Mechanical force induced reversible fluorescence switching of two 3-aryl-2-cyano acrylamide derivatives

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ABSTRACT

Two structural-simple 3-aryl-2-cyano acrylamide derivatives (CDPA-E and CDPA-P) were synthesized and characterized by NMR, MS, IR, and single crystal. It was found that both of them exhibited obvious piezofluorochromic properties. The as-prepared yellow-green compounds were both converted to orange-red after grinding with a spatula. All the ground samples can be recovered to its original color by heating at 80 °C over 5 min or fuming with solvents like DCM, ethanol, ethyl acetate etc. The changes in fluorescence color can be attributed to the phase transition between crystalline (order) state and amorphous (disorder) state according to the Powder XRD spectrum. At the molecular level, the extension of the conjugation length and the formation of excimers are confirmed to account for the color transition of CDPA-P and CDPA-E, respectively. In addition, CDPA-P exhibited AIE activity which was caused by the restricted rotation of the molecules in the crystal state.

Introduction

Stimuli-responsive materials have attracted much attention due to their potential applications in sensors,1–3 memories,4–7 and security inks.8 Piezochromic fluorescent (PCF) materials are a kind of materials that change their fluorescent properties in response to external pressure stimuli.9–11 The molecule packing in the solid state transforming between crystalline and amorphous states or between crystalline and crystalline states is responsible for the tunable fluorescence, which is accompanied by the changes in molecular conformation.12–18 The π–π overlap that is adequately altered by the reorganization of molecular packing modes would also result in delocalization of excited states and induces a shift of wavelength.

The adequate fluorescence efficiency is required for the organic luminescent materials. But lots of them often become very weak in the aggregated state because of the aggregation-caused quenching (ACQ) effect,19 which largely restricts their practical application. In 2001, Tang and co-workers reported an important class of aggregation-induced emission (AIE) materials, which can emit more efficiently in the aggregated state.20,21 In 2010, Park and co-workers reported an important class of AIE-active molecules, such as α-cyano-substituted stilbene derivatives, diphenyldibenzofulvenes, tetrphenyl-ethene, and 9,10-divinylanthracenes end-capped with or without other bulky or AIE-active moieties has also been reported.22–31

As we all know, adequate fluorescence efficiency is essential for people to investigate the PCF behaviors. In 2002, P. Bosch found that 2-cyano-3-(4-(diethylamino)phenyl)acrylamide can be used as fluorescent sensors to monitor the photopolymerization reactions for its good fluorescent efficiency and its sensitivity.32 Its simple structure and high fluorescence efficiency gave us deep impression.

To expand the PCF materials and investigate the relationship between the structure and piezochromism, we synthesized these two 3-aryl-2-cyano acrylamide derivatives that have the PCF behaviors by chemical modification based on its framework. And CDPA-P was also found to have the AIE activity. Though both of them exhibited the PCF properties, the different molecular stacking was observed by X-ray crystal structure.

Results and discussion

2-Cyano-3-(4-(diethylamino)phenyl)acrylamide (CDPA-E) and 2-cyano-3-(4-(diphenylamino)phenyl)acrylamide (CDPA-P) were synthesized by Knoevenagel reaction as shown in Scheme 1. The
products were fully characterized by spectroscopic methods from which satisfactory analysis data were obtained.

To determine whether the compounds have the AIE properties, the ultraviolet-visible (UV) absorption and photoluminescence (PL) emission behaviors of their diluted mixtures were studied in the THF–water mixtures. Both of the compounds were soluble in THF and insoluble in water. Thus, increasing the water fractions in the mixed solvents would cause the monomer in pure THF into aggregated particles. As depicted in Figure 1, the PL intensity of CDPA-P in dilute THF solution was rather weak. The emission intensity of sample was slightly decreased with water content increasing, but abruptly bounced (nearly 6 times higher than the intensity of 10%) when water content got to 90%. This may be caused by the restricted intramolecular rotation which inhibits the nonradiative decay as CDPA-P molecules aggregate. To confirm the assumption, the relationship between solution viscosity and fluorescent intensity was also investigated. As shown in Figure 2, the much stronger intensity was found in the mixture of ethanol and glycol than that in the ethanol. All these experiments verified the restricted intramolecular rotation mechanism which might be responsible for the aggregation induced emission behavior. In the dilute solution, the molecule of CDPA-P rotated freely which facilitated the non-radiative relaxation pathways and afforded weak fluorescent emission. However, the aggregates that were made by increasing the content of water or by adding the viscous glycol restricted the intramolecular vibration and rotation to endow the aggregated samples with enhanced emission. As can be seen from Figure 3, the CDPA-E did not have the same phenomena when the water was added to its THF solution. The intensity of CDPA-E was slightly increased when the water was added to 50%, but the intensity was decreased when the water was further increased.

The phenomenon may be explained by its planar configuration. For CDPA-E, upon adding low ratio water, it can bring a little aggregation with blocking the possible intramolecular rotation to some extent, resulting in a slight increase in fluorescence when the water was added to 50% (Fig. 3), but upon higher ratio of water, the intensity is decreased which might originate from the heavy π–π aggregation due to the good planar conformation of CDPA-E. The absorption spectra of CDPA-E in the THF–water mixtures (1 μM) are shown in Figure 4. The spectral profile was slightly increased with the continual add of water. As for the CDPA-P, a similar phenomenon was observed that the spectral was increased with the adding of water. But when 80% water was added, the spectral began to decrease. This may be attributed to the formation of the nanoaggregates. The light scattering or Mie effect of the nanoaggregates suspensions in the solvent mixtures effectively decreased the light transmission.

The two compounds show the similar piezochromic properties. Take dye CDPA-E for example, it emits yellow fluorescence under the UV lights (365 nm). Upon grinding with a spatula, the color subsequently becomes orange-red. The ground powders can also be recovered to the original state by heating at 80 °C over 5 min or fuming with the solvent vapors such as the dichloromethane, ethyl acetate, and tetrahydrofuran. The similar phenomena can also be seen in the compound of CDPA-P, the yellow-green solid is transformed into orange-red when grinding with a spatula as depicted in Figure 5.

To further investigate the piezochromic properties, spectroscopy measurements were performed in detail. As shown in Figure 6, the CDPA-E crystals revealed the emission peak at 524 nm and red-shifted to 556 nm after grinding (about 32 nm red shift), and the PL spectrum of CDPA-P crystals is red-shifted from 520 nm to 560 nm (about 40 nm red shift). All the ground samples can return to its original state. In general, the red-shift in the PL spectrum can be attributed to the increasement of the conjugate length. Besides, the excimer formation of the fluorescent molecules could also induce a red shifted emission. If the increasement of the conjugate length causes such a red shift in the emission spectra, the absorption spectra should also exhibit a similar change. As to the excimers' case, the absorption spectra of the as-prepared sample and ground sample should remain the same. As shown in Figure 7, the ground CDPA-P exhibits remarkable red-shift, indicating the piezochromism is probably caused by the extended molecular conjugation instead of the formation of excimer. As to the CDPA-E, the formation of excimer might be responsible for the piezochromism, since CDPA-E had almost the same curve UV spectrums. The experiment of time-resolved fluorescence further verified the guess we proposed above and the lifetime data.
are illustrated in Table 1. The fluorescence decay behavior of CDPA-E sample revealed a single-exponential decay with the lifetime of 6.84 ns. While the ground CDPA-E sample was fitted by a double-exponential decay which revealed the mixture of two distinguished emission states in the amorphous phase. The longer lifetime of 12.65 ns indicated the formation of excimers after pressing.

To further determine the piezofluorochromism mechanism, wide-angle X-ray diffraction (WAXD) and differential scanning calorimetry (DSC) were conducted. The WAXD curves of compound CDPA-E and CDPA-P showed different molecule stacking before and after pressing (see Fig. 8). The diffraction curve of the as-prepared samples all revealed numerous sharp and intense reflections which indicated an ordered structure. However, the diffraction curve of the ground CDPA-P sample became a weak, broad, and diffused peak due to an amorphous structure. While the ground CDPA-E sample showed the combination of the crystalline state and amorphous state. And the ground samples could be recovered to the crystal state after the treatment of fuming with solvents or heating. These observations demonstrated that the ground powders could return to the original phase by heating or recrystallization.
The WXRD curves confirmed that grinding had induced the phase transition between crystalline and amorphous states, which should be responsible for the PCF behavior. DSC experiments could also be used to indicate the phase transition. Figure 9 showed that no additional thermal transitions are detected for all the pristine solids before their melt transition \(T_m\). However, two obvious cold-crystallization peaks at approximately 59.3°C and 129.5°C were observed for the ground samples of CDPA-E and CDPA-P, respectively. All these findings suggested that the amorphous states existed and could be transformed into a more stable state through heating.

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### Table 1
Solid-state fluorescence lifetime data of CDPA-E and CDPA-P samples in original and ground state

<table>
<thead>
<tr>
<th>Type</th>
<th>(t_1^a) (ns)</th>
<th>(t_2^a) (ns)</th>
<th>(A_1^b) (%)</th>
<th>(A_2^b) (%)</th>
<th>(\tau^c) (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CDPA-E</td>
<td>Original</td>
<td>6.84</td>
<td>100</td>
<td>6.84</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Grinding</td>
<td>3.00</td>
<td>12.65</td>
<td>38.56</td>
<td>61.44</td>
</tr>
<tr>
<td>CDPA-P</td>
<td>Original</td>
<td>1.90</td>
<td>4.54</td>
<td>46.81</td>
<td>53.19</td>
</tr>
<tr>
<td></td>
<td>Grinding</td>
<td>1.10</td>
<td>4.59</td>
<td>70.77</td>
<td>29.23</td>
</tr>
</tbody>
</table>

\(^a\) Fluorescence lifetime.

\(^b\) Fractional contribution.

\(^c\) Weighted mean lifetime.

Figure 6. The normalized PL spectra of CDPA-E (left) and CDPA-P (right) with different treatment.

Figure 7. Normalized solid UV–vis absorption spectra of the as-prepared and ground of CDPA-E (left) and CDPA-P (right) samples.

Figure 8. WAXD curves of the sample CDPA-E (left) and CDPA-P (right).
Further single crystal structures of the compounds provided more insights into piezochromic mechanisms. The crystal structure of CDPA-P containing four molecules in the unit cell was monoclinic with the space group \( P_{2}(1)/c \). As can be seen from Figure 10, it had a highly twisted conformation to fit in the crystalline lattice. And C–O...H interaction and two types of N–H...O interactions were found between adjacent molecules with a distance of 2.177 Å, 2.409 Å and 2.702 Å, respectively (see Fig. 11). These multiple interactions locked and rigidified the molecular conformation which increased the fluorescence quantum efficiency. The twisted conformation and weak interaction made the structure to be easily destroyed and a planarity conformation may be formed when external force was applied which has been demonstrated by the UV–vis absorption. As for dye CDPA-E, the single crystal consisting of two molecules belong to the \( P-1 \) triclinic space group. As revealed in Figure 12, numerous intermolecular interactions were observed. Those interactions made the molecules stacked in a cofacial arrangement which caused the fluorescence quantum efficiency of CDPA-E (24.6%) much lower than CDPA-P (38.3%). Upon grinding, part of the intermolecular \( \pi-\pi \) interactions was found to be stronger as verified by the rather long fluorescence lifetime while part of them was weaker accompanied by the shorter fluorescence lifetime as revealed in Table 1.

In summary, two 3-aryl-2-cyano acrylamide derivatives were successfully synthesized and the relationship between structures and luminescent behavior was investigated. Both derivatives...
exhibited PCF properties and the CDPA-P also had the AIE activities. Their color changes were mostly due to the crystalline–amorphous phase transformation. The planarization of the molecular conformation and the formation of excimers can further account for the color transition of two different derivatives, respectively at the molecular level. And the AIE property of CDPA-P was caused by the restricted intramolecular rotation of the molecules at the aggregated state. We hope our study can increase the knowledge on the relationship between molecular structure and luminescent behavior.

Acknowledgments

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Supplementary data

Supplementary data (detailed synthesis of CDPA-E and CDPA-P, NMR and Crystal data for CDPA-E and CDPA-P) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2014.04.024.

References and notes

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