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An Organic Molecule with Asymmetric Structure Exhibiting Aggregation-Induced Emission, Delayed Fluorescence, and Mechanoluminescence**

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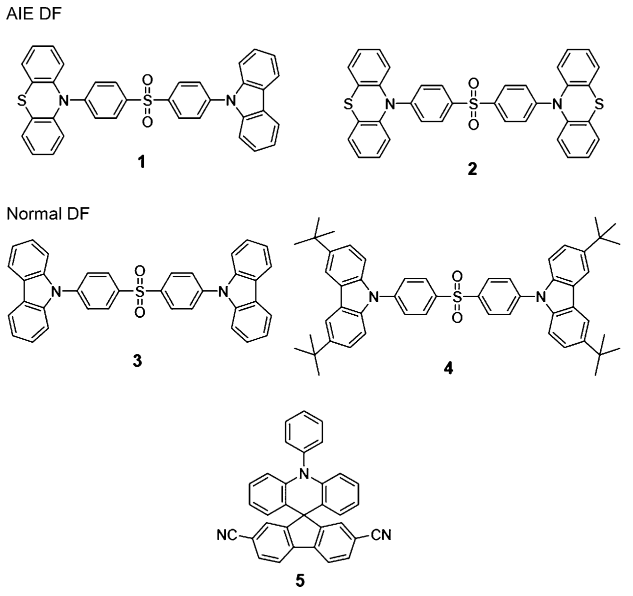
Abstract: *Compounds displaying delayed fluorescence (DF), from severe concentration quenching, have limited applications as nondoped organic light-emitting diodes and material sciences. As a nondoped fluorescent emitter, aggregation-induced emission (AIE) materials show high emission efficiency in their aggregated states. Reported herein is an AIE-active, DF compound in which the molecular interaction is modulated, thereby promoting triplet harvesting in the solid state with a high photoluminescence quantum yield of 93.3 %, which is the highest quantum yield, to the best of our knowledge, for long-lifetime emitters. Simultaneously, the compound with asymmetric molecular structure exhibited strong mechanoluminescence (ML) without pretreatment in the solid state, thus exploiting a design and synthetic strategy to integrate the features of DF, AIE, and ML into one compound.*

Delayed fluorescence (DF) is a long-lived triplet harvesting emission, which is rarely observed in organic fluorophores and metal complexes.[1] DF can be divided into P-type DF (triplet–triplet annihilation)[2] and E-type DF (thermally activated)[1f,g,3] based on the reverse intersystem crossing (RISC) from the lowest triplet (T_1) to the lowest singlet (S_1) states. A small energy gap between S_1 and T_1, ΔE_{ST}, is required to promote E-type DF because the rate of RISC is inversely proportional to the exponential ΔE_{ST}.[1b] Recently, Adachi et al. developed a series of E-type DF emitters with about 0 eV ΔE_{ST}, wherein the RISC process was strongly enhanced. They successfully achieved external quantum efficiencies (EQEs) higher than those obtained using conventional fluorescent emitters.[1f,g,3] Song et al. confirmed that the long-lived lifetime of E-type DF can be used in time-resolved fluorescence cell imaging.[4] Given its low cytotoxicity, E-type DF has good potential as a new time-resolved fluorescence-sensing platform to replace luminescent lanthanide complexes.

However, a common problem for DF, particularly for E-type DF, is the possibility of facile aggregation through π–π interactions as a result of the hydrophobicity and rigid, planar structure, thus leading to aggregation-caused quenching (ACQ).[1d,f] The compounds **4** and **5** (Scheme 1) are two typical DF compounds reported by Adachi et al. (2012). These two compounds are regarded as normal DF emitters in the current study. The luminescent efficiency (η_{PL}) value for the film of **5**, measured in air at atmospheric pressure, was only 5.5 %.[1f] The delayed component disappeared in the film of **4** and showed a short lifetime decay.[1d]



Scheme 1. Molecular structures of the compounds **1**–**5**.

These DF organic light-emitting diode devices (OLEDs) suffer from serious efficiency roll-off related to exciton

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concentration quenching caused by singlet–triplet annihilation and triplet–triplet annihilation.[3a,5] Additionally, these devices can only exhibit efficient DF (or triplet harvesting) in doping films, thereby restricting applications in nondoped materials.

To overcome this limitation, we considered a new approach toward an aggregation(concentration)-enhanced DF with efficient triplet harvesting in the solid state. These extremely concentrated materials would elicit more usage in nondoped devices if the performance of individual dyes can be cooperatively enhanced within the highly localized structure. Therefore, a special molecular design for a DF chromophore is required to ensure an efficient DF, and more importantly, to overcome fluorescence quenching at high concentration, which is generally observed in common organic fluorophores. Several studies have reported that, instead of concentration quenching, emission enhancement is observed in aggregate or solid-state form.[6] Investigations on this novel class of organic fluorophores, showing aggregation-induced emission (AIE), have recently begun, with some demonstrations of promising uses for electroluminescence devices, fluorescent sensing or switching, and optical storage.[6c,7]

In the current study, two AIE-active DF compounds (**1** and **2**; Scheme 1) were designed by modulation of molecular interactions. Both compounds revealed nondoped triplet harvesting. This report provides the first evidence of highly efficient DF without doping, and is significant for potential applications in bio- and nanomaterials science. The asymmetric compound **1**, in which molecules are artistically arranged, sequential, and closely packed without any π–π interaction, provided a high DF quantum yield (Φ_F) of 93.3 % in the solid state. Such a molecular design is simple, novel, and promising. Simultaneously, **1** exhibited strong mechanoluminescence (ML) without any pretreatment, and provided another breakthrough because almost all of the reported ML materials exhibited ACQ or weak emission in the solid state.[8] Such strong AIE-active ML is extraordinary and could facilitate potential applications of ML materials.

The compound **3** and its derivative **4** are strong DF emitters with high EL efficiency in doping films.[1d,3d] However, these substances are not very emissive in the solid state because of the involved ACQ process. The photoluminescence (PL) spectra (Figure 1 C,D) of **3** and **4** in tetrahydrofuran (THF)/water mixtures with different amounts of water (f_w), enabled fine-tuning of the extent of solute aggregation. The normal DF compounds showed a typical ACQ effect, and the emission intensity significantly decreased after the aggregation of molecules.

The compounds **1** and **2**, in which planar carbazole rings were replaced by nonplanar phenothiazine, were thus designed to modulate the molecular π–π interactions. The corresponding emission spectra of **1** and **2** in aqueous THF with different THF/water ratios are shown in Figure 1 A,B. Emissions from the pure THF solution of **1** and **2** were very weak. Hence, almost no PL signals were recorded. However, luminescence was significantly enhanced for approximately a 10:90 (v/v) THF/water mixture for **1** and **2**. For **2**, for example, the PL intensity in the THF was only 11, but this value increased to about 96 in 10:90 (v/v) THF/water. The emission enhancement was induced by the aggregation of molecules, thus suggesting that **1** and **2** are AIE active. Notably, **1** and **2** belong to a new class of AIE compounds because their structures are beyond the commonly reported AIE moieties, such as silole, tetraphenyl ethylene, and 9,10-distyrylanthracene.

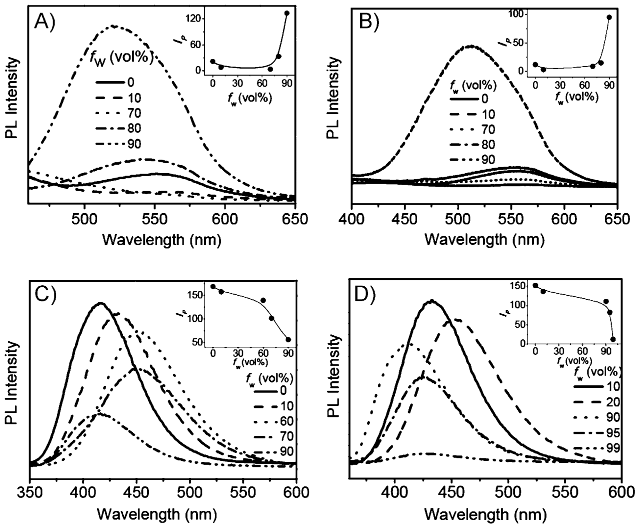

Figure 1. Photoluminescence (PL) spectra of **1**–**4** (A-D) in THF/water mixtures with different amounts of water (f_w). Insets depict the changes in PL peak intensity (I_P).

The single crystals of **1**–**3** were obtained by slow evaporation from the indicated solutions (see the Supporting Information). Careful inspection of the intermolecular interaction in the crystals of **1** and **2** revealed two modes of intermolecular interactions, including C−H···π and S=O···H−C weak hydrogen bonds (see Figure S1 in the Supporting Information). Thus, no typical π···π intermolecular interactions were observed for the single crystals of **1** and **2**, and can thus be ascribed to the nonplanar conformation of the phenothiazine moiety. Such a structure is unfavorable for face-to-face packing of the phenyl moieties between the molecules. However, in the crystal structure of **3**, except for the above-mentioned, two other modes of intermolecular interactions exist, namely, π···π and S = O···π intermolecular interactions (Figure 4; Figure S1). The π···π and S = O···π supramolecular interactions also play an important role in the triplet ACQ. This data shows that properly disturbing the close molecular packing and diminishing the intermolecular quenching effects are advantageous for increasing the Φ_F value.

The compound **1** showed delicate molecular packing like a Chinese "bagua", the so-called eight diagrams, in which each molecule has the planar carbazole moiety interlocked with the nonplanar phenothiazine moiety of another molecule, thus leading to a tightly packed and highly ordered alignment without any π–π interactions (Figure 2 A). In contrast, although **2** lacks π–π interactions, it shows loose packing (Figure S1) with weak molecular interactions, thus resulting in nonradiative deactivation of pathways through rotation or vibration.

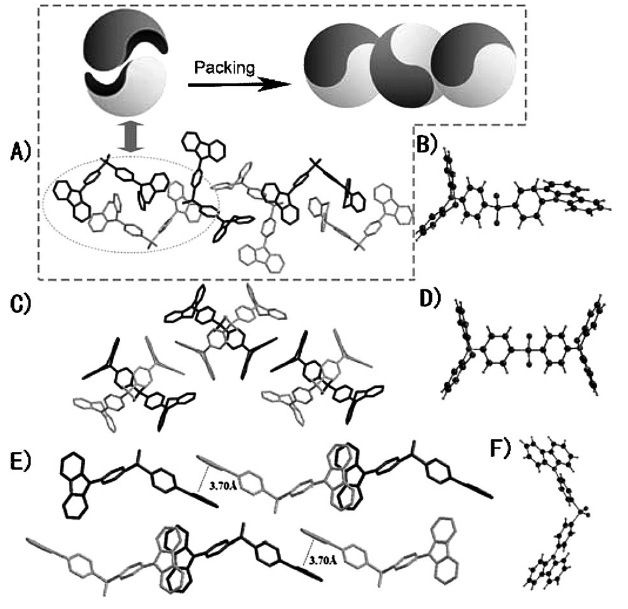

Figure 2. Molecular packing, interactions, and structures. Molecular packing and interactions for **1**–**3** (A, C, and E; hydrogen atoms and solvent molecules have been omitted for clarity) and molecular structures of single crystals of **1**–**3** (B, D, and F).[12] In (E), π–π interactions are shown at 3.70 Å.

Simultaneous consideration of a highly ordered alignment and intermolecular quenching has always been challenging when designing a fluorescent molecule. In this study, **1** set an equilibrium point through the bagua packing. This strategy appears to be simple, novel, and promising for the molecular design.

To predict the energy difference (ΔE_{ST}) between the lowest S_1 and the lowest T_1 levels, density functional theory (DFT) calculations were performed. The ground-state geometries were optimized using DFT with B3LYP hybrid function at the basis-set level of 6-31G*.[9] The geometrical parameters of the optimized ground state of **1**–**3** agreed well with those derived from the X-ray structure measurements. The molecular structures, as well as the highest occupied and lowest unoccupied natural transition orbitals (HOMO and LUMO, respectively) for the optimized ground-state geometries of the molecules are shown in Figure S2. The calculation results showed that the majority of the electron distribution of the HOMO was very similar for each of the three compounds and is located on the diphenylsulfone moiety. As expected, **2** and **3**, having symmetric molecular structures, showed similar electron distributions in the LUMO. The electron distributions were located on the two phenothiazine and two carbazole moieties. However, given the asymmetric structure, the electron distribution of the LUMO of **1** was significantly different from that of **2** and **3**, and was mainly located on the carbazole moiety. The asymmetric structure might be ascribed to the unique photophysical properties of **1**. As predicted by time-dependent DFT (TD-DFT), the ΔE_{ST} values of **1**, **2**, **3**, and **4** were 0.20, 0.03, 0.30, and 0.28 eV, respectively. These relatively small ΔE_{ST} values suggest a potentially high RISC, thus causing the DF.[1,3]

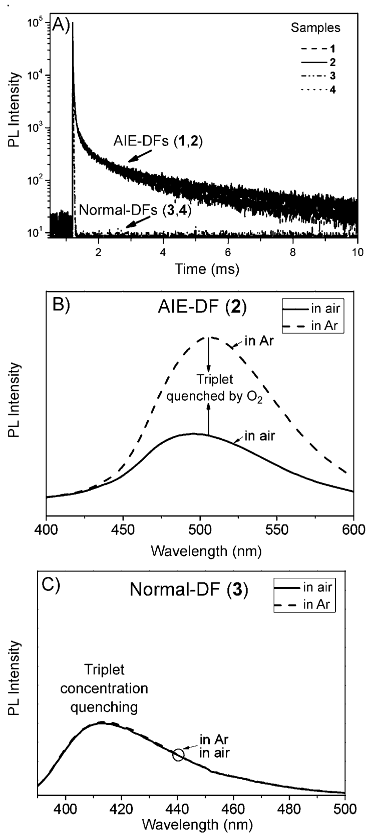

Figure 3. Emission decay of compounds **1** and **2** (AIE-DF), **3** and **4** (normal DF) in powder form in vacuo (A). PL spectra of powder samples of **2** (B) and **3** (C) in air and under an argon atmosphere.

Figure 3 A shows the transient PL decay curves measured for the powders of **1**, **2**, **3**, and **4** in the air, thus representing AIE-DF (**1** and **2**) and normal DF systems (**3** and **4**). Apparently, no delayed component was observed in the fluorescence decay transients of normal DF compounds, whereas AIE-DF samples showed a very strong delayed component with $\tau = 1.23$ ms. These results indicate that no upconversion of triplet excitons occurred in the powders of **3** and **4**, and is consistent with the results reported by Adachi et al.[1d,f] Briefly, these AIE-DF systems showed better solid-state triplet harvesting than the normal DF systems reported.

The oxygen-sensitive behavior of fluorescence indicates upconversion of triplet excitons for DF. Figure 3B,C depict the fluorescence emission of the powder samples of **2** and **3** before and after argon treatment. Argon treatment can eliminate the possibility of the deactivation of the photoexcited states by quenching with the low-energy triplet states of oxygen, thereby enhancing the emission. The AIE-DF sample was sensitive to oxygen, whereas normal DF systems displayed the same emission after argon treatment. These findings revealed that AIE-DF systems are triplet emissions available in the pure solid state. The PL Φ_{F} of **1** increased from 66.3 to 93.3 % after argon treatment, and can be ascribed to the elimination of the delayed component quenching by oxygen. This finding implies a very high value of for the solid-state Φ_{F} value, particularly for long-lifetime emitters. Such a high Φ_F value can be ascribed to the combination of DF and AIE properties. The Φ_F value of the nondoped phosphorescence emitter reported by Chou[10] was only 30%, which is much lower than that of this AIE-DF sample. The optical properties of **1**–**4** are listed in Table 1.

Table 1: Optical properties of **1**–**4**.

	λ_{max}^{abs} [nm]	λ_{max}^{em} [nm]	AIE/ACQ	Φ_F [%]		$\Delta\Phi$ [%]
				Air	Ar	
1	316	518	AIE	66.3	93.3	+27.0
2	324	510	AIE	30.2	52.8	+20.6
3	345	419	ACQ	32.1	32.3	+0.2
4	342	408	ACQ	25.4	25.0	−0.4

In addition to the high Φ_F value, **1** exhibited significant ML, which might represent the first reported mechanoluminesecent compound with both DF and AIE properties. ML is a type of luminescence induced by mechanical stimuli such as grinding, rubbing, cutting, cleaving, shaking, scratching, compressing, or crushing.[11] However, ML materials remain limited in number, and their emitting efficiency is generally low because almost all the reported ML materials exhibit ACQ or weak emission in the solid state, thereby limiting the application of ML materials.[8] The PL and ML spectra, as well as the ML image of **1** are depicted in Figure 4. When the powder sample was scratched by a stainless steel spoon against the side of a beaker, strong green luminescence could be observed without pretreatment, such as doping. The ML is very strong as it can be observed in daylight. The compound **1** exhibits the combined properties of ML, AIE, and DF. Thus, it appears to be extraordinary and would facilitate potential applications.

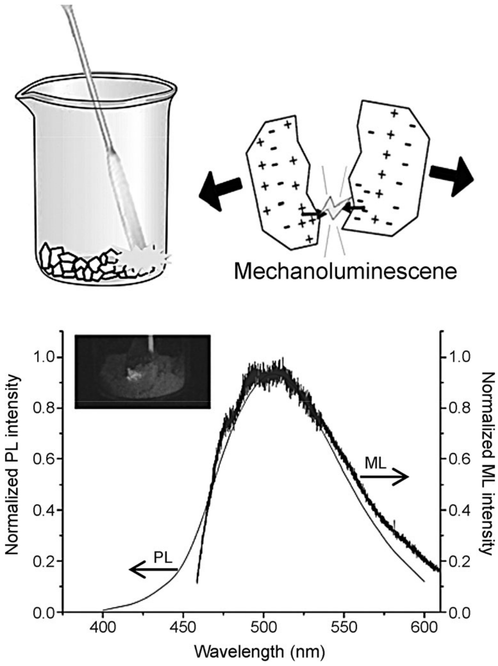

Figure 4. Schematic of ML, PL, and ML spectra, and ML image of **1** at room temperature.

The results of single-crystal X-ray diffraction analysis showed that the unit cells of **1** and **2** are orthorhombic with space groups $P_{na}2_1$ and P_{bcn}, respectively, whereas the unit cell of **3** is monoclinic with a space group $C2/c$ (see Table S1). Zink et al.[11a,b] has pointed out that the space group of $P_{na}2_1$ belongs to the piezo- and pyroelectric groups. When the piezoelectric crystal breaks, the crack surface is electrified. Electronic discharge at the crack surface induced the excited states of the compounds (Figure 4). The dipolar structures and non-centrosymmetric molecular arrangements in the crystals are necessary to achieve strong piezoelectric properties. Therefore, dissymmetrical molecular structural characteristics and formation of a non-centrosymmetric crystalline structure with a $P_{na}2_1$ space group may lead to ML of **1**.

In summary, novel AIE-DF compounds with phenothiazine moieties and/or asymmetric structures have been designed and synthesized. This report provides the first evidence of highly efficient DF without doping, and is significant for the potential application in nondoped devices, biomaterials, and nanomaterials. The asymmetric **1**, in which molecules exhibited artful packing and highly ordered alignment without any π–π interactions, provided a high DF Φ_F value of 93.3% in the solid state. Such a strategy appears to be simple, novel, and promising for the molecular design of this kind of compounds. Simultaneously, **1** exhibited strong ML without any pretreatment. It is believed that such strong AIE-active ML is extraordinary and would provide plenty of potential applications for ML materials. These novel AIE-DF materials might exploit a new pathway for organic fluorescence materials, and further studies are currently in progress in our laboratory.

Experimental Section

Synthesis of 4-carbazol-10-phenothiazine diphenyl sulfone (**1**): Bis(*p*-fluorophenyl) sulfone (1.91 g, 7.5 mmol) was added to a solution of sodium hydride (0.72 g, 30 mmol) in anhydrous dimethylformamide (DMF; 15 mL). After the solution was stirred at room temperature for 10 min, carbazole (1.25 g, 7.5 mmol) in dry DMF (10 mL) was added, and the mixture was stirred for 1 h. Phenothiazine (1.49 g, 7.5 mmol) in anhydrous DMF (10 mL) was then added. The mixture was stirred at 100°C for an additional 6 h. After cooling, the mixture was poured into 400 mL of water, and the white precipitate was filtered and dried. The crude reaction mixture was chromatographed on a silica gel column with *n*-hexane/CH_2Cl_2 (3:1 by volume) as eluent to obtain **1** (1.74 g) in 42% yield.

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[12] CCDC 981368 (**1**), CCDC 981369 (**2**), and CCDC 981370 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.