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A Novel Ultrasonic-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
10 **were greatly affected by the ultrasonic treatment and extremely sensitive to its power, which shows remarkable blue-shifting and enhanced emission. Moreover, Perfect ITPADA nano-sheets could be obtained by facile ultrasonic treatment.**

Introduction

15 Stimuli-responsive materials have been considered to be the fourth generation of materials after the natural materials, synthetic polymer materials and artificial design materials.[1] It is one of the important developing trends in high-tech new materials
20 and will support the development of modern high technology. Among them, mechanofluorochromic materials are rather rare and have aroused tremendous interests in recent years.[2] These materials show photoluminescence and colour change under external forces such as grinding,[3] crushing,[4] shearing,[5] rubbing[6]
25 and stretching,[7] and have an attractive application prospect in the field of fluorescence switches and probe, 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
30 study of the applied force to the assemble 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. Tian[9] used hydrostatic pressure to study the influence
35 and mechanism of applied pressure on the luminescence of a

piezochromic material BP2VA, which gives a clear picture of structure-properties relationship and is very important for the development of piezochromic materials. Immediately afterwards, Saito[10] found that some mechanochromic luminescent molecules
40 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 the requirement of high pressure.
45 Ultrasonic is a special way of energy input and widely used in various applications like industry, medical diagnosis, medicine, preparation of nano-materials, etc.[11] Recently, ultrasound was reported as an effective trigger for the formation of organogels[12] or to create the defect[5a] in fluorescent crystal materials.
50 Compared with the reported external stimuli, ultrasonic has overriding advantages such as high energy efficiency and quantitative controlling effect. Thus, ultrasound is likely to become a convenient, high-efficient and controllable external stimulus applied in mechanofluorochromic materials. But up to
55 now, it is extremely rare reported in the field.

Herein, we report a novel ultrasonic-sensitive mechanofluorochromic aggregation-induced emission (AIE)-compound, named ITPADA. The fluorescent properties of the ITPADA suspensions (such as multicolour change, blue-shifting and intensity
60 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 the molecular packing mode. ITPADA nano-sheets with perfect crystalline structure and high
65 purity could be obtained simply by a facile ultrasonic process with a proper power. Such interesting phenomena promote us to carry out systematic studies on the structure-property relationships. An effective mechanism of ultrasonic sensitive mechanofluorochromic phenomenon on the basis of the
70 molecular packing patterns was thus proposed, which might provide a theoretical basis for the molecular design strategies of new generation of controllable mechanofluorochromic materials. Such ultrasonic-sensitive materials may provide a suitable system for the mechanism studies of mechanofluorochromic behaviours
75 using ultrasound as a convenient and high-efficient external stimulus, which would be very important for the development and new application of stimuli-responsive materials.

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Results and Discussion

Synthesis and Characterization

The designed molecule ITPADA was synthesized from diphenylamine (DPA), which reacted with paranitrobenzoyl chloride (NBFC) using pyridine as the catalyst to afford 4-nitro-N,N-diphenyl-benzamide (IP-NO$_2$), followed by the reduction reaction to gain 4-amino-N,N-dipheny-lbenzamide (IP-NH$_2$). 4-(Bis(4-nitrophenyl)-amino)-N,N-diphenylbenzamide (ITPADN) was synthesized from IP-NH$_2$ and 4-fluoronitrobenzene under alkaline conditions. And finally, the reduction of ITPADN by hydrazine hydrate and Palladium/C catalyst gave the target molecule ITPADA. The detailed synthetic procedure was shown in **Scheme 1**. The chemical structure of the final product was confirmed by ^{1}H NMR, ^{13}C NMR (H-H COSY, C-H QC and C-H BC) spectra, HRMS, FT-IR and elemental analysis, respectively. The characterization of ITPADA was described in the Experimental Section and shown in **Fig. S1** in the Supporting Information. 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_g) was 117 °C (**Fig. S2** and **S3** in the Supporting Information).
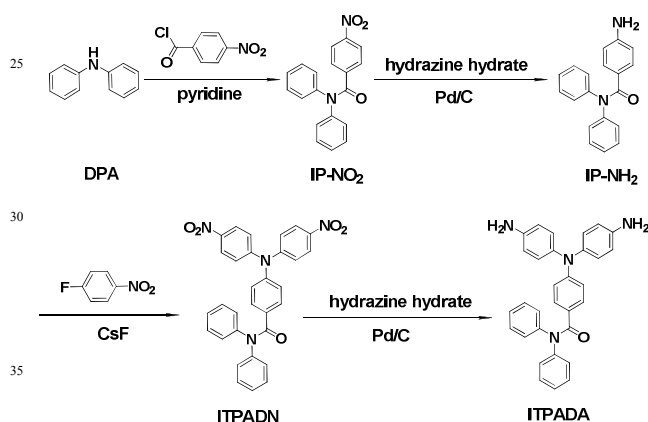

Scheme 1. Synthesis routes of the ITPADA.

Ultrasonic-Sensitive luminescent Behaviours

ITPADA showed interesting ultrasonic sensibility when we studied the luminescence behaviour of ITPADA. The experiments were carried out in the diluted mixed solvent system of THF/H$_2$O with different volume content of water under different mixing conditions. As shown in **Fig. 1a**, ITPADA showed non-luminescent when it was molecularly dissolved in pure THF (1 × 10^{-5} mol/L). Adding of a large amount of water (poor solvent of ITPADA) into its dilute THF solution (like 90% or more) caused the ITPADA molecules to aggregate and luminesce. It showed a yellow fluorescence with the maximum emission wavelength (λ^{em}_{max}) 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/H$_2$O 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/H$_2$O is typical of an AIE luminogen.
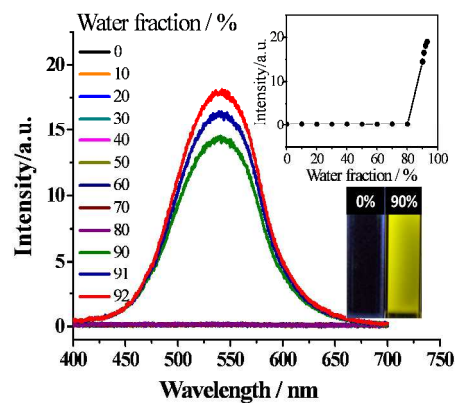
(a) non-ultrasonic
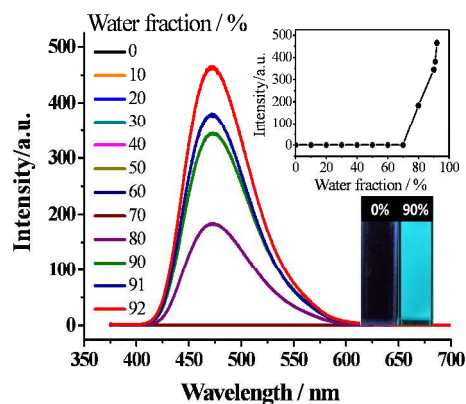
(b) ultrasonic (200W, 40kHz)

Fig. 1. PL spectra and pictures of ITPADA in the THF/H$_2$O mixtures with different water fractions. (a) non-ultrasonic condition; (b) ultrasonic conduction.
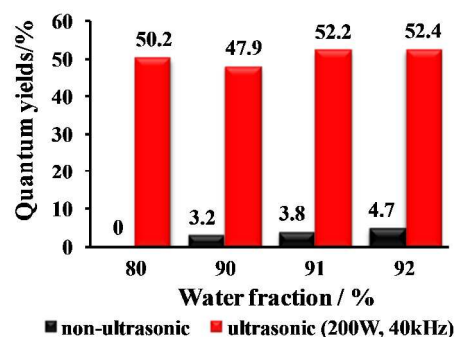

Fig. 2. Influence of ultrasonic treatment to the fluorescence quantum yield of ITPADA in the THF/H$_2$O mixtures with different water fraction.

The fluorescent characteristic of the ITPADA aggregates suspended in the THF/H$_2$O mixture was greatly changed when treated by ultrasonic, as shown in **Fig. 1b**. It showed a blue fluorescence with the λ^{em}_{max} 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 Φ_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
5 suspensions show notable and interesting ultrasonic sensitive mechanofluorochromic behaviours, which is abnormal as the 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
10 grinding.[2g, 3e, 5c, 6b, 9, 13] Such phenomena have not yet been reported in the literatures to the best of our knowledge.

We also tried other solvent/non-solvent combinations, such as THF/n-hexane system (where n-hexane is a non-polar solvent and a poor solvent of ITPADA) and DMF/H_2O system. The results
15 were shown in **Fig.S4** and **Fig.S5** in the Supporting Information. 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
20 suspensions doesn't seem like solvent dependent.

The fluorescence behaviours of the ITPADA aggregated suspensions also show a strong ultrasonic power-dependent manner, as shown in **Fig. 3**. Before treated with ultrasonic, ITPADA aggregations in the mixture solvent of THF/H_2O (90%
25 content of water) showed very weak fluorescence with the maximum wavelength at about 540 nm. When ultrasonic was performed, like 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
30 increase of the ultrasonic power strengthened the 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 treated with ultrasonic. Moreover,
35 before and after the ultrasonic treatment, the chemical structure of the ITPADA remained the same, as confirmed and shown in **Fig. S6** in the Supporting Information.
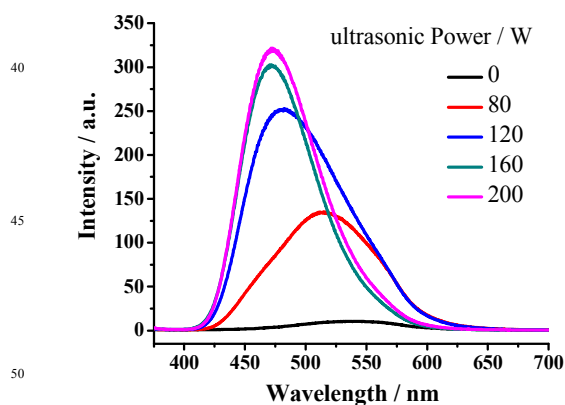

Fig. 3. PL spectra of ITPADA in the THF/H_2O mixtures (90% of water), with a frequency of 40 kHz and different ultrasonic power.

55 **Aggregated Morphology and Crystalline Structures**

The above interesting ultrasonic sensitive fluorescence behaviours of ITPADA suspensions spurred us to look into its aggregated morphology and crystalline structures before and after

ultrasonic treatment. The ITPADA aggregation obtained by
60 general mixing condition revealed to be spherical particle with a average diameter about 350 nm, which showed a yellow fluorescence with the λ^{em}_{max} at 540 nm, as shown in **Fig. 4a**. Such spherical precipitate turned to be in the amorphous form as revealed by powder XRD (blue pattern in **Fig. 5**). When a
65 ultrasonic with a power of 80 W was performed, the spherical particle 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
70 turned into thin slices, and the suspension color changed into bluish green, with the λ^{em}_{max} at about 480 nm (**Fig. 4c**). Further increasing the ultrasonic power, such as 160 W or 200 W, the ITPADA slices thinned down to transparent rhombic nano-sheets, and the fluorescent color was further blue-shifted to pure blue
75 (**Fig. 4d** and **4e**). 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
80 (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
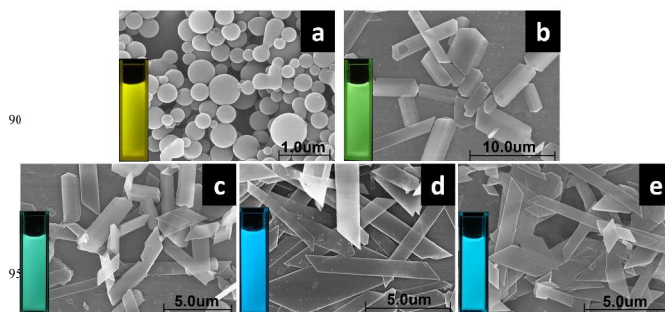85 point for the luminescent materials.

Fig. 4. Influence of ultrasonic power to the morphology and fluorescence color of ITPADA suspensions in the THF/H_2O mixtures (90% content of water) with a frequency of 40 kHz. (a)
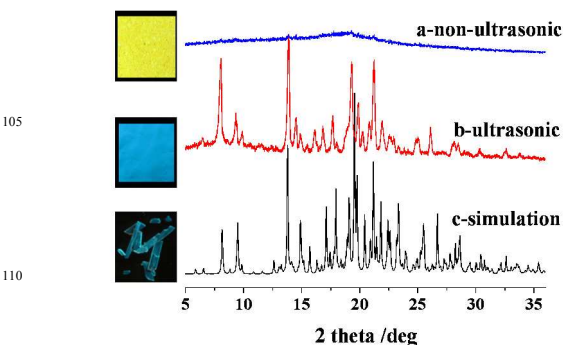100 Non-ultrasonic; (b) 80 W; (c) 120 W; (d) 160 W; (e) 200 W.

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

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The SEM studies revealed that the fluorescent properties of the ITPADA aggregates were mainly affected by its aggregated morphology, that is to say, it is able to control the aggregated structure 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 F2 by the full-matrix least-squares technique (**Table S1-S3** in the Supporting Information). The results showed that ITPADA molecules were crystallized in the triclinic system space group P-1. The basic unit of the single crystal was formed by four ITPADA molecules through three kind of strong hydrogen bond interactions, that is, N3-H3B...N7 hydrogen bond interaction with a distance of 2.37

Å, N3-H3A...O2 hydrogen bond interaction with a distance of 2.14 Å and N4-H4B...N8 hydrogen bond interaction with a distance of 2.21 Å. The four molecules could be divided into two types, which is **Type 1** (gray) and **Type 2** (red) shown in **Fig. 6a**. The crystals were grown along x-axis through short contact interaction of C47-C48…H54 with a distance of 2.776 Å and 2.882 Å (**Fig. 6b** and **6e**). Along y-axis, the crystals were grown through 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 x and y axis formed the basic planar structures of the nano-sheets, as shown in **Fig. 6f**. Outside the plane, the crystals were grown along the z-axis through short contact interaction 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 layer-by-layer growth pattern finally formed the four-side prism crystalline structure of the ITPADA single crystals (**Fig. 6g**).
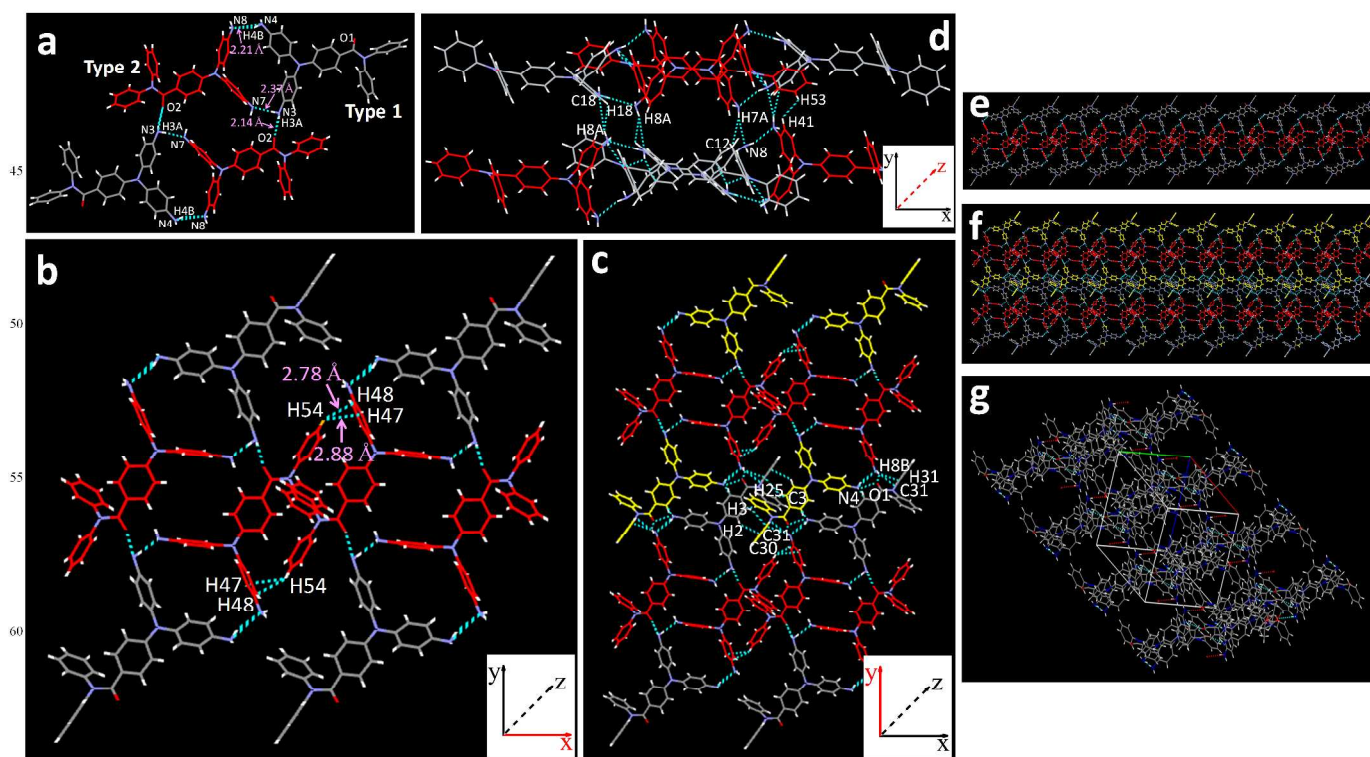

Fig. 6. Crystal packing of ITPADA single crystals. (a) basic unit of the single crystals; (b) interactions along x-axis; (c) interactions along y-axis; (d) interactions along z-axis; (e) ITPADA molecules grown along x-axis; (f) the in plane assembly of the ITPADA molecules; (g) the Lattice structure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

Discussion

Based on the above analysis, it now is clear that why the ultrasonic treatment would have such obviously effect to the morphologies of the ITPADA aggregations. By general mixing condition, the precipitate of ITPADA tended to form spherical aggregation because of the surface tension to obtain the minimal specific area and surface energy. Due to the special chemical structure and 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 bond and some other short contact interactions) by the application of low energy of ultrasonic, like 80 W. The ITPADA molecules finally formed the regular prism

through the mentioned x, y and z axis growing process.

Compared with the interaction strength among the x, y and z axis direction, one can see that because the existence of hydrogen bond interaction along the x and y axis, that is, the interaction in plane is much stronger than that along the z axis, which is aggregated only by short contact interaction. 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 as the increase of the ultrasonic power, and finally turned into rhombic nano-sheet structure, as shown in **Fig. 7**.
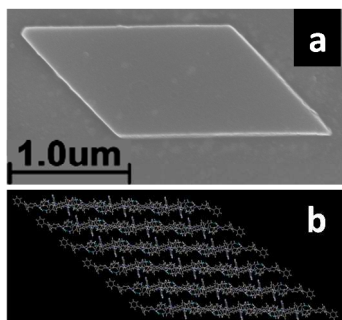

Fig. 7. (a) SEM image of ITPADA crystal obtained by ultrasonic treatment; (b) molecular packing of ITPADA in the single crystal.

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

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 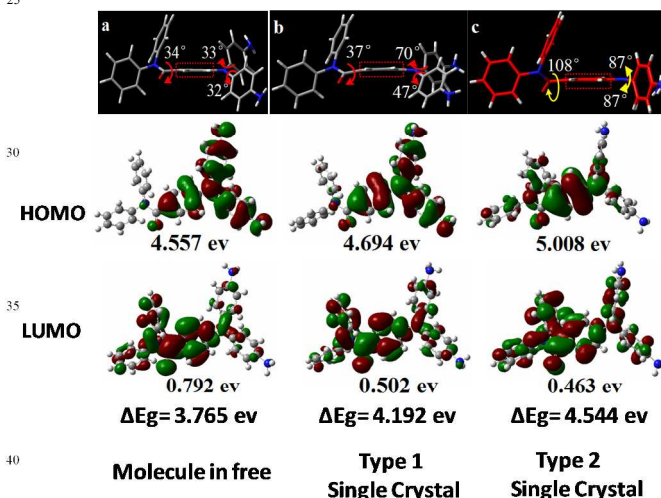by using Gaussian 09w at the B3LYP/6–31G(d) level. **Fig. 8** shows the optimization geometry structure, the spatial electron distributions and orbital energy of HOMO and LUMO of ITPADA in free and in single crystals by Gauss calculation. The optimization geometry structure in free can be used to estimate 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 to be more tortuous and non-coplanar due to the existence of the strong intermolecular interactions. Thus the band gap of the molecules in single crystals

(ΔE_g, 4.192 eV and 4.544 eV) was much higher than that in free (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 aggregations. On the other hand, compared with the ITPADA molecules in amorphous form, like the spherical particles, the intramolecular rotation of ITPADA molecule in the crystal lattice was greatly restricted, which would greatly reduce the energy relaxation of the excited state. Thus, the fluorescence intensity and fluorescent quantum yield were greatly enhanced.

Conclusions

In conclusion, a novel ultrasonic sensitive mechanofluoro-chromic 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 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 a proper power. 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, thus influence its fluorescent properties. Based on the above mechanism, we are using this strategy to exploit more ultrasonic sensitive mechanofluoro-chromic compounds in our lab.

Acknowledgements

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Huawei Sun, Yi Zhang,* Wei Yan, Wenxin Chen, Qi Lan, Siwei Liu, Long Jiang, Zhenguo Chi, Xudong Chen, and Jiarui Xu*

A ultrasonic-sensitive mechanofluorochromic AIE-compound has been synthesized, which shows remarkable blue-shifting, enhanced emission and the formation of perfect nano-sheets.