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### Hydrogen-Bonding Assisted Loosely Packing Crystals of a Diaminomaleonitrile-modified Tetraphenylethene Compound and their Photo- and Mechano-Responsive Properties

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In this study, loosely packing crystals with the building blocks of AIE active TPE-MN molecules were constructed with the assistance of intermolecular hydrogen bonding. Aggregation induced emission (AIE) properties of the compound TPE-MN were studied. From single crystal analyses, sandwich-like crystal structure with tightly packing areas (TPE moieties) and loosely packing areas were observed. Nevertheless, TPE-MN crystals display non-emissive properties in the loosely packing crystalline state. Differential scanning calorimetry (DSC) studies, powder X-ray diffraction analyses and various photophysical studies further reveal that the loosely packing crystal structure can provide enough space for significant molecular rotations and vibrations to occur, which leads to the emission quenching. By breaking the loosely packing crystal structure with mechanical force or UV irradiation, the emission band with the maximum at *ca*. 562 nm can be turned on. These results can serve as a basis for constructing multi-responsive materials with turn-on emissive properties.

#### Introduction

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Molecules in the crystalline state are stacked regularly and usually display more rigid packing modes than in amorphous states.<sup>[1]</sup> Many efforts have been tried to construct crystalline materials in the loosely packing mode for their widespread applications in gas storage, gas separation, catalysis and sensing.<sup>[2]</sup> To avoid a tightly parking mode, different types of intermolecular interactions have been used to decrease the energy of the loosely packing crystals. Many loosely packing crystalline material systems, especially porous organic crystalline materials including zeolites,<sup>[3]</sup> metal-organic frameworks (MOFs), <sup>[4]</sup> covalent organic frameworks (COFs) <sup>[5]</sup> and hydrogen-bonding organic frameworks (HOFs),<sup>[6]</sup> have aroused great attention. Compared with other types of loosely packing crystals, loosely packing crystals with intermolecular hydrogen bonding have outstanding features, such as solventprocess ability, facile regeneration by recrystallization and selfrepairing capabilities.<sup>[6h-6i]</sup> Constructed by weak noncovalent intermolecular interactions, these crystals may be sensitive to the external environment and to stimuli. Thus, it is possible to tune the crystal structure and the packing mode for the loosely

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packing crystals with drastic color and/or photophysical property changes.

The well-established concept of AIE was first reported by Tang in 2001.<sup>[7]</sup> By restriction of intramolecular vibrations and rotations, AIE compounds become much more emissive after "aggregation".<sup>[8]</sup> With the drastic emission enhancement in the aggregate state, compared to the dilute solution-state, these compounds show immense potential in many applications, especially in sensing and as mechanical responsive materials.<sup>[9]</sup> The restriction of the intramolecular rotations and vibrations of AIE-active materials in the aggregate state switches the fluorescence decay processes of the excited molecules from non-emissive to emissive. The majority of the reported AIE processes have been in a solution medium, which prevents the applications of AIE-active materials as responsive materials. If the rotational and vibrational restriction processes of AIE molecules can be realized in the solid-state, then the applications of AIE-active materials will become more useful in sensing and in mechano-responsive related fields. In previous studies several strategies have been reported for the production of high-contrast mechano-responsive materials.<sup>[9,10]</sup> For example, Tian and co-workers discovered that acridonyl-tetraphenylethene exhibits an intriguing turn-on luminescence by tuning the molecular conformation with mechanical stimuli.<sup>[10a]</sup> In addition, high-contrast mechanoresponsive properties were also achieved by breaking the intermolecular interactions ( $\pi$ - $\pi$  stacking, intermolecular hydrogen bonding and others), which could quench the emission bands, with mechanical stimuli.[10b-10e] However, highcontrast mechano-responsive materials are still rare and new strategies are quite urgent. As mentioned above, materials

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that exhibit hydrogen bonding assisted loosely packing crystal structures could allow



Figure 1. Synthetic route for compound TPE-MN.

enough space for significant intramolecular rotations and vibrations to occur even in the solid-state. In addition, the weak and sensitive structures which is attributed to the weak intermolecular interactions might bring about the restriction process with turn-on emission properties after external mechano- or irradiative-simulations. Therefore, designing AIE-active molecules with loosely packing crystal structures in the solid-state could become an appealing strategy for designing responsive materials.

Compounds containing diaminomaleonitrile moieties are prone to form intermolecular hydrogen bonds between the amino groups and the strongly electron-withdrawing cyan groups. Diaminomaleonitrile derivatives have been investigated as mechanoluminescent materials.<sup>[10b]</sup> In the present study, a TPE-modified diaminomaleonitrile derivative, TPE-MN, was synthesized and the synthetic scheme is shown in Figure 1. Hydrogen bonding assisted with loosely packing sandwich-type crystal structure was achieved. The mechanoluminescent properties and irradiation-induced emission properties were investigated in the loosely packing crystals. Various photophysical studies, DSC studies and powder x-ray diffraction (pXRD) studies were carried out to investigate the relationship between the multi-responsive properties and the loosely packing configuration.

#### **Result and Discussion**

#### **Experiment details**

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**Electronic absorption studies.** Dissolution of compound TPE-MN in dichloromethane solvent gives a pale-yellow solution at 298 K. The UV-vis absorption spectrum is shown in Figure 2(a) and shows two absorption bands at *ca.* 317 nm and *ca.* 391 nm. According to previous studies, the higher energy absorption band at *ca.* 317 nm is mainly attributed to the  $\pi$ - $\pi$ \* transition whilst the lower energy absorption band at *ca.* 391 nm mainly originates from intramolecular charge transfer between the tetraphenylethylene and the diaminomaleonitrile moieties.<sup>[10b,11]</sup>

**Aggregation Induced Emission Studies.** TPE is a typical AIE-active unit, in which its enhanced emission properties in the solid-state, compared to the dilute solution-state, is mainly attributed to the rotations and vibrations of the phenyl rings<sup>[7,8]</sup> With regards to TPE-MN, AIE properties can also be observed by recording the emission spectra after the gradual addition of water to a dilute solution of TPE-MN in THF (Figure 2).



**Figure 2.** (a) Electronic absorption spectrum of TPE-MN in dichloromethane solution, concentration =  $1.0 \times 10^{-5}$  mol/L, (b) Emission spectra of TPE-MN in THF/water solvent mixtures containing different water fractions (from 0% to 90%), concentration =  $1.0 \times 10^{-5}$  mol/L and excitation at 365 nm. The inset picture shows photographs of TPE-MN in THF solution (left) and THF/water (90% water fraction) (right).

The emission band of TPE-MN in pure THF is weak, which is due to the excessive intramolecular rotations in the dilute solution-state, and perhaps some contribution from the solvent polarity.<sup>[8]</sup> However, the emission intensity is enhanced considerably at 90% v/v water fraction with an emission peak located at ca. 530 nm. This dramatic enhancement of emission intensity indicates the formation of aggregate particles due to the poor solubility of TPE-MN in the mixed solvent system with high water content and the subsequent restriction of the internal motions. The emission band of TPE-MN in the aggregate state most likely originates from the intramolecular charge transfer (ICT) transition, owing to the push-pull characteristics of the TPE unit (donor) and the diaminomaleonitrile unit (acceptor).[10b]

Single crystal structure analysis. Single crystals of TPE-MN were obtained by recrystallization from dichloromethane and hexane mixed solvent system (CCreDC number: 1497597). The emission intensities of AIE-active materials usually stronger in their crystalline state than solids in the amorphous state.<sup>[1b,7]</sup> This is mainly ascribed to the more rigid packing mode in the crystalline state. However, the fluorescence of TPE-MN is almost quenched in the crystalline state compared to the emissive aggregates formed in 90% water/THF mixed solvent system. Therefore, the fluorescence quenching process for the TPE-MN crystals was sought. Single crystal analysis was carried out for TPE-MN and the single crystal structure of TPE-MN is based on the P-1 space groups. A sandwich structure can be observed in the view down in the b axis (Figure 3a). For the sandwich structures, TPE moieties are stacked tightly, which can be considered as the "hard-layer", while the diaminomaleonitrile moieties are packed loosely together acting as the "soft-layer". In the "soft layer", two CH-CN hydrogen bonds and one NH-CN hydrogen bond, with distances of 2.72 Å, 2.74 Å and 2.09 Å, respectively, are formed between connected TPE-MN molecules (Figure 3(b)).

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Figure 3. (a) Single crystal structure of TPE-MN; (b) the details of TPE-MN dimer with hydrogen bonding; (c) details of the repeat units for the layer-structure.

By forming these intermolecular hydrogen bonds in the softlayer, which could lower the energies of the aggregated systems, it is possible to avoid the tight packing modes in the crystalline state and form loosely packing structures. According to the single crystal analysis, the distance between the repeating units in the layered crystal structure is 10.58 Å, which is much larger than the diameter for the phenyl ring (ca. 5.8 Å). For crystals based on traditional AIE-active TPE derivatives, empty areas with the diameter larger than the diameter of phenyl ring is hardly observed. [7-9] This large distance could provide enough space for significant intramolecular rotations/vibrations to occur even in the solidstate, and not just in the solution-state. In the previous literature reports, several porous or loosely packing crystals were also formed with the assistance of hydrogen bonding.<sup>[6,12]</sup> The loosely packing areas in the crystal structure might be sufficient space for the internal molecular motions to be significant, causing the excited molecules to decay nonradiatively to the ground state. According to the previous literatures, the intramolecular rotations and vibrations can be restricted with decreased temperature.<sup>[13]</sup> Therefore, temperature-dependent emission studies were performed for TPE-MN to further demonstrate the emission quenching process is attributed to the molecular vibrations in the loosely packing areas in the crystalline state. For the non-emissive TPE-MN crystals, if the fluorescence quenching process is due to intramolecular rotations/vibrations, the emission band is predicted to be turned-on by decreasing the temperature. Temperature-dependent emission spectra for TPE-MN crystals were measured from 300 K to 145 K. As shown in Figure 4, no obvious emission band is detected when the temperature is above 300 K. When the temperature decreases to 200 K, the emission is turned on, and the intensities further drastically increase by decreasing the temperature further (up to 145 K). The temperature-dependent emission spectra of TPE-MN in the amorphous state (after grinding) upon cooling below room temperature is shown in Figure S2. The emission intensities are

also enhanced with decreasing temperature due to restriction of molecular vibrations, however, in contrast to TPE-MN crystals no emission "turn-on" process is observed due to significant emission observed at 293 K. Therefore, the internal molecular motions in the loose packing areas of the crystalline state lead to the emission quenching in the crystalline state, which is in accordance with the mechanism of the AIE phenomena.



Figure 4. Temperature-dependent emission spectra of TPE-MN in the crystalline state, with excitation wavelength = 365 nm. Mechanoluminescent Properties Studies. Constructed by the weak intermolecular hydrogen bonding, the loosely packing crystals with sandwich-type structure might easily collapse by mechanical force. In the AIE studies discussed previously, TPE-MN aggregates formed in solvent/anti-solvent (THF/water) systems were emissive. In contrast to the AIE studies, loosely packing TPE-MN crystals are nearly non-emissive. These TPE-MN crystals are shown to be "turn-on" mechanoluminescent materials. As shown in Figure 5(d), the characteristic peaks for the original crystalline TPE-MN pXRD spectrum are quite in accordance with the simulated pXRD spectrum. This reveals that the crystalline structures of the original TPE-MN crystals and the single crystal of TPE-MN are identical. Emission spectra and photographs of the turn-on and quenching processes are shown in Figure 5(a). After grinding, the non-

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emissive TPE-MN crystals become emissive with the emergence of a new emission band at *ca*. 561 nm originating from ICT transitions. The fluorescence quantum yield increases from <0.1% for TPE-MN in loosely packing crystalline state to 5.4% after grinding. Therefore, the fluorescence quenching process is attributed to the formation of the loosely packing crystal structures. In addition, the emission of ground TPE-MN can be quenched by heating or dichloromethane fuming (Figure 5(b)). DSC studies have been carried out on TPE-MN in the crystalline state and on ground TPE-MN, and the DSC scans are shown in Figure 5(c). For the ground TPE-MN, a glass transition temperature (Tg) is detected at *ca*. 110°C but not in the crystalline sample, which demonstrates the morphology of TPE-MN changes from crystalline to amorphous after grinding.

A temperature-dependent emission study for ground TPE-MN (from 303 K to 383 K) in the amorphous state was carried out. When the temperature increases from 300 K to 383 K the emission intensity for ground TPE-MN gradually decreases and finally quenches when the temperature reaches the  $T_g$  (383 K). After heating to the  $T_a$ , the emission properties of ground TPE-MN are quite similar to that of TPE-MN in the crystalline state. This suggests that as the material is heated to its  $T_g$  crystallization takes place due to thermal expansion and decrease in viscosity, which aids nucleation of the amorphous material with subsequent reduction in emission intensity. To further demonstrate the turn-on emission properties are considerably related to the loosely packing crystal structure, pXRD measurements were carried out for TPE-MN samples after different treatments (Figure 5d). According to the Bragg equation, the diffraction peak of  $2\theta$  = 4.1° and 8.3° corresponds to a distance of 10.6 Å. According to the single crystal structure, the distance between the repeat units in the loosely packing crystals is 10.6 Å (Figure 3). Therefore, the peaks of  $2\theta = 4.1^{\circ}$  and  $8.3^{\circ}$  can be tentatively assigned to the layer distance. Consistent with the emission changes, all these sharp peaks including the peaks of  $2\theta = 4.1^{\circ}$  and  $8.3^{\circ}$  in the pXRD spectra for the original loosely packing TPE-MN crystals disappear after grinding revealing that the loosely packing



**Figure 5.** (a) Emission spectra of TPE-MN crystals before and after grinding, excitation wavelength =  $\lambda$  = 365 nm. The inset shows the fluorescence photographs (under UV light) of the original and ground samples; (b) Emission spectra of ground TPE-MN sample, dichloromethane fumed ground sample and heated ground sample (to 200°C). (c) DSC spectra for the first heat processes of TPE-MN in the crystalline state and ground TPE-MN. (d) pXRD spectra of TPE-MN samples in the crystalline state (original), ground TPE-MN crystals, dichloromethane fumed ground TPE-MN sample, heated ground TPE-MN sample (to 200°C) and the simulated pXRD spectrum from the single crystal structure.

crystal structure is damaged after grinding. However, the defined peaks in the pXRD spectra can be partly reversed after heating or dichloromethane fuming. These changes further indicate that grinding/fuming and grinding/heating can damage or partly reconstruct the loosely packing crystal structures and thus drastically change the emission properties of the solid-state. By comparing the normalized emission spectra of TPE-MN in the crystalline state, ground TPE-MN, dichloromethane fumed ground TPE-MN and heated ground TPE-MN (Figure S4), it can be observed that the emission of the original crystalline sample can be recovered to some extent after dichloromethane fuming or heating. In accordance with the pXRD results (Figure 5(d)), the loosely packing crystal structure was only partly recovered during the heating or dichloromethane fuming processes. From these results above, it can be concluded that the loosely packing crystal structure, which provide sufficient space for the occurrence of significant internal molecular motions, can be easily damaged/ partly fuming. reconstructed by mechanical forces/solvent Mechanoluminescent properties were achieved bv manipulating the aggregation states between crystalline and amorphous.

Irradiation-Induced Emission Properties Studies. In TPE-MN, the TPE unit is connected to diaminomaleonitrile by a C=N bond. For the C=N bond, cis-trans isomerization occurs by UV-light irradiation according to the previous literature.<sup>[14]</sup> Based on this type of cis-trans isomerization, many photoresponsive materials have been designed and developed.<sup>[15]</sup> In the solution- state both the cis-isomer and trans-isomer (majority) can be observed in the <sup>1</sup>H NMR spectrum (Figure S5). UV-vis absorption studies were performed for TPE-MN before and after UV-light irradiation at 365 nm. As shown in Figure S6, the lower-energy absorption band is maintained whilst the higherenergy absorption band, which is assigned to the  $\pi-\pi*$ transition of the TPE-MN molecule, slightly increases. For the cis-trans isomerization, the cis-isomer usually displays a larger extinction coefficient for the  $\pi - \pi *$  transition.<sup>[14a]</sup> The slight enhancement of the higher-energy absorption band could be ascribed to the increased amount of the cis-isomer after UVlight irradiation. However, this is only cautiously reported due to the fast reverse isomerization from cis to trans after UVlight irradiation has ceased. In previous reports, some tetraphenylethylene and triphenylethylene derivatives display photo-responsive properties due to photocyclization reactions.<sup>[16]</sup> These materials display drastic color changes after irradiation, which is mainly due to the enhanced molecular conjugation after the photocyclization. To exclude the possibility that the photo-responsive properties are caused by photocyclization, UV-vis reflectance spectra were measured for TPE-MN in the crystalline state before and after UV-light irradiation. As shown in Figure S7, no new absorption bands can be detected after irradiation. The absorption band around 450 nm is slightly enhanced, which is mainly due to the increased amount of the cis-isomer after UV irradiation as mentioned above. This result can preclude the possibility that the photo-responsive properties of TPE-MN were caused by photocyclization or photooxidation. In the crystalline state, the well-aligned diaminomaleonitrile moieties might become disordered by UV-light irradiation and thus the emission is turned on by breaking the well-aligned loosely packing softlayer.

Similar to the predicted results, the non-emissive TPE-MN crystals become emissive with enhanced emission intensity and emission maximum at *ca*. 563 nm after UV-light irradiation, as shown in Figure 6(a). The emission spectra for the ground sample before and after UV-light irradiation were also measured. After the grinding process the crystal structure has already been destroyed due to a crystalline to amorphous morphology transition, therefore, the enhancement of emission intensity for ground TPE-MN cannot be observed after irradiation (Figure S8). To further investigate the irradiation-induced emission properties, pXRD studies were performed on the TPE-MN crystals before and after irradiation (Figure 5(b)). It can be observed that most of the peaks are still sharp after irradiation. Especially the peak at  $2\theta = 4.1^{\circ}$  and

#### 8.3°, which were assigned as the distance between repeat units of the loosely packing layer structure; 19.5tm/sharp after irradiation. These results demonstrate that the crystal structure is maintained after irradiation. On the contrary, some peaks such as $2\theta = 15.5^{\circ}$ , 17.6° and 27.2° are diminished, which indicates selective destruction of certain ordered packing in the TPE-MN crystals, which is in accordance with the prediction above. Without the orderly packing in the softlayer, the intermolecular rotations and vibrations are resisted to some extent and the emission is turned on. The photoresponsive property is irreversible and the enhanced emission after UV-light irradiation is maintained without any reversal back to the original species with comparatively lower emission intensity. The trans to cis transition merely aids the disordering of the well-aligned diaminomaleonitrile moieties with emission always originating from the trans isomer due to the rapid cis to trans back conversion after UV-light irradiation has stopped.



**Figure 6.** (a) Emission spectra of TPE-MN crystals before and after UV-light irradiation at 365 nm, excitation wavelength = 365 nm. The inset shows the fluorescence photographs (under UV-light) of the original and irradiated samples. (b) pXRD spectra of TPE-MN in the crystalline state before and after irradiation.

#### Conclusions

Loosely packing molecules in the crystalline state with sandwichtype structure has been demonstrated for compound TPE-MN. The loosely packing mode was formed with the assistance of intermolecular hydrogen bonding. With the loose-packing mode, the diaminomaleonitrile moiety of TPE-MN can rotate and vibrate and, therefore, fluorescence quenching in the crystalline state is observed. By destroying the loose-packing mode with mechanical force, the emission properties can be significantly enhanced (turnon). Oppositely, by solvent fuming or heating the emission can be turned-off. Moreover, by selectively breaking the orderly packing mode of the soft layer in the crystals by UV-light irradiation, the emission can also be turned on. These results provide a new strategy to design multi-responsive materials with turn-on emission properties by combining AIE-active molecules and loosely packing crystal structures.

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#### Title: Hydrogen-Bonding Assisted Loosely Packing Crystals of a Diaminomaleonitrile-modified Tetraphenylethene Compound and their Photo- and Mechano-Responsive Properties

**Loosely Packing Crystals:** This study reveals that loosely packing crystals can be constructed with the assistance of intermolecular hydrogen bonding. Combined with a traditional AIE building block, loosely packing crystals can be used as multi-responsive materials with turn-on emission properties.