Aggregation-Induced Emission

Synthetic Regulation of 1,4-Dihydropyridines for the AIE or AIEE Effect: From Rational Design to Mechanistic Views

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Abstract: Aggregation-induced emission/aggregation-induced emission enhancement (AIE/AIEE) has recently attracted intense research, and a large number of AIE/AIEE luminogens (AIE/AIEEgens) have been constructed for application in diverse scientific fields. The AIE and AIEE effects have similar, but not identical, photophysical behaviors, which are closely related to molecular architectures. However, the current understanding of the inherent differences between AIE and AIEE is still obscure. Herein, a rational design strategy is reported for achieving AIE and AIEE effects by simply incor-

Introduction

Aggregation-induced emission/aggregation-induced emission enhancement (AIE/AIEE) phenomena have attracted extensive interest because they are the exact opposite processes to the notorious aggregation-caused quenching (ACQ) effect and pave an avenue for creating aggregate-state emitters.^[1] The scaffolds of most AIE luminogens (AIEgens) feature multiple aromatic rotors linked to a stator by single bonds, and the construction of AlEgens generally complies with this principle.^[2] The rotation of the aromatic rings consumes most of the excited-state energy and results in near nonfluorescence in solution, whereas restriction of intramolecular rotation (RIR) in aggregates leads to conversion of the energy into photons and fluorescence turn-on. AIEEgens, which are similar to but not exactly the same as AIEgens, display gradually enhanced fluorescence with increasing degree of aggregation.^[3] These constructs generally contain smaller or/and fewer rotatable units and/or have smaller twisting amplitudes that weaken their capacity to serve as a relaxation channel for the deactivation of excitons.^[4] AIEE is considered to be a special case of AIE, and many AIEEgens are also arbitrarily classified as AIEgens from simple comparisons of the fluorescence efficiencies of the luminogens in the solution and solid states. However, the different photophysical behaviors of AIE/AIEEgens are closely associ-

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porating different substituents at the periphery of the same core skeleton. Experimental and theoretical studies on the series of compounds indicated that the restriction of intramolecular twisting motions or/and rotations plays an important role in regard to the corresponding AIE or AIEE behaviors. Moreover, compound **1a** (FW=203, Φ_F =80.9%) was discovered as the lowest molecular weight AIEEgen with a high quantum yield in the solid state despite having no rotatable units. Compound **2a** also exhibited an AIEE effect with the minimum necessary structure (a single ring).

ated with their structures, although their molecular frameworks may show only subtle differences. To date, the understanding of the relationship between molecular structure and the corresponding AIE/AIEE effect remains limited. Consequently, the rational design of luminogens with distinct AIE and AIEE effects from the same core has never been reported.

In contrast to their propeller-like counterparts, some newly emerging AIE/AIEE systems do not contain rotors, and these systems cannot simply be interpreted by the RIR model.^[5] Thus, the mechanisms of the AIE/AIEE effects are further unified under the more universal term of restriction of intramolecular motion (RIM).^[6] Deciphering the AIE/AIEE processes enables the design and synthesis of novel AIE/AIEEgens.^[7] Although numerous AIE/AIEE molecules have been constructed, most of them are very complex with high molecular weights and low quantum efficiencies, and they are often produced in tedious reaction steps. Such hurdles have greatly impeded the advancement of AIE/AIEEgens. Therefore, the development of small structures (M < 300) with high fluorescence quantum yields is appealing from both fundamental and practical viewpoints, yet a significantly challenging task.^[8]

1,4-Dihydropyridines (1,4-DHPs) and related heterocyclic compounds, which have a broad spectrum of biological properties, are usually obtained by the convenient Hantzsch-type reaction.^[9] Over the past few decades, the photophysics and photochemical behavior of structurally diverse 1,4-DHPs have been widely investigated.^[10] Recently, we reported a series of single-ring 1,4-DHPs as the minimal structural requirement for establishing the AIEE effect.^[11] The series of compounds also exhibited high specificity toward mitochondria with excellent photostability and storage stability. For these single-ring systems, gradually restricting rotations of the small ester groups and distortions of the DHP core in aggregates enables them to

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show increased fluorescence in a typical AIEE phenomenon. Considering the facile modification of 1,4-DHP through a simple one-pot multicomponent reaction, 1,4-DHP may be an ideal candidate for constructing AIE/AIEEgens with different mechanisms. Following this train of thought, we envisioned that the compounds could also show an AIEE effect through restriction of the small-amplitude intramolecular motions when the ester groups are replaced with carbonyl groups. Further attachment of large phenyl rings to the compounds is expected to create an AIE effect through the strong ability of the phenyl rotors to consume energy through large-amplitude rotations.

Herein, we report the design and synthesis of several 1,4-DHP derivatives by a Hantzsch-type reaction. The introduction of different substituents at the periphery of the DHP core not only expanded the structural types but also provided insights into the relationship between the structure and the photophysical properties. We explored the fluorescence properties of these compounds in detail and found that the 1,4-DHPs exhibited distinct AIE/AIEE phenomena: 1) compounds with open carbonyl groups showed an AIEE effect depending on the restriction of intramolecular rotation and twisting motion (RIR-RITM), 2) compounds with both open carbonyl and phenyl groups showed an AIE effect depending on the RIR-RITM process, and 3) compounds with enclosed carbonyl groups showed an AIEE effect depending on the restriction of intramolecular twisting motion (RITM). To the best of our knowledge, no single luminogen system has yet been developed whose emission behavior could be regulated between AIE and AIEE by simply altering the peripheral substituents of a single core framework.

Results and Discussion

Molecular design

In our previous work, a series of single-ring 1,4-DHPs were prepared, and their progressively enhanced fluorescence intensities on adding water to their solutions in THF manifested their AIEE behavior.^[11] Restriction of the twisting motions of the core ring along with the rotations of the two ester groups favors efficient radiative decay, and thus the fluorescence intensities of the compounds are enhanced on aggregation. We envisaged that the attachment of phenyl rotors to the core skeleton would further improve the ability of the molecule to dissipate its excited-state energy through intramolecular rotation compared to that containing small ester groups (Figure 1A). On the basis of this hypothesis, we presumed that the compounds would be non-emissive in the dissolved or loosely aggregated state but display bright fluorescence in the closely aggregated state, as the molecular motions would be almost completely restricted in the last-named state. Such a photophysical process is consistent with a representative AIE phenomenon.

Moreover, Tang et al. recently investigated the optical properties of two coumarin derivatives, **CD-5** and **CD-7**, containing five- and seven-membered aliphatic rings, respectively, without any rotors (Figure 1 B).^[12] The size of the aliphatic ring played a crucial role in controlling the molecular rigidity and twisting



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Figure 1. Molecular design based on 1,4-DHP for the AIE or AIEE effect.

motions. Thus, the two compounds had very similar molecular structures but completely opposite emission behaviors. Although CD-5 exhibited an ACQ effect, CD-7 showed typical AIE characteristics, which originated from its twisting motion and structural nonplanarity. We proposed that the same strategy could also be applied to the construction of rotor-free AIE/ AIEEgens based on the DHP core to further increase the scope of the AIE/AIEE family (Figure 1C). Three 1,4-DHP derivatives that contained two five-, six-, and seven-membered rings on both sides of the core framework were designed. The rules of geometry state that the three adjacent vertices of a heptagon are fixed, which allows this polygon to fold, whereas a pentagon is unable to fold. This difference in ring flexibility between five- and seven-membered rings was responsible for the opposite emission behaviors of the two coumarin derivatives. In the 1,4-DHP system, only two adjacent vertices of each polygon are fixed, which allows the pentagon to also twist. Furthermore, we deduced that the twisting motions of the flexible aliphatic rings would impart weaker nonradiative deactivation ability than phenyl rotors on aggregation and thus result in an AIEE process, which is in complete contrast to the ACQ effect observed for CD-5.

With the molecular design protocols in mind, several 1,4-DHP derivatives were first synthesized to test the hypothesis. The derivatives were readily prepared by one-pot Hantzsch reactions of acetaldehyde, ammonium acetate, and various β -dicarbonyl compounds as substrates according to the published procedure (Scheme 1).^[13] All the desired products were purified by column chromatography with petroleum ether/ethyl acetate or recrystallized from ethanol. The 1,4-DHPs were characterized by ¹H and ¹³C NMR spectroscopy and high-resolution mass spectrometry (see Supporting Information), which confirmed their molecular structures. The 1,4-DHPs were relatively

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Scheme 1. Synthesis of enclosed/open 1,4-DHPs.

insoluble in water but soluble in common organic solvents such as THF.

AIE/AIEE properties

Three different types of movable parts were incorporated in the design of the target luminogens, including open carbonyl groups, enclosed carbonyl groups, and open carbonyl/ester groups with phenyl groups around the DHP core. On the basis of the RIM mechanism and our deductions, all of these compounds were expected to exhibit AIE/AIEE characteristics. Having obtained a series of structurally diverse 1,4-DHP derivatives, we then evaluated their photophysical properties. The absorption maxima, fluorescence emission maxima, quantum yields $arPsi_{\mathrm{F}}$ and fluorescence lifetimes au of the derivatives in both the solution and solid states are summarized in Table 1 and Figures S1-S3 in the Supporting Information. The guantum yields of all these 1,4-DHPs were much higher in the solid state than in the solution state, and this clearly suggests that they are indeed AIE/AIEE-active (high $\Phi_{\rm F}$ values up to 0.809). We also calculated the radiative (k_r) and nonradiative (k_{nr}) rate constants from the corresponding $\Phi_{\rm F}$ and τ values. In pure THF solution, the k_{nr} value of each compound was larger than its k_r value by 1–3 orders of magnitude, which implies that nonradiative decay was the dominant decay channel. However, the k_{nr} value was substantially lower in the powder samples than in solution and was close to or even smaller than the k_r value. These results suggest that aggregation greatly suppressed the nonradiative pathway of energy dissipation through RIM.

To gain insight into the emission processes of the 1,4-DHPs on gradual aggregation with AIE or AIEE characteristics, we measured the fluorescence intensity changes of the compounds in THF/water mixtures with varying water fractions f_{w} . As shown in Figure 2A-C and F, compounds 1a-c exhibited faint emissions in pure THF at a concentration of 10 $\mu \textrm{M}$ with maxima at 395, 421, and 442 nm, respectively. When f_w was increased in small increments, the fluorescence intensities of the compounds also gradually increased due to aggregation, with a slight redshift in the maximum emission wavelengths. Thus, this class of compounds clearly exhibited AIEE behavior, as expected. The redshift in the fluorescence implied narrowing of the bandgap, possibly because the increased solvent polarity elevated the energy level of the HOMO.^[14] However, the addition of more water lowered the fluorescence intensity, which can be attributed to a corresponding decrease in the solubility. Dynamic light scattering (DLS) measurements demonstrated that large nanoaggregates started to form once a small amount of water was added. When f_w values were further increased, the increasing trend of the particle sizes became slower (Figure S4 in the Supporting Information). The average sizes of the nanoparticle were 300–400 nm at $f_w = 90\%$ (Figure S5 in the Supporting Information).

Unlike in the propeller-shaped AIE/AIEEgens containing rotatable phenyl rings, the common RIR model cannot explain the AIEE effect observed for these rotor-free fluorogens. According to a previous report, the fluorescence enhancement might stem from the restriction of the out-of-plane twisting motion of the aliphatic ring in the aggregated state.^[12] Notably, the emission behavior of compound **1a** was exactly opposite to that of **CD-5**. The AIEE effect of **1a** indicates that a fivemembered ring backbone can still be distorted after fixation of two adjacent vertices, which proves the feasibility of our molecular design strategies developed on the basis of geometry.

We next investigated the fluorescent signatures of the opentype 1,4-DHPs (**2a**,**b**) under the same experimental conditions (Figure 2D–F). Interestingly, compound **2a** showed a very similar gradual increase in emission intensity with increasing f_w to

Table 1. Photophysical properties of 1a-2c in the solution and solid state.												
Compound	Solution ^(a) λ_{abs} λ_{em} $\tau^{[b]}$ $\Phi_{F}^{[c]}$ $k_{rr} k_{nr}^{[d]}$ [nm] [ns] [10 ⁷ s ⁻¹]					Solid state λ_{ex} λ_{em} $\tau^{[b]}$ $\Phi_{F}^{[c]}$ $k_{\#} k_{nr}^{[d]}$ [nm][nm][ns][10 ⁷ s ⁻¹)						
1a	340	395	0.5	0.067	12.6, 175.0	325	420	1.2	0.809	67.4, 15.9		
1b	357	421	3.1	0.162	5.1, 26.6	325	455	3.7	0.712	19.2, 7.8		
1c	367	442	0.2	0.002	0.9, 509.3	365	475	1.4	0.037	2.6, 68.8		
2a	365	449	< 0.1	0.009	37.5, 3915.0	340	480	3.4	0.275	8.1, 21.3		
2b	380	-	< 0.1	0.004	3.9, 1077.2	380	510	4.8	0.196	4.1, 16.8		
2c	351	-	< 0.1	0.009	18.4, 1977.6	345	480	5.0	0.204	4.1, 15.9		

[a] Measured in THF. [b] On excitation at 371 nm. [c] Absolute quantum yield determined with an integrating-sphere system. [d] Rate constants for radiative (k_r) and nonradiative (k_{rr}) decay were calculated from the Φ_F and τ values according to the formulas $k_r = \Phi_F/\tau$ and $k_n = (1 - \Phi_F)/\tau$.

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Figure 2. Fluorescence spectra of A) **1a**, B) **1b**, C) **1c**, D) **2a**, and E) **2b** in THF/water mixtures with different f_w values. F) Normalized maximum emission intensity of **1a–2b** as a function of f_w . G) Photographs of **1a** and **2a,b** in THF/water mixtures with different f_w taken under UV illumination. Concentration: 10 μ m; excitation wavelength: 340 (**1a**), 357 (**1b**), 367 (**1c**), 365 (**2a**), 380 nm (**2b**).

that observed for the enclosed-type counterparts. In contrast to the mechanism of AIEE activity for compound 1, the two carbonyl groups of 2a act as rotatable moieties and are mainly responsible for the AIEE activity through an RIR process. Compound 2a has the minimal structure necessary to elicit AIEE behavior, namely, a single ring. Considering the strong energyconsumption ability of aromatic rotors, we further explored the fluorescence spectra of compound 2b in THF/water mixtures with increasing f_w values. As illustrated in Figure 2E, no discernible emission peaks were observed as f_w was increased from 0 to 80%; however, an abrupt emission enhancement was observed at $f_w \ge 90$ %. Compound **2** c also showed a similar phenomenon due to the similarity of its scaffold to that of 2b (Figure S6 in the Supporting Information). These results are indicative of a typical AIE process, which is in good agreement with the behavior observed for the propeller-like AIEgens with multiple aromatic rotors.

Crystal structures

To better understand the AIE/AIEE characteristics of the 1,4-DHPs, we obtained five single-crystal structures to determine the molecular conformation and packing modes (**1a-2a** and **2c**).^[15] Our repeated attempts to grow single crystals of **2b** were unsuccessful. In general, the DHP core frameworks of all

these AIE/AIEEgens adopted a nonplanar conformation. Therefore, we used four atoms in the central ring (C², N¹, C⁴, and C⁵) to define a dihedral angle θ for quantitative analysis of the degree of distortion (Figure 3 A).^[16] The θ value varied from 152.85 to 173.79° depending on the different substituents at the periphery (Figure 3 and Figure S7 in he Supporting Information). For compound **2c**, three independent molecules with different dihedral angles (151.63, 158.46, and 161.82°) existed in the crystalline state. The twisted nature of the 1,4-dihydro-N-heterocyclic architecture may help to prohibit close π - π stacking interactions in the aggregated state and thus avoid the formation of species that are detrimental to emission.

We further scrutinized the packing modes of the 1,4-DHPs. Compound **1a** crystallized in the orthorhombic space group $Cmc2_1$ in the presence of several drops of water. Multiple intermolecular hydrogen bonds of the form O–H···O and N–H···O (H···O 1.864 and 1.903 Å, respectively) were observed between the DHP core/carbonyl groups and water molecules, which stabilized the edge-to-face packing. More importantly, the carbonyl groups of the five-membered ring on both sides of the central ring adopted slightly twisted conformations with torsion angles of 173.56°. The present system was packed in a loose pattern owing to the nonplanar three-ring skeletons and hydrogen-bonding interactions with water, and the conformation of the molecules was rigidified by the collective forces of the

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Figure 3. Chemical structure of the 1,4-DHPs (A). Single-crystal structures and molecular packing modes of 1a (B and C) and 2a (D and E) showing various key dihedral angles [°] (blue dashed lines) and N–H--O and O–H--O interactions with distances [Å]. Carbon, oxygen, and nitrogen atoms are shown in gray, red, and light blue, respectively.

weak interactions. The results differ from the hypothesis that a planar conformation and tight packing of **CD-5** were responsible for the severe quenching of the emission intensity in the aggregate state due to the induced π - π interactions. On the basis of geometric analysis, a fixed number of vertices in a five-membered ring alters the mobility of the ring.

Compounds 1b and 1c crystallized in triclinic space group $P\bar{1}$ and monoclinic space group P2/c, respectively. As shown in Figure S7 of the Supporting Information, an antiparallel packing structure with a face-to-face orientation (interplanar distances of 4.30 and 4.78 Å) is clearly observed in the crystal structure of 1b, while several different molecular stacking modes can be identified in 1c. Intermolecular N-H-O hydrogen bonds with a distance of about 2.9 Å were formed between the carbonyl groups and DHP rings of neighboring molecules. Furthermore, the six/seven-membered carbonyl rings exhibited large twisting amplitudes and impeded close $\pi - \pi$ stacking. Therefore, the AIEE effects of compounds 1 a-c can be attributed to their intrinsic twisting motions. When fully dissolved in solution, the dynamic intramolecular twisted motions of the isolated molecules promote nonradiative excited-state decay, and thus result in poor fluorescence. Such motions are impeded in the aggregated state due to physical constraints, which block the nonradiative relaxation channels and enable strong fluorescence.

Both open carbonyl-substituted molecules (**2a** and **2c**) stack head-to-tail and participate in hydrogen-bonding interactions (NH···O 2.943 Å for **2a** and 2.991 Å for **2c**) in the crystalline state (Figure 3 and Figure S7 in the Supporting Information). The face-to-face antiparallel packing structure of **2a** is similar to that of **1b** and has an interplanar distance of 4.86 Å (triclinic space group $P\bar{1}$). The introduction of the two phenyl groups into the backbone of DHP in compound **2c** resulted in a zigzag arrangement to avoid steric repulsion and strong π - π interactions (monoclinic space group $P2_1/c$). Overall, the loose molecular packing structure and RIR of the multiple rotatable blades are crucial for the enhanced emission in the aggregated state.

In our previous study, the distorted DHP core framework was forced to change continuously from a puckered to spread geometry along with rotation of the ester groups. Because the molecules in the current study are from the same family, we rationalized that the present AIE/AIEEgens would exhibit similar behavior. In combination with the results described above, we therefore concluded that all of the collective factors including twisted annular conformations, rotatable units, intermolecular interactions, and packing modes, would endow the luminogens with distinct AIE/AIEE properties.^[17]

Theoretical calculations and mechanisms

The electronic structures of the AIE/AIEEgens were calculated by DFT at the B3LYP/6-311 + G(d) level of theory by using the Gaussian program. The optimized structures, molecular orbital diagrams, and energy levels are plotted in Figure 4. The frontier molecular orbitals of compounds 1a-2a are distributed across the entire conjugated framework. The similarity in the orbital distributions implies that the luminogens have similar photophysical properties. The HOMOs of 2b and 2c are centered on the DHP backbone, whereas the LUMOs are delocalized on the two phenyl groups, which exhibit partial chargetransfer character. Moreover, we performed time-dependent DFT calculations on the 1,4-DHPs and found that the emission bands can be predominantly ascribed to the electronic transition from the LUMO to HOMO (Table S1 in the Supporting Information). Such predicted results are consistent with the experimental spectroscopic data.

To quantitatively interpret the geometric relaxations of the AIE/AIEEgen single molecules, we analyzed the structural changes $|\Delta(S_0-S_1)|$ on photoexcitation in the gas phase. The simulated structures of the S_0 and S_1 states and the corresponding key distortion angles are summarized in Figure S8 and Table S2 of the Supporting Information, respectively. The

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Figure 4. Optimized structures, frontier molecular orbitals, and energy levels of the HOMOs and LUMOs of 1a-2c.

geometries of the S₁ state are obviously different from those of the S₀ state. First, the 1,4-DHPs with open carbonyl groups (2a,c) have larger twisting amplitudes than those with ring substituents, because they are not restricted by covalent bonds. The extent of deformation in the compounds is correlated to the distortion angles $|\Delta|$ in the decreasing order of $2c > 2a \approx 1c > 1b > 1a$. Second, the two large seven-membered rings in 1c enhance the flexibility and greatly facilitate out-of-plane movements of the molecular skeleton, which are similar to the free rotations of the carbonyl groups in 2a. Third, although 1a experiences the least motion among the studied compounds, it is still very different from CD-5, which has a more planar conformation because of its intrinsic structural rigidity. Fourth, the dihedral angles θ in the DHP core rings are highly dependent on the peripheral substituents, and thus illustrate that the distorted core framework could be forced to change along with the motion of the peripheral groups.

We subsequently modeled the effect of aggregation by calculating the geometric structures (S₀ and S₁ states) of a large enough cluster of the crystal structures (taking **1 a**, **2 a**, and **2 c** as representatives of the three types of substituents) through a combined quantum mechanics/molecular mechanics (QM/ MM) approach (Figures S9–S11 in the Supporting Information).^[18] The geometric modifications between the S₀ and S₁ states of these compounds were smaller in the solid phase than in the gas phase because the intramolecular motions were largely constrained in the solid state (Figure 5 and Table 2). For instance, the changes in the torsion angles between the two phenyl groups and the DHP core in **2 c** were smaller ($\Delta \varphi 3$, $\Delta \varphi 4 = 12$, 11°) in the solid phase than in the gas phase ($\Delta \varphi 3$, $\Delta \varphi 4 = 27^{\circ}$, 18°). Meanwhile, the change in the di-



Figure 5. Optimized S_0 and S_1 geometric structures of **1 a**, **2a**, and **2 c** in the gas and solid phases. The rules for defining the relevant distortion angles are shown in the upper panel. The key changes in the distortion angles from the S_0 state to the S_1 state are listed in the lower panel.

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Table 2. Distortion angles [°] of 1a, 2a, and 2c in the gas and solid phases and the changes in the distortion angles from the S₀ state to the S₁ state ($|\Delta|$ $= |(S_0 - S_1)|).$

Distortion angle	a 1 a gas phase		1 a solid phase			2 a gas phase		2 a solid phase		2 c gas phase		2 c solid phase						
	S ₀	S ₁	$ \Delta $	S ₀	S ₁	$ \Delta $	S ₀	S ₁	$ \Delta $	S ₀	S ₁	$ \Delta $	S ₀	S ₁	$ \Delta $	S ₀	S ₁	$ \Delta $
θ	171	179	8	178	179	1	151	165	14	151	164	13	153	170	17	162	173	11
φ1	-178	-179	1	-177	-179	2	173	156	17	18	20	2	-6	-13	7	3	2	1
φ2	178	-179	3	179	180	1	-5	-2	3	-143	-140	3	-167	-166	1	-163	-167	4
φ3	-1	8	9	-0.2	-0.5	0.3	-	-	-	-	-	-	-123	-150	27	-127	-139	12
<i>\ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ </i>	1	2	1	2	6	4	-	-	-	-	-	-	121	139	18	125	136	11

hedral angle $\Delta\theta$ in the DHP core ring also decreased to 11°. These results are consistent with the stronger fluorescence observed for the aggregate state relative to the solution state, which reveals that the excited-state energy was converted into photons via RIR and RITM.

Considering the influence of the aggregation behavior on the photophysical phenomena (induced emission or emission enhancement), we attempted to develop a tentative explanation for the AIE/AIEEgens with different substituents on the basis of the above experimental and theoretical results as well as the mechanism proposed by Tang et al. The mechanisms of 1 a, 2 a, and 2 c are shown in detail in Figure 6 as illustrative ex-



Figure 6. Proposed AIEE mechanisms for 1 a and 2 a and AIE mechanism for 2 c.

amples of the three types of substituents. As an archetype of the AIE/AIEE family, 2a contains two small rotatable units that give rise to AIEE characteristics. We inferred that the rotations of the carbonyl groups are easily restricted by adjacent molecules on aggregation, and this leads to gradual switching of the energy loss of excitons from the nonradiative pathway to the radiative channel. Compound 2c has four rotatable units, including two ester groups and two large phenyl rotors. The molecules are loosely packed in the crystalline state owing to steric repulsion imposed by the aromatic rings, which results in a large intermolecular free volume in small aggregates. Therefore, the motions of the rotatable blades cannot be totally suppressed, and the fluorescence intensity of the compound remains low. When clustered into larger aggregates, a large number of molecules become entrapped inside the particles, and this results in almost complete RIM and fluorescence turnon (AIE effect). For the enclosed analogue of 2a, that is, compound 1 a, out-of-plane twisting deformation is the major nonradiative decay channel in solution. The limited twisting motions of the carbonyl rings are sensitive to and readily inhibited by the surrounding molecules on aggregation and thus favor the radiative channel and an AIEE effect.

Conclusion

We constructed a series of 1,4-DHP derivatives by simple reactions and investigated their AIE and AIEE properties in detail (1 a is the lowest molecular weight AIEEgen with a high absolute quantum yield in the solid state; 2a contains a single ring, which is the minimum structure necessary for AIEE). The emission behaviors of these compounds were readily regulated by altering the substituents at the periphery of the core framework. On the basis of the experimental and theoretical results, the relationship between the molecular structures and the corresponding AIE/AIEE processes was attributed to three factors (Table 3). First, the DHP core inherently adopted a twisted conformation, which hampered strong $\pi - \pi$ intermolecular interactions. Second, the types of substituents played critical roles in creating the AIE or AIEE signature. Finally, the mechanisms used to explain the main cause of the AIE/AIEE effect included RIR/RITM. Overall, AIE and AIEE are two similar photophysical properties but not exactly the same in detail. We believe that this study will enable the more flexible design of novel AIE/ AIEEgens for high-tech applications in biotechnology and materials science.

Table 3. Factors summarizing the relationship between the molecular structures and the corresponding AIE/AIEE effect.										
Compound	Substituent	Туре	Motion capacity	Mechanism ^[a]	Phenomenon					
2a 2b,c 1a-c	carbonyl carbonyl/es- ter + phenyl carbonyl	open open enclosed	weak strong weak	RIR RIR BITM	AIEE AIE AIEF					
[a] In addition to RITM of the 1,4-DHP core.										

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Conflict of interest

The authors declare no conflict of interest.

Keywords: aggregation · aggregation-induced emission · fluorescence · nitrogen heterocycles · polycycles

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FULL PAPER

Rational design strategy: By incorporating different substituents at the periphery of the same core, the 1,4-dihydropyridines show aggregation-induced emission or aggregation-induced emission enhancement effects (see figure). Experimental and theoretical studies indicated that the restriction of intramolecular twisting motions or/and rotations played important roles in the corresponding photophysical behaviors.



Aggregation-Induced Emission

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Synthetic Regulation of 1,4-Dihydropyridines for the AIE or AIEE Effect: From Rational Design to Mechanistic Views