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Novel highly emissive H-aggregates with aggregate fluorescence change in phenylbenzoxazole-based system

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Fibrous nanoaggregates of a new benzoxazole-based derivative have been reported. It exhibit not only H-aggregates but also highly yellow fluorescence, which is different from the traditional understanding of H-aggregates.

Designing novel chromophores with excellent optical properties in the condensed state have been a popular research for their potential applications in organic light emitting diodes (OLEDs), fluorescent sensors and sensors. The restriction of intramolecular rotation (RIR) or planarization and J-aggregation reported by Tang and Park are in favor of enhancing emission. The frequently reported aggregation-caused quenching fluorescence (ACQ) in H-aggregates has greatly limited their potential applications. At present, various excellent chromophores with aggregation-induced emission or enhanced emission (AIE/AIEE) properties have been developed by many research groups, such as tetraphenylethene, cyanostilbene and 9, 10-distyrylanthracene derivatives, which all avoid the H-aggregate.

Scheme 1 (a) The molecular structure of 2a, 2b and 2c, (b) The photos of powder and crystal of 2b under UV light.

Considering interesting fluorescence properties of benzoxazole, we utilized benzoxazole as building blocks and changed the terminal substituents to build new phenylbenzoxazole-based chromophores. The structures of targeted molecules are shown in Scheme S1. In this communication, we reported the highly emissive H-aggregate 2b and the unique AIEE phenomenon with large red shifts and remarkable color change. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) results indicate that all compounds hold high melting points with T_m at 139.9, 235.8 and 201.9 °C (Tab 1), respectively, and high thermal stability with T_g at 294, 273 and 294 °C (Tab 1), respectively.

We initially investigated the absorption and fluorescence spectra of 2a-2c (10 µM) in various polarity solvents (Tab S1 and Fig. S1, ESI†). The absorption and fluorescence spectra of 2a-2c demonstrate quite similar maxima in the different solvents meaning the slight solvent-dependence. The targeted molecules show strong absorption bands at 388, 327 and 414 nm, respectively, and emission maxima (λem) at 499, 389 and 495 nm, respectively. The weak absorption peaks at 300-320 nm that are mainly attributed to π-π* electronic transitions derived from the benzoxazolyl-benzene unit. The molar extinction coefficient values also are in agreement with π-π* transitions. Theoretical calculations are liable method for qualitative indication of the absorption properties. We calculated frontier molecular orbital potential applications in organic light emitting diodes (OLEDs). Further details are given in the ESI and the results are in good agreement with the experimental absorption spectra. All data indicate that the introduction of diethylamino groups can change the π-conjugated degree of benzoxazolyl compounds.

Tab 1 Optical properties of the targeted molecules.

<table>
<thead>
<tr>
<th>Compd</th>
<th>λ_{max}/nm</th>
<th>Pure</th>
<th>Mixed</th>
<th>Powder</th>
<th>Crystal</th>
<th>T_m/(°C)</th>
<th>T_g/(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>388</td>
<td>499</td>
<td>518</td>
<td>552</td>
<td>593</td>
<td>139.9</td>
<td>294</td>
</tr>
<tr>
<td>2b</td>
<td>327</td>
<td>389</td>
<td>542</td>
<td>581</td>
<td>588</td>
<td>235.8</td>
<td>273</td>
</tr>
<tr>
<td>2c</td>
<td>414</td>
<td>495</td>
<td>564</td>
<td>564</td>
<td>564</td>
<td>201.9</td>
<td>294</td>
</tr>
</tbody>
</table>

λ_{max} = the maxima absorption peak, λ_em = the maxima emission peak, in dilute ethanol solution (10⁻³ mol L⁻¹), Pure = the pure ethanol solution, Mixed = the mixed water/ethanol solution with f_w = 90%, T_m = temperature for 5% weight loss, T_g = melting temperature recorded by differential scanning calorimeter.

Fig 1. The fluorescence spectra of 2b and 2c in water/ethanol mixtures with different water fraction (f_w). The inset depicts the changes of PL peak intensity with different f_w. Photos of 2b and 2c in the water/ethanol mixtures with different f_w are taken under UV light. Concentration: 50 μM.

2a-2c molecules exhibit weak green, blue and cyan emission in diluted ethanol solution under UV light (The inset in Fig S2, ESI† and Fig 1), respectively. Firstly, the fluorescence intensity of 2a is almost linearly increasing step by step with the increasing of water fraction, accompanying with red-shift in the λ_em values. The light emission reaches its maximum value when f_w = 70%, which is 6.4-fold higher than that in pure ethanol solution. 2b plays different fluorescent behaviors in ethanol/water solutions with different f_w values. Upon addition of water, the emission intensity and wavelength show a slight decrease and red shift, respectively. When f_w ≥60% (Fig 1), the yellow emission band centred at 542 nm rapidly turn on. The inset photos (Fig 1) taken under UV light describe the color change and we can clearly see that the blue the solution vividly transfer into yellow. In addition, 2c also exhibits...
the changes of the emission from cyan to orange with red-shift of 70 nm after addition of different amount of water. The fluorescence intensity remain unchanged until the f<sub>em</sub> is increased to 60%, the solutions emit bright yellow light with λ<sub>em</sub> at 528 nm. The emission intensity reaches its maximum value at f<sub>em</sub> = 70% and the λ<sub>em</sub> red shift to 564 nm when f<sub>em</sub> = 90%. Such ratiometric fluorescence changes with a large red-shift of 150 and 70 nm for 2b and 2c in benzoxazole-based compounds has so far never been reported, not to mention the impressive color changes. These nanoparticle in ethanol/water mixtures (Fig S3c, ESI†). These unique AIEE behaviors are very significant in the field of fluorescent probes. The absorption spectra of 2a and 2c show a slight bathochromic shift and level-off tail in the long-wavelength regions. The tail is caused by the Mie scattering effect, which suggests the formation of nanomaterials. While the absorption spectrum of 2b exhibits a slight blue-shift and arises a few new absorption peaks between 370 and 420 nm when f<sub>em</sub> ≥60%, which indicate the formation of new species.

To gain further insight into the unique morphology of the nanoaggregates of these benzoxazole-based compounds in the mixture system, the mixture solutions was subjected to the scanning electron microscopy (SEM) observation. As can be seen from the photos shown in Fig 2a and Fig S3, three benzoxazole-based compounds aggregate to form three different shapes in the mixture system. A large number of block nanoparticles of 2a formed immediately in the mixture of ethanol/water with f<sub>em</sub> = 80% (Fig. S3a, ESI†). It is noteworthy that 2b molecules aggregate to form entangled three-dimensional networks consisting of the interconnected fibrous nanomaterials, which has so far never been reported in benzoxazole-based compounds (Fig. 2a). For 2c, it aggregates into the rice-like shape nanoparticles in ethanol/water mixtures (Fig S3c, ESI†). These above mentioned images must be responsible for the observed enhanced emission and the impressive color changes.

All compounds exhibit the minimum emission wavelength in the pure ethanol solution and the maximum emission wavelength in the crystal state. 2a and 2b show the same trend: λ<sub>em/Pure</sub> < λ<sub>em/Mixed</sub> < λ<sub>em/Powder</sub> < λ<sub>em/Crystal</sub>, while 2c displays λ<sub>em/Pure</sub> < λ<sub>em/Mixed</sub> ≈ λ<sub>em/Powder</sub> ≈ λ<sub>em/Crystal</sub>. According to some other AIE/AIEE-active system, the reasons for these unique fluorescent behaviors can be tentatively ascribed to the different molecular conformations and packing modes in the different states. In the pure ethanol solution, these compounds molecules are molecularly isolated without any interactions between the adjacent molecules, and the molecules have highly twisted conformations due to the intramolecular steric hindrance, which leads to the minimum λ<sub>em</sub>. The molecules of 2b-2c in the crystal state are arranged so regularly that the rotatable single bonds are locked due to the multiply physical intermolecular interactions (see the following crystal discussions). These increase the molecular planarity and strengthen the π-intermolecular interactions, which contribute to the maximum λ<sub>em</sub>. While the powder states have less regularity compared with that in the crystal states. In condensed solution, 2a shows the common feature just like some other AIE/AIEE-active systems, 2b may form multimers in the mixture with high water content. The emission wavelength of 2c in the mixed solution is close to that in the powder and the crystal state, suggesting that they originate from the same emitting species with similar molecular conformation and interactions.

To obtain a better understanding of the enhanced emission and impressive color change of 2a-2c, we investigated their crystal structures. The single crystals were obtained by slow evaporation from ethanol, CH<sub>3</sub>Cl<sub>2</sub>/ethanol and CH<sub>3</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN solution, respectively and their crystallographic data are summarized in Tab S2.

Fig 3. Formation scheme of two dimensional expanded cross packing layer structure of the 2b molecules. All the hydrogen atoms are omitted for clarity.

As shown in Fig S5, due to the existence of intramolecular hydrogen bonds, they all have a better planarity. The ORTEP diagram with atom numbering and high dimensional structures of 2a is shown in Fig S6. The adjacent three molecules are cross-linked into one dimensional band in face-to-face edge via multiple C-H···π interactions (d = 2.743, 2.823, 2.964 and 2.905 Å) and C-H···N hydrogen bonds (d = 2.780 and 2.747 Å). Furthermore, the more molecules are interconnected by above-mentioned intermolecular interactions to form two dimensional layer structures. The molecular structure of 2b in the crystal state is nearly coplanar (Fig S7, ESI†). We can clearly see from Fig S7c that the two molecules are initially cross stacked in edge-to-face type to form an L-shaped dimmer through C-H···O hydrogen bonds between the hydroxystyryl hydrogen atoms and the hydroxy oxygen atom, with the distance measured at 2.716 and 2.680 Å, respectively. As shown in Fig S7b, two 2b molecules are slip-stacking together in face-to-face type to form H-aggregates through π···π stacking interactions with the distance measured at 3.477 Å. The two dimmers are then connected with each other in middle-to-middle way to form H-shaped tetramer through C-H···N (d = 2.564 Å) and C-H···O (d = 2.668 Å) hydrogen bonds between the hydrogen atoms of the benzoxazolyl and phenyl groups of one molecule and the nitrogen...
and oxygen atoms of the benzoazoyl group of the adjacent molecule. The #-aggregations are further expanded to form two dimensional multimer cross layer structure by above-mentioned type of hydrogen bonds and π-π stacking interactions. The formation scheme of the two dimensional expanded cross packing layer structure is shown in Fig. 3. For 2c, its crystal structures are similar to that of 2a. Fig S9b shows all intermolecular interactions on one molecule, including C-H...π (d = 2.735, 2.844 and 2.852 Å), C-O...π (d = 3.010 Å) and C-H...N (d = 2.847 and 2.699 Å) interactions. 2c molecules are linked into two dimensional bands via the above intermolecular interactions (Fig. S9c, ESIF). Furthermore, these bands structures are connected in head-to-head way to form a three dimensional W-shaped stacking structure by another type of hydrogen bonds between the nitrogen atoms on the oxaazoly rings and the hydrogen atoms of phenyl rings, with the distance measured at 2.796 Å. According to the crystal structures, the obvious enhanced emission and unique color change can be well explained by these existing multiply interactions. Under the synergetic effect of intra- and intermolecular interactions, intramolecular motions are locked and the molecular conformations are more rigid and planar. Thus, the physical restriction of intramolecular motions and aggregation-induced planarization induced by the molecular aggregation can be considered as the mechanisms of the enhanced emission phenomena of 2a and 2c. For 2b, it is obvious that 2b molecules have better planarity and aggregate to form multimer in face-to-face type according to its crystal structure. In general, the formations of H-aggregate where molecules are aligned parallel to each other with strong intermolecular interactions are characterized by blue-shifted absorption bands, which tend to induce the nonradiative deactivation process.14 The absorption bands and the crystal structures all prove that 2b molecules aggregates to form H-aggregates. The formation of multimer shows obvious concentration-dependence. When the concentration of 2b is lower than 1µM in the ethanol/water (2:8) mixtures, the yellow emission at 542 nm disappeared (Fig 2b and Fig. S13, ESIF), which indicate the absence of the special emissive species that show yellow emission. Thus, we can speculate that the emission in yellow region is attributed to the emission of H-aggregates, which is quite different from the traditional understanding of H-aggregates. Generally, high radiative rates can efficiently enhance emission, while the active exciton migration is detrimental to emission.15 Whether the emission quenches or strengthens is determined by the competition between the two opposite factors. Obviously, the positive effect is dominant in the emission process of 2b. It is very likely that the specific slip-stacking and the dimmer formed by multiple intermolecular hydrogen bonds play essential roles in its high emission, which effectively slow down exciton motion, turn on radiative decay channel and avoid strong H-type coupling to some extent, thus H-aggregates of 2b exhibit high emission. Considering the color changes in solution and nanoaggregates, the application of 2b nanoaggregates to detect highly volatile organic solvents was investigated on thin-layer chromatography plates (Fig. S12, ESIF). Under the 365 nm of UV light at room temperature, 2b nanoaggregates show bright yellow fluorescence which turn into blue in the atmosphere of dichloromethane vapour. The color can be recovered after the vapour is removed. Such fluorescence switches indicate that 2b exhibits different states in different condition. Similar fluorescence change of 2b can also be observed for other solvents, such as tetrahydrofuran and chloroform. Thus, the fluorescence color changes can be used in detecting highly volatile organic solvents because it can be distinguished easily by eye.

Conclusions
In conclusion, we have revealed enhanced emission with large red shifts and color change of a novel benzoxazole-based derivative. In contrast to the general observation that H-aggregates formation quenches the light emissions of chromophores, 2b exhibit H-type aggregates and efficient emission in the aggregate state. The specific slip-stacking and the dimmer formed by multiple intermolecular interactions avoid strong H-type coupling and are responsible for highly emissive H-type aggregates. The response to volatile organic solvents with blue/yellow fluorescent switching was also demonstrated. 2a and 2c show the common AIEE feature. The unique enhanced emission with color changes and efficient emission is suitable for fluorescent probes and OLEDS and also provide new ideas for emissive chromophores. We acknowledge the financial support from New Century Excellent Talents in University (China), the Doctoral Program Foundation of the Ministry of Education of China (20113401110004), the National Natural Science Foundation of China (21271003, 21271004 ), the National Science Foundation of Education Committee of Anhui Province (KJ2012A024), the Natural Science Foundation of Anhui Province (1208085MB22), the 211 Project of Anhui University, the Ministry of Education Funded Projects Focus on Returned Overseas Scholar, Higher Education Revitalization Plan Talent Project of (2013) and the College Students Innovative Entrepreneurial Training Program of Anhui University(201310357025, 201310357155).

Notes and references