From A Fluorescent Chromophore in Solution to An Efficient Emitter in the Solid State

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Abstract: Polycyclic aromatic hydrocarbons (PAHs) normally exhibit efficient fluorescence in dilute solutions, whereas their emission is significantly quenched in the aggregated state due to the formation of π -aggregates/excimers. The rigid and planar structure of PAHs plays a positive role in terms of fluorescence in solution but a negative one in the aggregated state. To bestow PAHs a luminescent ability in the solid state, we constructed a non-coplanar PAH-substituted ethene. By using the

Keywords: aggregation-induced emission • fluoranthene • polycyclic aromatic hydrocarbons planar PAH fluoranthene as a building block, a highly efficient solid-state emitter with a fluorescence quantum efficiency of unity in the aggregated state was obtained. OLEDs with contain the molecule as an emitter reach a luminance up to 20520 cd m⁻² and an efficiency of 10 cd A⁻¹.

Introduction

Fluoranthene is a polycyclic aromatic hydrocarbon (PAH) consisting of a naphthalene and a benzene unit connected by a five-membered ring (Scheme 1). The chemistry of fluoranthene and studies of the photophysical properties evolved rapidly after the elucidation of its structure;^[1] however, the interest in fluoranthene faded fast, especially in applications as a solid-state fluorophore in optoelectronics.^[2] Like other planar PAHs, the utility of fluoranthene and its derivatives as emitting materials has been greatly restricted due to aggregation between the planar chromophores. This kind of aggregation usually leads to the formation of π -aggregates/excimers and causes low solid-state fluorescence quantum yields.^[2] On the other hand, it is well known that

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Scheme 1. Chemical structures of fluoranthene, tetraphenylethene (TPE), and 1,2-bis(8-fluoranthenyl)-1,2-diphenylethene (DFAE).

the rigid and planar chemical structures benefit the fluorescent ability of chromophores in solutions. Hence, if the aggregation between molecules of PAH derivatives can be alleviated, their emissive nature will be regained in the solid state. To meet the practical demand for highly efficient solid-state emitters in the fields of organic optoelectronics such as organic light-emitting diodes (OLEDs) and organic laser diodes, much effort has been devoted to eliminate the notorious effect of aggregation-caused quenching (ACQ) of PAHs.^[3] For fluoranthene in particular, a highly luminescent solid-state light-emitting molecule, 7,8,10-triphenylfluoranthene, has been designed. The steric hindrance of the perphenylated PAH was believed to reduce facial contacts that led to excimer quenching and bathochromic shifts. This derivative reached a maximum efficiency of $3.02 \text{ cd } \text{A}^{-1}$ (1.83% external quantum yield) in OLEDs.^[4] However, because every luminophore has an inherent tendency to aggregate in the condensed phase, the resistance against the intrinsic aggregation nature is not good enough to make use of it. From this viewpoint, the characteristics of aggregationinduced emission (AIE) will serve the role. By introducing AIE into fluoranthene, we hope to take advantage of the rigid and planar structure of this compound and turn it into

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an efficient solid-state emitter. In this report, a non-coplanar fluoranthene-substituted ethene was designed and synthesized (Scheme 1). This analogue of tetraphenylethene (TPE) possesses the same AIE property as TPE and does not suffer from the ACQ effect.

Results and Discussion

In our previous works, we have succeeded in converting the typical ACQ chromophores triphenylamine and pyrene into efficient solid-state emitters with AIE characteristics by decorating them with TPE as peripheries.^[5] Herein, we report another facile strategy to generate AIE-active luminogens from planar PAH chromophores, that is, using them as building blocks to construct directly the corresponding analogue of TPE. Since the origin of the unusual AIE effect of TPE has been identified as restriction of rotations of its multiple benzyl blades in the aggregate,^[6] we expected that their analogues should possess similar AIE features as TPE. This speculation has been proved in our previous experimental results.^[7] By using one or more aromatic substituents to replace the benzyl ones, the resultant tetrasubstituted ethenes luminesce indeed efficiently in the solid state. Based on this idea, an ethene substituted by two fluoranthenes and two phenyls, 1,2-bis(8-fluoranthenyl)-1,2-diphenylethene (DFAE) was designed and synthesized. Scheme 2 shows the



Scheme 2. Synthetic route to DFAE and its optimized geometry.

synthetic route to DFAE. The procedure is quite facile and efficient. The fluoranthene was first incorporated into 8-benzoylfluoranthene by AlCl₃-catalyzed Friedel–Crafts acylation. A subsequent $Zn/TiCl_4$ -mediated McMurry coupling reaction produced the target compound in high yield. Details of the synthetic procedures and characterization data are presented in the Supporting Information. The identity

Abstract in Chinese:

很多多环芳烃在其稀溶液中表现出不错的荧光,在固态 下却由于形成分子间π聚集或是 excimer 等而导致显著的 荧光猝灭。如何使多环芳烃刚性且平面化的分子骨架在 固态荧光性能中发挥正面作用,是本工作的目的。我们 设计了一种方法,将多环芳烃荧蒽作为取代基利用 McMurry 偶联直接构建螺旋桨结构的非平面化的四取代 乙烯。得到的产物表现出典型的聚集态荧光增强特性, 在固态下的荧光量子产率接近100%。 and purity of the product were verified by ¹H and ¹³C NMR spectroscopy and high-resolution mass spectrometry. The purity of the material was also assessed by elemental analysis with satisfactory results.

The molecular conformation of DFAE was analyzed by density functional theory calculation at the DFT/B3LYP/6-31G(d) level. The result shows a typical propeller-like nonplanar conformation. The dihedral angles between the two fluoranthenes and the two phenyl rings are 78.2° and 75.4°, respectively. Such propeller-shaped geometry will hamper a close intermolecular π - π stacking and facilitate the molecules to adopt a loose packing in the condensed state. However, the non-coplanar structure does not disrupt the conjugation of the whole molecule. Figure 1 shows the molecular



Figure 1. Molecular orbital amplitude plots of HOMO and LUMO energy levels of DFAE.

orbital amplitude plots of HOMO and LUMO energy levels. It can be seen that all four aryl substituents contribute to the molecular orbitals. This is different to the dyes decorated with TPE as peripheries, in which the orbitals are mainly dominated by the core part. Moreover, the emission wavelength for that kind of luminogens changed only slightly from that of their core part.^[5] In other words, using TPE as peripheries of PAHs hardly changes their electronic nature, while building the TPE analogues with PAHs directly enables uniform electron delocalization along the whole molecule. The higher extent of conjugation and lower intermolecular π - π interactions make the molecule an efficient solid-state emitter. Figure 2 shows the fluorescent micro-



Figure 2. Fluorescence microscopic images of microspheres of DFAE.

scopic images of the microspheres of DFAE. Perhaps also due to its propeller-shaped structure, DFAE is morphologically quite stable. Hence, many efforts to grow crystals failed; instead we always obtained microspheres. The microspheres shown in the images were obtained from a solution of DFAE in dichloromethane/ethanol after slow evaporation

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Figure 3. Photoluminescence spectra of A) fluoranthene and C) DFAE in THF/water mixtures with different water fractions (f_w). Plots of (I/I_0) values as a function of solvent composition of B) fluoranthene and D) DFAE. E) Fluorescent images of DFAE in THF/water mixtures with different water fractions.

of solvent. Under UV irradiation, the spheres emit a strong greenish yellow light.

Figure 3 depicts the change in fluorescence of DFAE from the solution state to the aggregated state in aqueous suspension. For comparison, the fluorescence of fluoranthene was recorded under the same conditions. In pure THF solution, fluoranthene displays a nice fluorescence with a quantum yield (Φ_{Fs}) of about 30%. Upon the addition of the non-solvent water, its fluorescence intensity increased slightly initially, which is attributed to the increase in solvent polarity.^[8] When the water fraction (f_w) becomes high (> 80%), the dissolved fluoranthene starts to aggregate, which is accompanied by a decrease in fluorescence. At a f_w of 95%, the fluorescence intensity is reduced to about 60% of its original value. Thus, fluoranthene is a typical ACQ fluorophore. In sharp contrast, the propeller-shaped tetrasubstituted ethene DFAE is nearly non-emissive when dissolved in a good solvent (THF, chloroform, dichloromethene, etc.). As shown in Figure 3C, very weak photoluminescence (PL) signals are recorded in a THF/water mixtures of $f_{\rm w} < 60\%$, in which the DFAE molecules are genuinely dissolved. The increase in polarity of the solvent does not promote the fluorescence as in the case of fluoranthene. The emission intensity starts to increase upon increasing the f_w to values larger than 60%; in such mixtures the solvating power of the mixture is worsened to such an extent that the luminogen molecules begin to aggregate. From the solution in pure THF to the aggregate suspension in 5% aqueous THF (f_w = 95%), the fluorescence intensity of DFAE at 526 nm increases approximately 25-fold. The change from the none-missive to the emissive state of DFAE with increasing f_w , which demonstrates that DFAE is AIE-active, can clearly be observed visually (Figure 3E).

The fluorescence quantum yields of DFAE in the solution and in the solid state were quantitatively measured by a reference and absolute method, respectively. The obtained results further validated its AIE activity. The quantum yield of DFAE in THF is as low as 0.68%, while that of its solid thin film reaches 100%. Accordingly, DFAE behaves just like its analogue TPE, displaying enhanced emission in the solid state. Intramolecular rotations along the single bonds between the central ethene and the peripheral fluoranthenyl or phenyl rings are likely responsible for its AIE behavior. That is, the aromatic rings undergo an active intramolecular rotation process in solution at the excited states, which nonradiatively annihilates their energy and renders the molecules non-luminescent, while the rotation process is impeded in the aggregated state, thus blocking non-radiative decay channels.^[9] Moreover, the propeller-shaped structure prevents the luminogens from packing in a close π - π stacking mode. The emission of DFAE exhibited a bathochromic shift of about 70 nm as compared to that of fluoranthene, thereby suggesting electron delocalization along the entire molecule. Thus, the restriction of intramolecular rotations and the lack of intermolecular interactions account for the restraint of the solid-state emission quenching. Upon overcoming the ACQ effect, the large conjugation and rigid structure of fluoranthene facilitate its luminescent ability.

Next, the thermal stability of DFAE was investigated by thermogravimetric (TGA) and differential scanning calorimetry (DSC) analyses. As shown in Figure 4, DFAE had a degradation temperature (T_d) of 366 °C. The DSC measurement on the second heating cycle showed a glass transition tem-



Figure 4. TGA and DSC thermograms of DFAE recorded under N_2 atmosphere at a heating rate of 20 (TGA) and 10 (DSC)^oC min⁻¹.

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perature (T_g) at 137 °C, which is quite a high value compared to most of the electroluminescence materials. A good thermal and morphological stability is essential to improve the performance and lifetime of optoelectronic devices.

The high thermal stability and efficient solid-state emission of DFAE prompted us to study its electrolumi-

nescence (EL) properties. The device architecture was designed according to the energy level of the material, and the electrochemical property of DFAE was studied by cyclic voltammetry. The HOMO energy level determined from the onset of the oxidation is 5.5 eV (relative to the vacuum energy level). The LUMO energy level deduced from the difference between the HOMO level and the optical band gap is located at 2.8 eV. Thus, in a device structure as shown in Figure 5 A, the luminogen should work well under a balanced charge transport.

Figure 5B–E show the EL performances of the device based on DFAE. The device emits yellow light with an EL maximum (λ_{EL}) of 548 nm, which is quite close to that of the PL in thin film. The device based on this AIE luminogen exhibits good EL performances. The maximum current efficiency (η_c), power efficiency (η_p), and external quantum efficiency (η_{ext}) attained are 10 cd A⁻¹, 5.7 Lm W⁻¹, and 3.1%, respectively (Table 1). The device reaches a maximal bright-



Figure 5. A) Energy level diagram and device configuration of multilayer EL devices of DFAE. B) PL and EL spectra of a solid thin film of DFAE. C) Current density and luminance as a function of voltage for the device containing DFAE. D) Power efficiency and current efficiency as a function of voltage for the device containingDFAE. E) External quantum efficiency as a function of voltage for the device containing DFAE.

ness of 20520 cd m⁻². At a practical brightness of 500 cd m⁻² (with an applied voltage of 8 V and a current density of 5.3 mA/cm^2), the device can still maintain a high efficiency (9.4 cd A⁻¹). For the fluorescence OLEDs, the EL performance of DFAE is really a good result.^[10]

Table 1. Electroluminescence performances of a device based on DFAE.

V _{on} [V]	$L \left[cd m^{-2} \right]$	$\eta_C \left[cd A^{-1} \right]$	$\eta_P \left[lm W^{-1} \right]$	$\eta_{\rm ext}$ [%]	λ_{em} [nm]
Maximum Values 3.8	20520	10 (at 6.6 V)	5.7 (at 4.6)	3.1 (at 6.6 V)	548
Values at 500 cd m ⁻² $\frac{8}{3}$	500	9.4	3.7	2.9	548

Conclusions

In summary, a new facile strategy of generating highly solidstate emitters from planar PAH chromophores was developed in this work. By using the planar fluoranthene as a building block for a tetrasubstituted ethene, the resulting DFAE is endowed with an AIE effect. Efficient solid-state fluorescence ($\Phi_F = 100\%$) was achieved. DFAE works well as a solid emitter in OLEDs, with a maximum luminance of up to 20520 cdm⁻² and an efficiency of 10 cdA⁻¹. Thus, fluoranthene, a PAH with an intrinsic ACQ effect, was successfully incorporated into an AIE luminogen. We are hopeful to create more efficient solid emitters with other PAHs by using this strategy.

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Solid-State Fluorescence

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From A Fluorescent Chromophore in Solution to An Efficient Emitter in the Solid State



Switching roles: As a polycyclic aromatic hydrocarbon, fluoranthene efficiently emits in dilute solution but displays quenched fluorescence in the aggregated state due to its rigid and planar structure. By incorporating it into a tetrasubstituted ethene, the resulting compound, 1,2-bis(8-fluoranthenyl)-1,2-diphenylethene (DFAE), is endowed with an aggregation-induced emission effect. Efficient solid-state fluorescence ($\Phi_{\rm F}$ =100%) was achieved.

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