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Aggregation-Induced Emission Enhancement of Aryl-Substituted Pyrrole Derivatives

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The relationship between the structures and light emission properties of five aryl-substituted pyrrole derivatives was studied during aggregation in THF−water mixtures. Only pentaphenylpyrrole clearly shows, however, an aggregation-induced emission enhancement (AIEE) phenomenon. On comparison of the optical properties and single-crystal structures of these pyrrole derivatives, it is suggested that the more twisted configuration which prevented parallel orientation of conjugated chromophores combined with the restricted intramolecular rotation (RIR) effect was the main cause of the AIEE phenomenon.

1. Introduction

Development of luminescent materials is a hot topic of current interest because of their applications to the development of fluorescence sensing and light-emitting diode fabrication.[1] Although many luminophores are highly luminescent in dilute solutions, their light emissions are often quenched in the solid state due to aggregation of their chromophoric units in the condensed phase.[2] This aggregation-caused emission quenching (ACQ) is a notorious problem that has seriously obstructed advancement in the development of efficient organic light-emitting diodes (OLEDs), chemosensors, biosensors, etc. It is thus highly desirable to develop "unconventional" luminophoric systems that can overcome this obstacle.[3−5]

Development of luminogens whose films emit more efficiently than their solutions has aroused much interest in recent years. Tang's group in 2001 first reported that the luminescence of silole molecules is stronger in the aggregate state than that in the solution state.[6−9] A variety of luminogens, including distyrylbenzene, fluorene, pentacene, and pyrene derivatives,[10−13] were successively proved to have the same properties. These molecules can be generally categorized into two groups. In the first group, the luminogenic molecules are nonemissive when dissolved in good solvents but become highly luminescent when aggregated in the solid state, thus behaving exactly opposite to the conventional ACQ luminophores. Since the emission is induced by aggregation, Tang coined "aggregation-induced emission" (AIE) for this unusual phenomenon.[6] In the second group, the luminogens are luminescent in solution and become more emissive in the aggregate state. Because the light emission is enhanced by aggregate formation, the effect is referred to as "aggregation-induced emission enhancement" (AIEE).[7]

Such compounds were regarded as competitive candidates for practical use as highly emissive materials, and they seem especially ideal for the nondoped red[14] or blue[15] organic light-emitting diodes (OLED). Moreover, some functional groups introduced into AIE molecules will favor new development of chemo- or biosensors for detecting metal cations, biomolecules, organic vapors, chiral molecules, and explosives.[16]

The novel AIE(E) effects challenge our current understanding of photoluminescence (PL) processes; investigating the causes and mechanisms may help develop new photophysical theories and technological innovations. The ACQ process may generally be attributed to a nonradiative deactivation process, such as excitonic coupling, excimer formation, and excitation energy migration to the impurity traps.[17] What then is the exact cause for the "abnormal" AIE phenomenon? Several models, such as restricted intramolecular rotations (RIR),[18] excimer formation,[19] fluorescent organic nanoparticles (FON) formation,[20] and configuration changed,[21] have previously been proposed for enhanced emission in the solid state, compared with lower PL quantum yield or PL quenching in solution. However, the effect of molecular structure and packing arrangement on the AIE(E) processes has rarely been investigated, although the structure−property relationship is of great value in terms of gaining new insights into AIE(E) mechanisms and guiding further research efforts in the development of new AIE(E) luminogens.

Herein, a series of aryl-substituted pyrrole derivatives, 1,2,5-triphenylpyrrole (TriPP), 1,2,3,5-tetraphenylpyrrole (TetraPP), 1,2,3,4,5-pentaphenylpyrrole (PentaPP), 2,5-di(anthracen-9-yl)-1-phenylpyrrole (DiAnPP), and 2,5-di(phenanthren-9-yl)-1-phenylpyrrole (DiPhenPP), was designed and easily synthesized. In these pyrrole derivatives, the structure of PentaPP is very similar to that of silole. We show that the molecular structure, conformational twisting, structural rigidification, and morphological packing play important roles in the photophysical processes of aryl-substituted pyrrole derivatives, which provide us a convenient way to have a better understanding on the influence of the aryl-substituted numbers and structures to the AIE(E) phenomenon.

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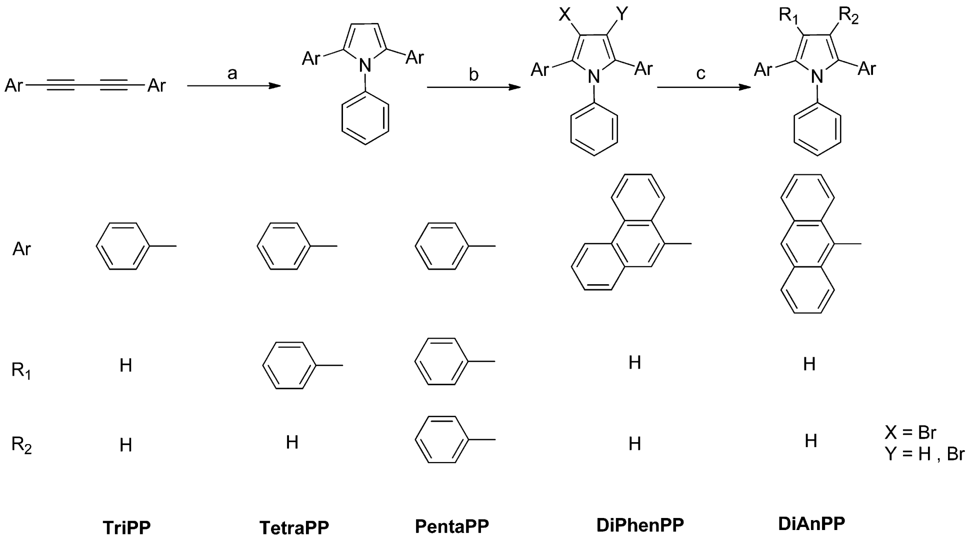
SCHEME 1: Synthetic Routes of Aryl-Substituted Pyrrole Derivatives



(a) Aniline, 100 °C; (b) NBS, DMF, (1) 0 °C and (2) room temperature; (c) Phenylboronic acid, Pd(PPh_3)$_4$, toluene/K_2CO_3 aqueous solution, 110 °C.

2. Results and Discussion

Synthesis. Scheme 1 shows the synthesis routes and molecular structures of the aryl-substituted pyrrole derivatives, TriPP, TetraPP, PentaPP, DiPhenPP, and DiAnPP. Aryl-substituted pyrrole derivatives can be efficiently synthesized in less than four steps from the starting material aryl acetylene. The oxidative coupling reaction gives 1,4-bisaryl butadiyne in good yield.[22] TriPP, DiPhenPP, and DiAnPP were synthesized by reaction of 1,4-bisaryl butadiyne with aniline employing copper chloride.[23] Then TetraPP and PentaPP were readily obtained by Suzuki coupling reaction of phenylboronic acid with aryl bromide pyrroles which were synthesized by *N*-bromosuccinimide (NBS) bromination of TriPP.[24] The reaction products were characterized spectroscopically and crystallographically, from which satisfactory analysis data corresponding its expected structure were obtained.

Aggregation-Induced Emission Enhancement. The photophysical properties of PentaPP during aggregation were first studied due to its similarity structure of silole. The UV−vis absorption spectra and PL spectra of PentaPP were measured in THF/water mixtures with different volume fractions of water, and the final concentrations were kept constant at 1 × 10^{-5} mol/L according to the previous methods.[25]

As can be seen from Figure 1, when the water content in the aqueous THF mixture is ≤60 vol %, the absorbance of PentaPP is almost decreased. At 60% water content, the absorption peak of PentaPP is bathochromically shifted with a big decrease in intensity. At high water contents (≥90%), the absorption peaks of PentaPP are shifted back to the position of its THF solution with moderate decreases in intensity. The absorption spectra of PentaPP in the aqueous THF mixtures with ≥70% water contents contain light-scattering tails in the long wavelength region, suggesting that the molecules of PentaPP have clustered into nanoaggregates in the poor solvents.[25,26] The morphologies of PentaPP aggregates obtained in water/THF solution with different fraction volume of water were observed by FE-SEM measurements (Figure S1a−c, Supporting Information). The experimental results show that the sizes of most PentaPP aggregates obtained in THF−water mixtures with 70% and 80% volume fractions of water are about 140−300 nm × 80−100 nm and 200−400 nm × 50−100 nm with an irregular rectangle, respectively. Thus, the absorption spectra of PentaPP in the aqueous THF mixtures with 70% and 80% water contents are revealed in the light-scattering tails in the long wavelength region. However, the size of PentaPP aggregates (20−30 nm diameter) obtained in THF−water mixtures with 90% volume fractions of water is much smaller than that in 70% and 80% water content. It caused the decreasing of light-scattering tails in the long wavelength region observed in the absorption spectrum for 90% water content solvent (Figure 1).

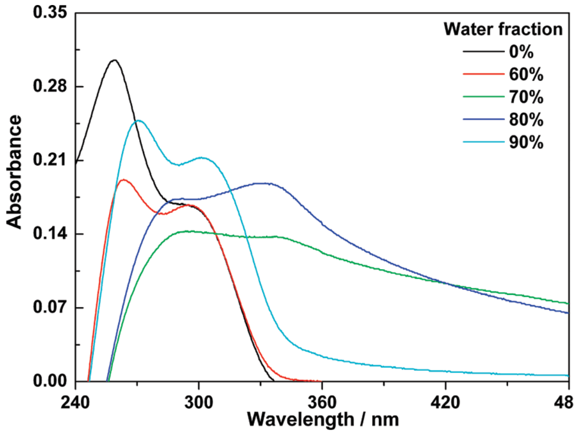


Figure 1. UV spectra of PentaPP in THF−water mixtures with different volume fractions of water. PentaPP concentration: 5 × 10^{-5} mol/L.

Upon photoexcitation, the dilute THF solution of PentaPP shows a PL spectrum with an emission peak at 386 nm (Figure 2). When water is continually added into the THF solution of PentaPP while keeping the luminogen concentration unchanged at 1 × 10^{-5} mol/L, the PL intensity of PentaPP is slowly increased when the water content in the aqueous THF mixtures is "low" (≤60%) but greatly increased when the water content is "high" (>60%) (Figure 2). Since water is a poor solvent for PentaPP, the molecules of PentaPP must have aggregated in the aqueous THF mixtures with high water contents, in agreement with observation of the light-scattering tails in the absorption spectra discussed above (cf., Figure 1). Evidently, the emission of PentaPP is spectacularly boosted by aggregation; in other words, PentaPP is AIEE active. Compared with the

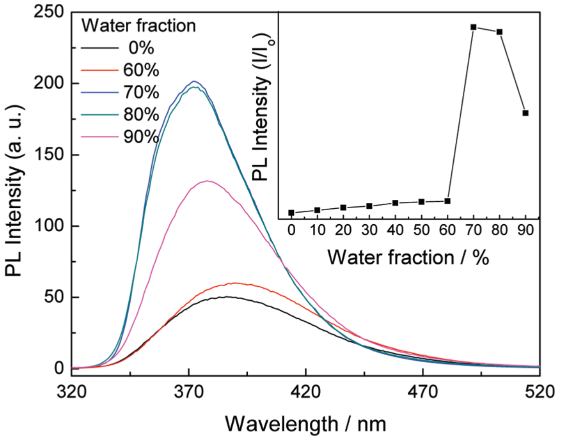


Figure 2. PL spectra of PentaPP in THF−water mixtures. The inset plot indicates the relationship between PL intensities of PentaPP at maximum intensity and water volume fraction in THF−water mixtures. PentaPP concentration: 1 × 10^{-5} mol/L. Excitation wavelength: 310 nm.

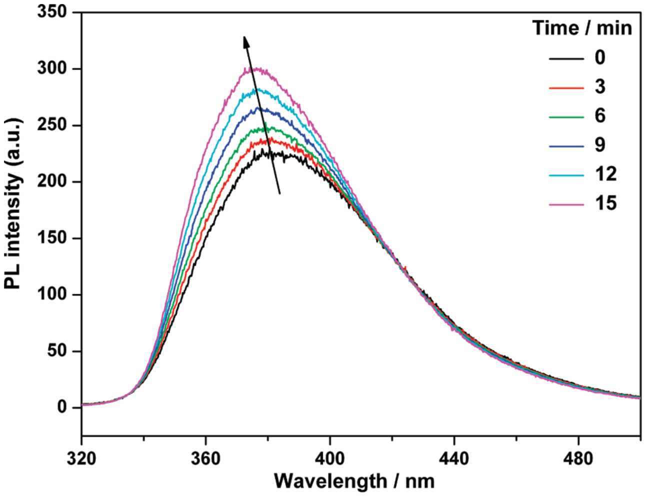


Figure 3. Dependence of the PL intensity of PentaPP to aggregating time in THF−water mixture (20:80 v/v). PentaPP concentration: 1 × 10^{-5} mol/L. Excitation wavelength: 310 nm.

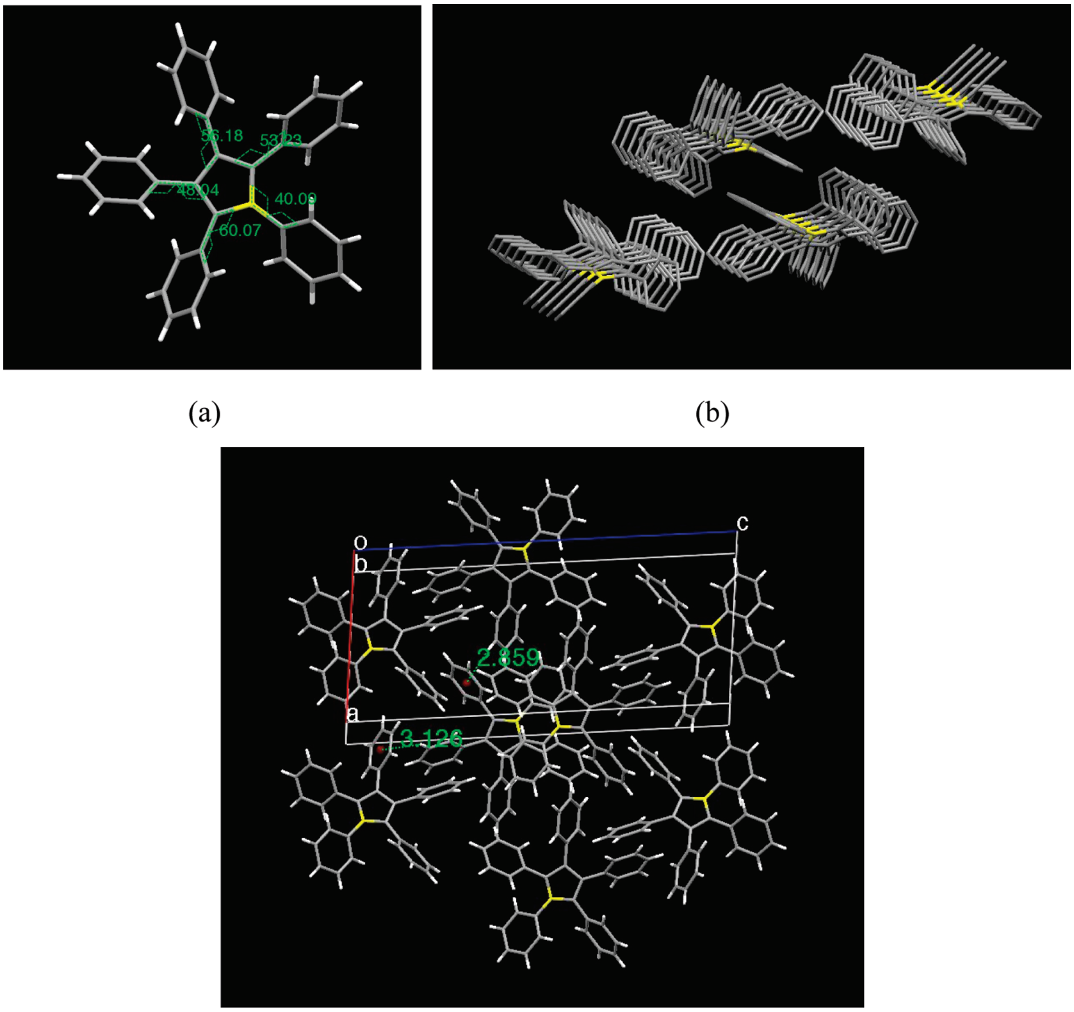
PL spectrum of silole, a moderate blue shift (ca. 15 nm) in the emission peak was observed when the water fraction is increased from 60% to 80%. However, the PL intensity is decreased and a red-shift in the emission peak is from 372 to 378 nm when the water fraction is from 80% to 90%. Careful inspection of the PL spectra of PentaPP in the aqueous mixtures reveals an increase/decrease in the intensity ratio and a blue/red shift in the emission peak, while increasing the water fraction from 60% to 90% agreed well with the absorbance spectra shown in Figure 1. This is probably due to the change in the packing mode of the PentaPP molecules in the aggregates. In the mixture with the "low" water content, the dye molecules may steadily assemble in an ordered fashion to form more emissive, bluer crystalline aggregates. In the mixture with the "high" water content, however, the dye molecules may quickly agglomerate in a random way to form less emissive, redder, and smaller particles (Figure S1a−c, Supporting Information).

To further investigate the process of AIEE phenomenon, we studied the relationship between the PL intensity of PentaPP and the aggregating time in the THF/water mixture with 80% water content. Water was injected to the THF solution of PentaPP with vigorous stirring at room temperature. PL detection was done after stirring for 2 min. The spectra show that the rate of the fluorescence enhancement is first order with respect to the time prolonged, and at the same time the maximum peak gradually blue shifts from 381 to 374 nm (Figure 3). It is assumed that, initially, the mechanical shear stress leads to the raising of valid collision chance; thus, a potion of the dye molecules clustered together to form tiny particles. The portion of the dye molecules remaining in the solvent mixture then gradually deposits onto the initially formed particles in a way similar to recrystallization. Thus, the size of PentaPP aggregates and the arranging degree between PentaPP molecules in the aggregates can be increased with the increasing of the aggregating time, which are more propitious to enhance restricted intramolecular rotations effect. This is the reason why the peak is blue shifted and enhanced.

Mechanism for AIEE. The crystal structures of the fluorophores in the aggregation state are the most direct evidence to help us to explain the mechanism of AIEE. Single crystals of PentaPP were grown through its slow crystallization in a THF/water mixture. Crystals of high quality were used for the XRD analysis. The crystal structure of PentaPP belongs to the monoclinic system with space group *P*2(1)/*c* (Table S1, Supporting Information). In the crystal, PentaPP adopts a highly twisted conformation with torsion angles between the pyrrole group and the neighboring phenyl groups of 40.09°, 53.23°, 56.18°, 48.04°, and 60.07°, respectively (Figure 4a). As shown in Figure 4b, the molecules of PentaPP are packed into molecular columns that are perpendicular to the plane of the central pyrrole rings. The distance between two molecules within one column for PentaPP is 5.14 Å, which is too large to form the $\pi-\pi$ interaction. As shown in Figure 4c, there is no face-to-face $\pi-\pi$ stacking but edge-to-face interactions such as aromatic CH$\cdots\pi$ hydrogen bonding in the crystal structure.[9,11,27] The delocalized system of sp^2-hybridized covalent bonds can act as an acceptor group, and hydrogen atoms serve as proton donors for the formation of aromatic CH$\cdots\pi$ hydrogen bonds. The difference in the torsion angles is caused by the CH$\cdots\pi$ interaction, which in turn stabilizes the twisted conformation of the dye molecule, which helps to hinder rotation of the σ bond between the phenyl rings and the pyrrole group. This structural rigidification may have made the crystals stronger emitters.[7−9]

The fluorescence quenching of PentaPP in solution might be understood as dominant nonradiative decay. In dilute solution, twisting of the σ bond between phenyl and the pyrrole group might facilitate approach between the excited and the ground states of PentaPP and, thus, efficient rapid radiationless decay occurrence. Once the water content is above 70%, however, the degree of internal conversion is insignificant because the rigid environment (C−H$\cdots\pi$ bond formed) restricts intramolecular rotations of PentaPP, resulting in the observed enhanced emission. Furthermore, crystallographic analysis indicates that a long molecular distance (∼5.14 Å) reduces the distance-dependent intermolecular quenching effects to produce intense fluorescence in the aggregation state. Therefore, the enhanced emission of PentaPP is attributed to the synergistic effect of restricted intramolecular rotations with a twisted geometry configuration.

On the basis of B3LYP/6-31G* calculation, Liu et al. found that the filled π orbitals (or HOMOs) and the unfilled orbitals (or LUMOs) are mainly dominated by orbitals originating from the silole ring and two phenyl groups at the 2,5-positions in all cases, while the LUMOs have significant orbital density at two exocyclic σ bonds on the ring silicon, implying that $\sigma^*-\pi^*$ conjugation plays an important role.[8a] The HOMO and LUMO



(a) (b)

(c)

Figure 4. (a) Molecule structure of PentaPP. (b) Stacking image of PentaPP. The hydrogen atoms have been omitted for clarity. (c) The schematic intermolecular interactions in the crystal of PentaPP. The interaction distance of C−H···π center is 2.86 Å (carbon, gray; hydrogen, white; nitrogen, yellow).

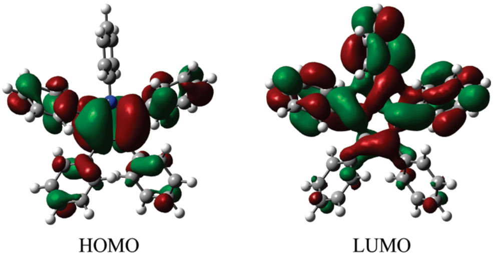


Figure 5. Molecular orbital amplitude plots of HOMO and LUMO energy levels of PentaPP calculated using the B3LYP/6-31+G** basis set.

of PentaPP were calculated by using the B3LYP/6-31+G** method (Figure 5). The results revealed that the HOMO of PentaPP is similar to that of 1,1,2,3,4,5-hexaphenylsilole (HPS),[8a,g] which is located on the core ring (pyrrole or silole) as well as on the phenyl rings. The LUMO wave function of PentaPP is, however, found to be localized on both the pyrrole ring and the three phenyl rings at the 1,2,5-positions with a staggered distribution, which is much more complicated than that of HPS. It may cause the decrease of the fluorescence in the solid state, leading to weaker AIEE response compared to HPS.

To gain insight into the relationship between structures and AIEE phenomenon, we further checked the PL spectra of other

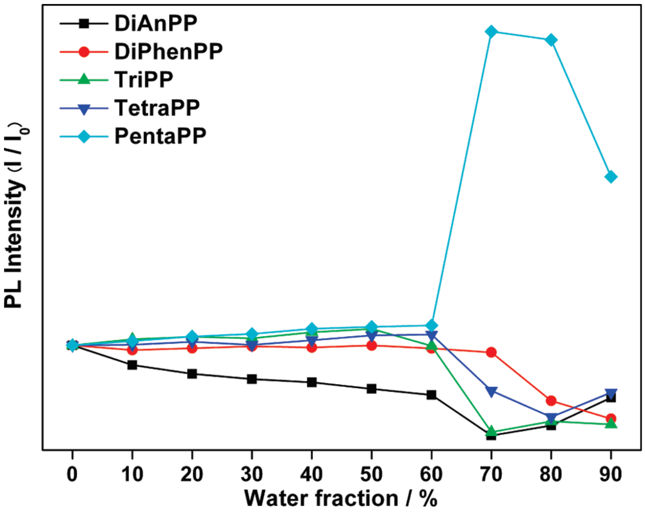


Figure 6. Relationship between PL intensity of aryl-substituted pyrrole derivatives and different water volume fraction in THF−water mixtures.

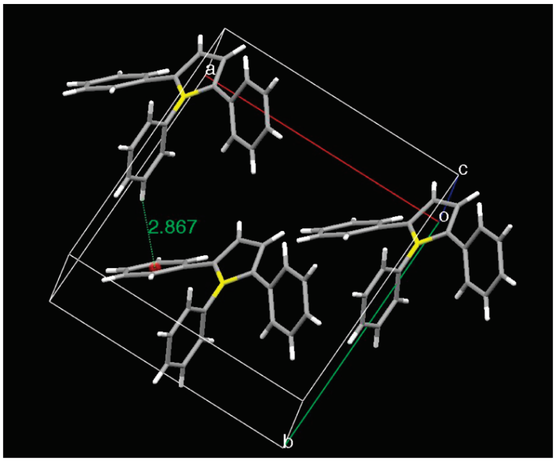


Figure 7. Molecule structure of TriPP. The interaction distance of C−H⋅⋅⋅π center is 2.86 Å (carbon, gray; hydrogen, white; nitrogen, yellow).

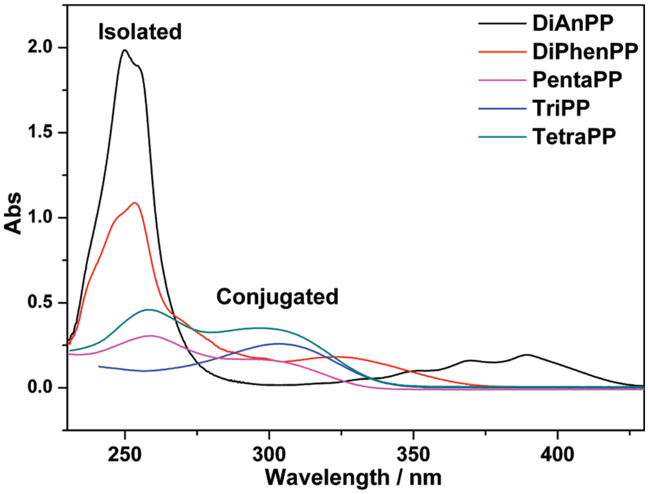


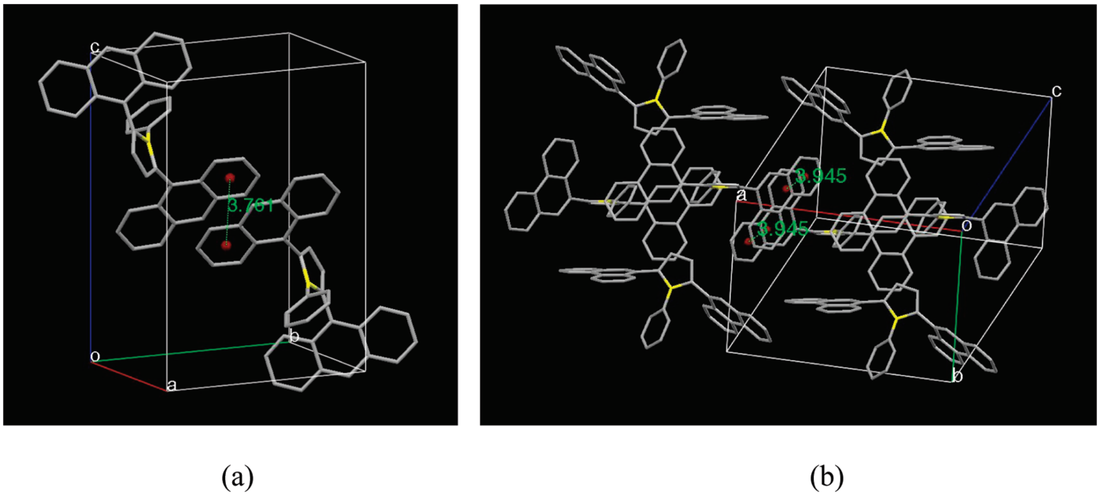
Figure 8. UV spectra of aryl-substituted pyrrole derivatives in THF solution.

aryl-substituted pyrrole derivatives containing different substituted groups numbers and structures.

As shown in Figure 6, PL intensities of TriPP and TetraPP remained unchanged when the water fraction in THF−water mixtures is gradually increased to 60% and begin to decrease after 70% water fraction. To explain the reason, the single-crystal structure of TriPP was emphatically studied. The single-crystal structure of TriPP belongs to the monoclinic system with a space group of C_2, which is different from that of PentaPP. The analysis revealed that the CH⋅⋅⋅π bond also plays an important role in stabilizing the crystal structure instead of π−π interactions in the crystal structure of TriPP (Figure 7).

We compared the UV spectra of these compounds (Figure 8). The π−π* transition of isolated phenyl groups in TetraPP and PentaPP occurs at 258 nm, whereas in TriPP it is hard to find the absorbance of isolated phenyl groups. The bathochromic shift of absorption bands to 303 nm in TriPP is due to the conjugation of the phenyl groups and pyrrole group, which can be explained in terms of interaction or delocalization of the π and π* orbital of each chromophore to produce a new orbital in which the highest π orbital and the lowest π* orbital are closer in energy. It indicates that the lowest energy, most stable conformation of TriPP in solution is coplanar with extension of π-delocalization. However, it is hard to find face-to-face π−π stacking in the single-crystal X-ray diffraction of TriPP, which means that the conformation of the pyrrole system in the single crystal favored the nonplanar structure instead of the planar structure in the solution state. Thus, we consider that aggregation, which happened while adding water into THF solutions, is the process under kinetic control; π−π stacking, which is the nonradiative de-excitation pathway, happened during collisions of the chromophores. It is not similar to the conformation of TriPP in the single crystal we obtained, which is under thermodynamic control.

Furthermore, anthracenyl and phenanthrenyl groups with a bigger conjugated structure and steric hindrance were used to substitute phenyl groups in TriPP and induced to the pyrrole system, respectively. The bigger conjugated substitutes did restrict rotation of the single bond between the pyrrole group and the neighboring aryl groups in DiAnPP and DiPhenPP as we expected (the torsion angles between the pyrrole group and the neighboring aryl groups in the single crystal reach almost 80° (Figure 8a and 8b); the UV spectra also indicate that in the solution state the structures of these two compounds are isolated (Figure 7)), which made the conjugation in these two compounds totally destroyed. However, the changing trend of PL intensities of the two compounds with the water fraction remained almost the same as TriPP, which are not AIEE properties (Figure 3). We found that the distance between the π−π stacking of the



(a) (b)

Figure 9. Molecule structure of (a) DiAnPP and (b) DiPhenPP (carbon, gray; hydrogen, white; nitrogen, yellow. Hydrogen atoms of DiAnPP and DiPhenPP have been omitted for clarity).

anthracenyl groups and the phenanthrenyl groups is 3.76 and 3.94 Å (Figure 9a and 9b) in the single-crystal structure of DiAnPP and DiPhenPP, respectively. The anthracenyl and phenanthrenyl groups are so big that they can stack by themselves, which provide a nonradiative route to dissipate the energy from de-excitation.

3. Conclusions

In summary, we successfully synthesized a series of aryl-substituted pyrrole derivatives and investigated the mechanism for the AIEE effect. On consideration of the difference in the chromophore structures and their steric hindrance, it is concluded that the RIR process combines with the huge steric hindrance to void the intermolecular $\pi-\pi$ interactions during the aggregation state, which might play a crucial role in overcoming fluorescence quenching in the solid state, proving the value of our molecular-design strategy.

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Supporting Information Available: General procedure for the synthesis of five aryl-substituted pyrroles; analytical data of NMR, elemental analysis, mass spectroscopy, and single-crystal structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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