynamic controlling of solid state fluorescence with high efficiency, reversibility, and reproducibility, successful examples are quite limited because most chemical reactions in the solid state frequently encounter insufficient conversion, irreversible reactions, or loss of their fluorescence ability. To overcome this problem, a very attractive approach is to control the fluorescence properties dynamically by altering the mode of solid state molecular packing without changing the chemical structure of the constituting molecules. However, piezofluorochromic materials depending on the change of physical molecular packing modes remain extremely rare. Recently, many wholly aromatic aggregation-induced emission enhancement (AIEE) compounds containing phenylvinylanthracene have been synthesized in our laboratory, and it is very interesting to find that some of them have piezofluorochromic nature. These compounds have been called piezofluorochromatic aggregation-induced emission or piezofluorochromic aggregation-induced emission enhancement (PAIE) materials by us as they possess both piezochromatic fluorescence and aggregation-induced emission enhancement properties. AIEE materials are an important class of antiaggregation-caused-emission-quenching materials first reported by Tang and have attracted considerable research attention due to their potential application in various fields such as organic light-emitting devices and chemosensors. Although Park’s group in 2010 reported an AIEE compound [DBDCS, 2,2'-(1,4-phenylene)bis(3-(4-butoxyphenyl) acrylonitrile)] possessing piezofluorochromic property, they did not recognize the existence of a structural relationship between the AIEE compound and the piezofluorochromatic nature.

In this article, we find that 9,10-bis(2-(10-hexyl-10H-phenothiazin-3-yl)vinyl)anthracene, whose structure has already appeared in a patent, has PAIE properties and the piezofluorochromatic nature of AnPh is generated through phase transformation under the stimulus of external pressure.

EXPERIMENTAL SECTION

Materials and Measurements. 9,10-Bis(chloromethyl)anthracene, phenothiazine, and 1-bromohexane purchased from Alfa Aesar were used as received. All other reagents and solvents were purchased as analytical grade from Guangzhou Dongzheng Co. (China) and used without further purification. Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Ultrapure water was used in the experiments. Intermediates 1, 2, and 3 were synthesized according to the literature methods.

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\(^1\)H NMR and \(^{13}\)C NMR spectra were measured on a Mercury-Plus 300 spectrometer [CDCl\(_3\) as solvent] and tetramethylsilane (TMS) as the internal standard. Mass spectra (MS) were measured on a Thermo DSQ MS spectrometer. Elemental analyses (EA) were performed with an Elemental Vario EL elemental analyzer. Fluorescence spectra were measured on a Shimadzu RF-5301pc spectrometer with a slit width of 1.5 nm for both excitation and emission. Differential scanning calorimetry (DSC) curves were obtained with a NETZSCH thermal analyzer (DSC 204 F1) at heating and cooling rates of 10 °C/min under N\(_2\) atmosphere. Wide-angle X-ray diffraction (WAXD) measurements were performed by using a Rigaku X-ray diffractometer (D/max-2200) with an X-ray source of Cu K\(\alpha\) (\(\lambda = 0.15406\) nm) at 40 kV and 30 mA at a scan rate of 4° (2\(\theta\)) per min. Pressed samples or ground samples were prepared by pressing in an IR pellet at 1500 psi for 5 min or by grinding using a mortar and pestle. Annealing experiments were done on a hot stage with an automatic temperature control system. Single crystals of the compound were grown from ethyl acetate solvent. X-ray crystallographic intensity data were collected at 110 K using a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromated Enhance (Mo) X-ray source (\(\lambda = 0.71073\) Å). The structures were solved by direct methods following difference Fourier syntheses and refined by the full-matrix least-squares method against \(F^2\) using the SHELXTL software. The water/THF mixtures with different water fractions were prepared by slowly adding ultrapure water into the THF solution of THF under ultrasound at room temperature. For example, a 70% water fraction mixture was prepared in a volumetric flask by adding 7 mL of ultrapure water into 3 mL of THF solution of the sample. The concentrations of all samples were adjusted to 10 \(\mu\)M after adding ultrapure water.

**Synthesis of 9,10-Bis(10-hexyl-10H-phenothiazin-3-yl)vinyl) Anthracene (AnPh).** Tetraethyl anthracene-9,10-diyliblsis(methylene)diphosphonate (1) (0.10 g, 0.21 mmol) and 10-hexyl-10H-phenothiazine-3-carbaldehyde (3) (0.157 g, 0.50 mmol) were dissolved in THF (20 mL), and then t-BuOK (0.2 g) was added under argon. The solution was stirred at room temperature overnight. After removing the solvent under reduced pressure, the residue was recrystallized with THF/ EtOH to give AnPh (0.16 g, 97% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\): 0.91 (t, 6 H, \(J = 6.6\) Hz), 1.30–1.52 (m, 12 H), 1.87 (qui, 4 H, \(J = 7.2\) Hz), 3.90 (t, 4 H, \(J = 6.9\) Hz), 6.77 (s, 1 H), 6.83 (s, 1 H), 6.86–6.97 (m, 6 H), 7.12–7.21 (m, 4 H), 7.38–7.52 (m, 8 H), 7.75 (s, 1 H), 7.80 (s, 1 H), 8.35 (g, 4 H, \(J = 3.3\) Hz). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) (ppm): 145.15, 136.35, 132.83, 132.05, 129.79, 127.68, 127.47, 126.66, 126.13, 125.53, 125.36, 125.28, 124.53, 123.60, 122.68, 115.60, 47.94, 31.85, 27.28, 27.04, 22.99, 129.79, 127.68, 127.47, 126.13, 125.53, 125.36, 125.28, 124.53, 123.60, 122.68, 115.60, 47.94, 31.85, 27.28, 27.04, 22.99, 14.39. MS (EI), \(m/z\): 792, calcld for C\(_{54}\)H\(_{52}\)N\(_2\)S\(_2\), 792. Anal. Calcld for C\(_{54}\)H\(_{52}\)N\(_2\)S\(_2\): C, 81.77; H, 6.61; N, 3.53; S, 8.09. Found: C, 81.69; H, 6.58; N, 3.49; S, 8.15.

**RESULTS AND DISCUSSION**

The target compound 9,10-bis(10-hexyl-10H-phenothiazin-3-yl)vinyl) anthracene (AnPh) was synthesized according to the routes depicted in Scheme 1. The synthesis of AnPh started from 9,10-bis(chloromethyl)anthracene and phenothiazine, which were purchased from a commercial source. The intermediates tetraethyl anthracene-9,10-diyliblsis(methylene)diphosphonate (1), 10-hexyl-10H-phenothiazine (2), and 10-hexyl-10H-phenothiazine-3-carbaldehyde (3) were synthesized according to literature methods.

\(^{1}\)Wittig–Horner reaction of 1 and 3 afforded the target product AnPh in high yield (97%). The chemical structures of these products were confirmed with proton and carbon-13 nuclear magnetic resonance spectra (\(^1\)H NMR and \(^{13}\)C NMR), mass spectrometry, and elementary analysis. To confirm whether a compound is AIEE active or not, the fluorescent behaviors are usually studied with a poor solvent added to a solution of the compound. As the compound is insoluble in water, increasing the water fraction in the mixed solvents can change its existing form from a solution or well-dispersed state in pure tetrahydrofuran (THF) to aggregated particles in mixtures with high water content. The photoluminescence (PL) spectra of 10 \(\mu\)M of AnPh in the water/THF mixtures with different water contents are shown in Figure 1, which shows that the PL intensity is very weak and observed almost no change as the water fraction of the water/THF mixture increases from 0% to 50%. However, a significant enhancement of luminescence is observed in the water/THF mixture with water fraction >50%. The 5.0 PL intensity (au) in pure THF is elevated to 125.0 in the water/THF mixture with a water fraction of 95%, about 25 times higher than that in the pure THF solvent, which indicates that the compound has strong AIEE activity. However, the PL spectra with 55–65% water fractions are unusual either in intensity or in wavelength. The PL spectra exhibit a significant blue shift with two peaks at 530 and 556 nm, respectively. However, the other PL spectra show only one peak around 570 nm.

The emission images of AnPh in pure THF and 60% and 95% water fraction mixtures under 365 nm ultraviolet (UV) illumination are also shown in Figure 1 (inset). In pure THF, the emission of the compound is very weak and virtually invisible. However, in 60% and 95% water fractions of water/THF mixtures the compound exhibits green and strong yellow emissions, respectively. The images and PL spectra of the compound
in the mixture with 60% and 95% water fractions are different because of the difference in molecular packing mode in the aggregates. Molecules of AnPh form crystal-like aggregates and amorphous aggregates in mixtures with 60% and 95% water fractions, respectively. This phenomenon is evident in many AIEE systems, but the reason for this is still not clear yet. It is generally believed that in the mixture with a "low" water fraction the solute molecules steadily assemble in an ordered fashion to form more emissive, bluer crystalline aggregates, and in the mixture with the "high" water content the solute molecules quickly agglomerate in a random way to form less emissive, redder amorphous particles.24

The common structural feature for the reported AIEE compounds, such as triphenylethylene, tetraphenylethylene, silole and cyano distyrylbenzene, and distyrylanthracene derivatives,25–34 is that the multiple phenyl peripheries are linked to an olefinic core via rotatable C—C single bonds to form an AIEE moiety. The steric effect between the phenyl rings forces the AIEE moieties or the molecules to take a twisted conformation. The optimized geometry of AnPh by Gaussian 0335 at the B3LYP/6-31G level also shows a twist configuration. Between two phenyl rings as defined in Scheme 1 (bottom), dihedral angles for A—B (B—C) and A—C are 66° and 54°, respectively. The twisted configuration makes it difficult for the AnPh molecules to assume a dense packing structure. Thus, the AnPh crystals formed have low lattice energy and some structural defects (cavities) and are easily destroyed by external pressure. It is suggested that this "destroy" may be triggered by slip deformation under external pressure. Destruction of crystalline structure leads to the release of binding energy (lattice energy) and thus planarization of the molecular conformation resulting in a red shift in the PL spectrum. Therefore, we propose that if an AIEE compound exists in two different pressure-dependent stable or metastable states it will exhibit piezofluorochromic activity. As expected, this AIEE compound does exhibit significant piezofluorochromic property. Under 365 nm UV light, the as-synthesized sample (also the annealed sample or fumed sample with a good solvent) shows strong green emission and the pressed (or ground) sample shows orange—red emission (Figure 2, right). In addition, the colors of the samples are also different: the former is yellow and the latter is red (Figure 2, left). This indicates that the pressing (grinding) treatment changes not only its emission spectrum but also its absorption spectrum.

The two colors, either emission or absorption, are completely reversible under treatment with annealing (or fuming) and pressing (or grinding). Therefore, the reversible color change (switchable) features of the compound make it a promising candidate as optical recording, anticounterfeiting, and temperature- or pressure-sensing systems.

If a drop of dichloromethane was dropped onto the surface of pressed or ground sample, the soaked area immediately changed its emission from orange—red to green as well as sample color from red to yellow (Figure 3a). Interestingly, a strong green-emitting yellow solid was converted to an orange—red solid with strong red luminescence even when pressed simply with a metal spatula. The change occurred only at the written area (Figure 3b). Under natural light, it can also be seen red "A&P" on yellow "paper". The results suggest that the material has potential for application as an optical recording material.

Figure 4 shows the PL spectra of AnPh after grinding and annealing treatments. The wavelength changes in solid-state emission could be repeated many times without fatigue, suggesting excellent reversibility in the switching processes. The cycle could also be achieved when ground and fumed with dichloromethane vapor.
To determine the mechanism of the piezo-fluorochromatic effect, we carried out wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) measurements for the samples. According to the WAXD measurements (Figure 5), the compound exhibited different structures of molecular aggregation before and after pressing or grinding treatment. The diffraction patterns of the as-synthesized, annealed, and fumed samples display sharp and intense reflections at \(2\theta = 8.3^\circ, 12.7^\circ, 21.3^\circ,\) and \(36.4^\circ,\) which are indicative of some crystalline order. The diffraction pattern of the sample after pressing or grinding shows a weak, broad, and diffuse peak except for a peak at \(36.4^\circ,\) indicating that after pressing or grinding most of the ordered structures have been destroyed. However, the ordered structures destroyed by pressing or grinding treatment can be restored by annealing or fuming with a good solvent such as dichloromethane for a short time (i.e., 1 min).

In the AIEE section we mentioned that the molecules of AnPh form crystal-like aggregates and amorphous aggregates in mixtures with 60% and 95% water fractions, respectively. We tried to consider the difference in the driving forces of microphase separation between “low” and “high” water fraction systems to explain these findings. In the “high” water fraction system, the driving force must be greater because of the lower solubility of solute molecules in the mixtures. The driving force should play the same role as the external macroscopic pressure. As the compound is piezoresponsive and the external macroscopic pressure causes a change from the crystalline state to the amorphous state, we assume that the driving force of the microphase separation causes formation of amorphous aggregates in mixtures with a high water fraction.

The heating DSC results of the compound (Figure 6) show that after being pressed or ground the samples reproducibly observed a melting—crystallization transition before melting, indicating that the aggregation structure of the pressed sample is in a metastable state which would transfer to a more stable state referring to the crystals of the main melting peak around 202 °C. After being treated by annealing at 100 °C or solvent fuming by dichloromethane for 1 min, the melting—crystallization transition disappears and the shapes of the two DSC curves are almost the same as that obtained from the as-synthesized sample. These results indicate that pressing or grinding treatment causes the change of morphology of the compound, and the change was recoverable through annealing or fuming.
The crystalline structure of AnPh was successfully grown from the ethyl acetate solvent, and its crystalline structure was determined by single-crystal X-ray diffraction analysis. The X-ray crystallographic intensity data were collected at 110 K using a Bruker Smart 1000 CCD diffractometer equipped with a graphite-monochromated Enhance (Mo) X-ray source (λ = 0.71073 Å). The structures were solved by direct methods following difference Fourier syntheses and refined by the full-matrix least-squares method against \( F^2 \) using the SHELXL software. Selected crystallographic data are given in Table 1.

The crystalline structure shows the AnPh molecules are packed in a head-to-head fashion (Figure 8a). Due to the highly twisted conformation and steric hindrance of the bulky phenothiazinyl groups in the molecule, the backbone of the molecule largely deviates from a plane and typical cofacial \( \pi-\pi \) stacking becomes impossible. Instead, the molecules are first packed in clusters via synergetic weak C−H···S, S···π, and C−H···π interactions, and the clusters are followed forming lamellar layer structures via C−H···π interactions. From Figure 9 it can be seen that the interaction between each cluster is not the same. The layers are subsequently connected via the phenyl rings in the phenothiazinyl groups with weaker sparse \( \pi-\pi \) interactions. Due to the twisted conformation and weaker \( \pi-\pi \) interactions, the interfaces between the layers are relatively loose with some defects and the interfaces are the feeblest parts in the crystalline structures. Thus, the interfaces are readily destroyed through slip deformation by external pressure. The dihedral angle of the A−B pair in the single-crystal structure is 71°, which is 7° higher that calculated (64°). The difference between the single-crystal structure and the isolated molecule may suggest that great twist stress exists in the molecule of the crystalline state. Such twist stress is believed to be released when triggered by external pressure, which causes the loss of the long-ranged order of the crystal structure and planarization of molecular conformation. Planarization of the molecular conformation results in an increase of the molecular conjugation and a red shift of the PL spectrum.

Table 1. Crystallographic Data of AnPh

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<th>Value</th>
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<tr>
<td>( fw )</td>
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<td>temp., K</td>
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<td>wavelength, Å</td>
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<tr>
<td>cryst syst</td>
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<tr>
<td>space group</td>
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<tr>
<td>( a ), Å</td>
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<tr>
<td>( b ), Å</td>
<td>17.681(3)</td>
</tr>
<tr>
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<td>111.793(3)</td>
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<tr>
<td>( \beta ), deg</td>
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<td>( \gamma ), deg</td>
<td>92.295(3)</td>
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<td>( V ), Å(^3)</td>
<td>2054.4(6)</td>
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<tr>
<td>( Z )</td>
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<tr>
<td>( d(\text{calcld}), \text{Mg/m}^3 )</td>
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<tr>
<td>( F(000) )</td>
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<td>no. of independent refinfs</td>
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<td>R indices (all data)</td>
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<tr>
<td>largest diff. peak and hole</td>
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</table>

Figure 8. Molecules packing in a crystal cell (a), and the schematic intermolecular interactions in a cluster (green dashed lines, hydrogen atoms omitted for clarity) (b).

Figure 9. Molecules packing in single-crystal structure.
room temperature (Figure S1, Supporting Information) the major reflections were almost the same, indicating both of them had the same crystal structure and it was considered that the analysis on the mechanism was suitable by the single-crystal structure. In other words, this proposed mechanism is suitable to explain the piezofluorochromic phenomena.

**CONCLUSIONS**

A piezofluorochromic compound was synthesized. The spectroscopic properties and morphological structures were reversibly and repeatedly exhibited upon pressing (or grinding) or annealing (or fuming). The piezofluorochromic nature is believed to be generated through phase transformation. It is proposed that the twisted conformation of an aggregation-induced emission enhancement compound is the key factor in determining its piezofluorochromic activity, and the common structure–property relationship will guide researchers in identifying and synthesizing more piezofluorochromic materials.

**ASSOCIATED CONTENT**

Supporting Information. CIF file of the compound and Figure S1. This material is available free of charge via the Internet at http://pubs.acs.org.

**AUTHOR INFORMATION**

Corresponding Author

*E-mail: chizhg@mail.sysu.edu.cn; xjr@mail.sysu.edu.cn.

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