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A novel ultrasound-sensitive mechanofluorochromic AIE-compound with remarkable blue-shifting and enhanced emission[†]

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A novel ultrasonic-sensitive mechanofluorochromic AIE-compound (ITPADA) has been designed and synthesized. The fluorescent properties of the ITPADA suspensions were greatly affected by the ultrasonic treatment and extremely sensitive to its power, which show remarkable blue-shifting and enhanced emission. Moreover, perfect ITPADA nano-sheets could be obtained by facile ultrasonic treatment.

Introduction

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Stimuli-responsive materials have been considered to be the fourth generation of materials after natural materials, synthetic polymer materials and artificial design materials.¹ It is one of the important developing trends in high-tech new materials and will support the development of modern high technology. Among them, mechanofluorochromic materials are rather rare and have aroused tremendous interest in recent years.2 These materials show photoluminescence and colour change under external forces such as grinding,³ crushing,⁴ shearing,⁵ rubbing⁶ and stretching,⁷ and have attractive application prospects in the field of fluorescence switches and probes, mechanosensors, optoelectronic devices, data storage, indicators of mechanohistory, and so on.8 However, most of the reported studies are usually confined to the description of the phenomenon. The quantitative study of the applied force to the assembled structure and the fluorescent properties of the mechanofluorochromic materials, such as color change and fluorescent intensity, is still pending as an important and tough topic due to the lack of effective research methods. Tian⁹ used hydrostatic pressure to study the influence and mechanism of applied pressure on the luminescence of a piezochromic material BP2VA, which gives a clear picture of the structure-property relationship and is very important for the development of piezochromic materials. Immediately afterwards, Saito10 found that some mechanochromic luminescent molecules might show distinct responses to the mechanical grinding (anisotropic) and hydrostatic pressure (isotropic), which accelerated and enriched the chemistry of the mechanochromism. However, the application of hydrostatic pressure is limited in practical applications because of the requirement of high pressure.

Ultrasonication is a special way of energy input and widely used in various applications such as in industry, medical diagnosis, medicine, preparation of nano-materials, *etc.*¹¹ Recently, ultrasound was reported as an effective trigger for the formation of organogels¹² or to create defects^{5*a*} in fluorescent crystal materials. Compared with the reported external stimuli, ultrasonication has overriding advantages such as high energy efficiency and quantitative controlling effects. Thus, ultrasound is likely to become a convenient, highly efficient and controllable external stimulus applied in mechanofluorochromic materials. But until now, it is extremely rarely reported in the field.

Herein, we report a novel ultrasonic-sensitive mechanofluoro-chromic aggregation-induced emission (AIE)-compound, named ITPADA. The fluorescent properties of the ITPADA suspensions (such as multicolour change, blue-shifting and intensity enhancement) and the aggregation morphologies were found to be greatly affected by the ultrasonic treatment and extremely sensitive to its power. In other words, the luminescent properties are tunable through controlling of the molecular packing mode. ITPADA nano-sheets with perfect crystalline structure and high purity could be obtained simply by a facile ultrasonic process with an appropriate power supply. Such interesting phenomena promote us to carry out systematic studies on the structure-property relationships. An effective mechanism of the ultrasonic-sensitive mechanofluorochromic phenomenon on the basis of the molecular packing patterns was thus proposed, which might provide a theoretical basis for the molecular design strategies of a new generation of controllable mechanofluorochromic materials. Such ultrasonic-





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Paper

sensitive materials may provide a suitable system for the study of the mechanism of mechanofluorochromic behaviours using ultrasound as a convenient and highly efficient external stimulus, which would be very important for the development and new application of stimuli-responsive materials.

Results and discussion

Synthesis and characterization

The designed molecule ITPADA was synthesized from diphenylamine (DPA), which reacted with para-nitrobenzoyl chloride (NBFC) using pyridine as the catalyst to afford 4-nitro-N,N-diphenyl-benzamide (IP-NO₂), followed by the reduction reaction to obtain 4-amino-N,N-diphenyl-benzamide (IP-NH₂). 4-(Bis(4-nitrophenyl)-amino)-N,N-diphenylbenzamide (ITPADN) was synthesized from IP-NH₂ and 4-fluoronitrobenzene under alkaline conditions. And finally, the reduction of ITPADN by hydrazine hydrate and the palladium/ C catalyst gave the target molecule ITPADA. The detailed synthetic procedure is shown in Scheme 1. The chemical structure of the final product was confirmed by ¹H NMR, ¹³C NMR (H-H COSY, C-H QC and C-H BC) spectra, HRMS, FT-IR and elemental analysis, respectively. The characterization of ITPADA is described in the Experimental section and shown in Fig. S1 in the ESI.† The original ITPADA powder showed good thermal stability. The 5% and 10% weight-loss temperatures (T_d) of ITPADA in nitrogen were 399 and 419 °C, respectively, and the glass transition temperature (T_{σ}) was 117 °C (Fig. S2 and S3 in the ESI[†]).

Ultrasonic-sensitive luminescent behaviours

ITPADA showed interesting ultrasonic sensitivity when we studied the luminescence behaviour of ITPADA. The experiments were carried out in the diluted mixed solvent system of THF-H₂O with different volume contents of water under different mixing conditions. As shown in Fig. 1a, ITPADA showed non-luminescent behaviour when it was molecularly dissolved in pure THF ($1 \times 10^{-5} \text{ mol L}^{-1}$). Addition of a large amount of water (poor solvent of ITPADA) into its dilute THF



Scheme 1 Synthesis routes towards the ITPADA.



Fig. 1 PL spectra and pictures of ITPADA in the THF-H_2O mixtures with different water fractions. (a) Non-ultrasonic conditions; (b) ultrasonic conduction.

solution (like 90% or more) caused the ITPADA molecules to aggregate and luminesce. It showed a yellow fluorescence with the maximum emission wavelength (λ_{max}^{em}) at about 540 nm. The fluorescence quantum yield (Φ_F) of the THF solution of ITPADA was virtually nil, and the Φ_F value of its aggregates suspended in the THF-H₂O mixture is obviously enhanced, which is 4.74% when the water content reached 92%. Clearly, the photoluminescence (PL) behaviour of ITPADA in the mixed solvent of THF-H₂O is typical of an AIE luminogen.

The fluorescent characteristics of the ITPADA aggregates suspended in the THF–H₂O mixture were greatly changed when treated by ultrasonication, as shown in Fig. 1b. It showed a blue fluorescence with the λ_{max}^{em} at about 470 nm. The maximum emission wavelength was remarkably blue-shifted by approximately 70 nm as compared with that determined without ultrasonic treatment. More importantly, the fluorescence intensity was greatly enhanced by the ultrasonic treatment. The suspended system began to luminesce strongly when the water content reached 80%, and the $\Phi_{\rm F}$ value was as high as 50.2% (red column in Fig. 2). After that, the fluorescence quantum yield of the mixture maintained at a high level, which was 52.4% when the water content reached 92%. The ITPADA aggregated suspensions show notable and interesting ultrasonic sensitive mechanofluorochromic behaviours, which is abnormal as the



Fig. 2 Influence of ultrasonic treatment on the fluorescence quantum yield of ITPADA in the THF-H₂O mixtures with different water fractions.

stimuli-induced emission of the most reported mechanofluorochromic compounds was found to be red-shifted and the intensity tended to be decreased or even quenching upon grinding.^{2g,3e,5c,6b,9,13} Such phenomena have not yet been reported in the literature to the best of our knowledge.

We also tried other solvent/non-solvent combinations, such as the THF/*n*-hexane system (where *n*-hexane is a non-polar solvent and a poor solvent of ITPADA) and the DMF-H₂O system. The results are shown in Fig. S4 and S5 in the ESI.† As can be seen, the fluorescent properties of the ITPADA suspensions also showed similar ultrasonic-sensitive behaviour, such as remarkable blue-shifting and enhanced emission. The interesting ultrasonic-sensitive phenomenon of the ITPADA suspensions does not seem to be solvent dependent.

The fluorescence behaviours of the ITPADA aggregated suspensions also show a strong ultrasonic power-dependent behaviour, as shown in Fig. 3. Before being treated with ultrasonication, ITPADA aggregates in the mixture solvent of THF- H_2O (90% content of water) showed very weak fluorescence with the maximum wavelength at about 540 nm. When ultrasonic treatment was performed, at a power of 80 W and a frequency of 40 kHz, the fluorescent intensity was enhanced by almost 10 times and the maximum wavelength was blue-shifted to 513 nm. Further increase of the ultrasonic power strengthened the



Wavelength / nm

Fig. 3 PL spectra of ITPADA in the THF $-H_2O$ mixtures (90% of water), with a frequency of 40 kHz and different ultrasonic powers.

fluorescent intensity and the blue-shifted effect. When the power reached 200 W, the intensity of the mixture was enhanced by 25 times, and the maximum wavelength was blue-shifted by about 70 nm, as compared with that without being treated with ultrasonication. Moreover, before and after the ultrasonic treatment, the chemical structure of the ITPADA remained the same, as confirmed and shown in Fig. S6 in the ESI.†

Aggregated morphology and crystalline structures

The above interesting ultrasonic sensitive fluorescence behaviours of ITPADA suspensions motivated us to look into their aggregated morphology and crystalline structures before and after ultrasonic treatment. The ITPADA aggregates obtained under general mixing conditions revealed to be spherical particles with an average diameter of about 350 nm, which showed a yellow fluorescence with the λ_{max}^{em} at 540 nm, as shown in Fig. 4a. Such spherical precipitates turned amorphous as revealed by powder XRD (blue pattern in Fig. 5). When an ultrasonic power of 80 W was used, the spherical particles of ITPADA changed into regular four-side prism crystals, and the fluorescent color of the suspension changed into green (Fig. 4b). When the ultrasonic power was increased to 120 W, the thickness of the four-side prism became thinner, most of them turned into thin slices, and the suspension color changed into bluish green, with the λ_{\max}^{em} at about 480 nm (Fig. 4c). On further increasing the ultrasonic power, such as 160 W or 200 W, the ITPADA slices thinned down to transparent rhombic nanosheets, and the fluorescent color was further blue-shifted to pure blue (Fig. 4d and e). The XRD results showed that the ITPADA nano-sheet possessed very perfect crystal structures (red pattern in Fig. 5), which is almost the same as its single crystalline structure, as shown in the black pattern of Fig. 5. The ITPADA single crystal was transparent and emitted blue fluorescence (picture in Fig. 5), which is similar to the nano-sheets of ITPADA. In other words, it is applicable to get highly purified single crystals of ITPADA by a facile ultrasonic process, which should be extremely important to the practical application as purification of the as-synthesized compounds is generally a choke point for the luminescent materials.

The SEM studies revealed that the fluorescent properties of the ITPADA aggregates were mainly affected by their aggregated



Fig. 4 Influence of the ultrasonic power on the morphology and fluorescence color of ITPADA suspensions in the THF–H₂O mixtures (90% content of water) with a frequency of 40 kHz. (a) Non-ultrasonic; (b) 80 W; (c) 120 W; (d) 160 W; (e) 200 W.



Fig. 5 Powder XRD patterns of ITPADA with and without ultrasonic treatment; simulated powder XRD pattern of the single crystal. The inset pictures are the corresponding photos under 365 nm UV light.

morphology, that is to say, it is able to control the aggregated structures and fluorescent properties of ITPADA by adjusting the ultrasonic power. The improvement in the crystallinity and especially the formation of the ITPADA nano-sheet crystalline structure greatly enhanced its fluorescent properties, such as the fluorescence quantum yield and the blue-shift effect.

To thoroughly understand the mechanism of the ultrasonic effects on the formation of nano-sheets of ITPADA, systematic X-ray diffraction studies were performed on the single crystal of ITPADA to determine the growth process of the crystals. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix least-squares technique (Tables S1–S3 in the ESI†). The

results showed that ITPADA molecules were crystallized in the triclinic system space group $P\overline{1}$. The basic unit of the single crystal was formed by four ITPADA molecules through three kinds of strong hydrogen bond interactions, that is, the N3-H3B…N7 hydrogen bond interaction with a distance of 2.37 Å, the N3-H3A…O2 hydrogen bond interaction with a distance of 2.14 Å and the N4-H4B...N8 hydrogen bond interaction with a distance of 2.21 Å. The four molecules could be divided into two types, which are Type 1 (gray) and Type 2 (red) shown in Fig. 6a. The crystals were grown along the *x*-axis through a short contact interaction of C47-C48…H54 with distances of 2.776 Å and 2.882 Å (Fig. 6b and e). Along the y-axis, the crystals were grown through a weak hydrogen bond of N8-H8B…O1 (2.48 Å) and N4-H4A…O1 (2.54 Å), as well as short contact interactions of C5-H4A…O1 (2.54 Å and 2.828 Å), C31-H8B…H31 (2.39 Å and 2.619 Å), C30–H2 (2.886 Å), C31–H3 (2.795 Å) and C3–H25 (2.858 Å), as shown in Fig. 6c. The growth of the crystals along the xand y axes formed the basic planar structures of the nanosheets, as shown in Fig. 6f. Outside the plane, the crystals were grown along the z-axis through short contact interactions such as C18-H8A…H18 (2.216 Å and 2.784 Å), C12-H7A-N3 (2.448 Å and 2.871 Å) and H53-H41 (2.375 Å), as shown in Fig. 6d. Such a layer-by-layer growth pattern finally formed the four-side prism crystalline structure of the ITPADA single crystals (Fig. 6g).

Discussion

Based on the above analysis, it now is clear why the ultrasonic treatment would have such an obvious effect on the



Fig. 6 Crystal packing of ITPADA single crystals. (a) Basic unit of the single crystals; (b) interactions along the *x*-axis; (c) interactions along the *y*-axis; (d) interactions along the *z*-axis; (e) ITPADA molecules grown along the *x*-axis; (f) the in-plane assembly of the ITPADA molecules; (g) the lattice structure of the ITPADA crystals.

morphologies of the ITPADA aggregates. Under general mixing conditions, the precipitates of ITPADA tended to form spherical aggregates because of the surface tension to obtain the minimal specific area and surface energy. Due to the special chemical structure and the polar molecular nature of ITPADA (imide and amino groups in one molecule), the spherical structure seems to be destroyed and the ITPADA molecules underwent a self-assembled process through the mentioned intermolecular forces (five kinds of hydrogen bonds and some other short contact interactions) by the application of a low energy ultrasonic power such as 80 W. The ITPADA molecules finally formed the regular prism through the mentioned *x*, *y* and *z* axis growing processes.

Compared with the interaction strength among the x, y and z axes directions, one can see that because of the existence of hydrogen bond interactions along the x and y axes, that is, the interaction in plane is much stronger than that along the z axis, which is aggregated only by short contact interactions. So when the ultrasonic power was increased, the layer-by-layer structure would be easily peeled off. So the four-side prism became thinner and thinner with the increase of the ultrasonic power, and finally turned into a rhombic nano-sheet structure, as shown in Fig. 7.

To obtain further insight into the mechanism of the ultrasonic effect on the fluorescent properties of ITPADA at the molecular level, DFT calculations were performed by using Gaussian 09w at the B3LYP/6-31G(d) level. Fig. 8 shows the optimization geometry structure, the spatial electron distributions and the orbital energies of the HOMO and LUMO of ITPADA in free and in single crystals by Gauss calculation. The optimization geometry structure in free crystals can be used to estimate the geometry structure of ITPADA in its diluted solution or in its amorphous form. Compared with these two situations, the molecules in the single crystals (Type 1 and Type 2) turned more tortuous and non-coplanar due to the existence of the strong intermolecular interactions. Thus the band gaps of the molecules in single crystals (ΔE_g , 4.192 eV and 4.544 eV) were much higher than that in free crystals (3.765 eV). Higher energy was thus needed for electronic transitions; as a result, the maximum fluorescent wavelength of the crystals was obviously blue-shifted than that in diluted solution or in its amorphous aggregates. On the other hand, compared with the



Fig. 7 (a) SEM image of the ITPADA crystal obtained by ultrasonic treatment; (b) molecular packing of ITPADA in the single crystal.



Fig. 8 The optimization geometry structure, the spatial electron distributions and the orbital energy of the HOMO and LUMO of ITPADA in free and in single crystals by Gauss calculation.

ITPADA molecules in amorphous form, like the spherical particles, the intramolecular rotation of ITPADA molecules in the crystal lattice was greatly restricted, which would greatly reduce the energy relaxation of the excited state. Thus, the fluorescence intensity and the fluorescent quantum yield were greatly enhanced.

Conclusions

In conclusion, a novel ultrasonic sensitive mechanofluorochromic AIE-compound (ITPADA) has been designed and synthesized. The fluorescent properties of the ITPADA suspensions and its aggregation morphologies were greatly affected by the ultrasonic treatment and extremely sensitive to its power. The maximum fluorescent wavelength of ITPADA suspensions was abnormally blue-shifted, the fluorescent quantum yield was greatly enhanced, and the aggregation structure was changed from an amorphous form into regular crystals by sonication. Moreover, the ITPADA nano-sheets with perfect crystalline structure could be obtained simply by a facile ultrasonic process with an appropriate power supply. The theoretical studies by systematic X-ray diffraction and DFT calculations at the molecular level showed that in the ITPADA molecule, the imide and the amino groups play a significant role. The special intermolecular interactions among them and the crystalline growth mode made the ITPADA molecules extremely sensitive to the external forces, like ultrasound. Such strong interactions would affect the geometry structure and spatial electron distributions of ITPADA molecules, and thus influence their fluorescent properties. Based on the above mechanism, we are using this strategy to exploit more ultrasonic-sensitive mechanofluoro-chromic compounds in our lab.

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