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A Family of Planar Luminogens with Active Photoluminescence in both Dispersion and Aggregation States

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Molecular skeletons with active photoluminescence emission in both dispersed and aggregated states are important for diverse applications. As planarization of molecular configuration in the excited state has been shown to be a critical precondition for efficient emission, developing luminogens with pristine planar geometry seem to be the most straightforward approach. However, conventional planar ACQ-type (aggregation-caused quenching) luminogens (e.g. perylene) or novel planar AIE-type (aggregation-induced emission) luminogens exhibit week emission in the aggregated or dispersed states, respectively. Herein, we describe the synthesis of a family of pristine planar luminogens which demonstrate photoluminescence in both the dispersion and aggregation states. The avoidance of a concentration quenching effect in the solid state could be attributed to weakened π–π interactions within the herringbone featured crystal structures based on experimental and theoretical evidence. We further investigated the potential applications of these luminogens in cell imaging.

Introduction

Planar aromatic building blocks prove to be pivotal elements through the construction of highly efficient solid-state luminescent materials.[1] However, planar luminogens tend to be closely packed in their crystal structure with tight π–π interaction between aromatic moieties in common sense.[2] This facilitates the formation of energy dissipative species as excimer or exciplex under excitation and brings about the exhausting aggregation-caused quenching (ACQ) effect at solid-state.[3] Meanwhile, progressively more research articles recommend that planar molecular geometry favors increasing emission efficiency of specific luminogen.[4] Thus, sketching and reaping of emissive molecular ensemble bearing planar geometry and suppressing the troubling aggregation quenching behavior stimulates our research interest ambitiously.

To date, few luminogens with both pristine (quasi-) planar molecular structure and active solid-state emission have been reported. The majority of them work through Excited-State Intramolecular Proton Transfer (ESIPT) type procedure,[5] which involves a tautomerism pathway (enol-keto transformation most of the time). As illustrated in Figure 1a, formation of intramolecular hydrogen bond with restriction of intramolecular rotation at aggregation state impedes the concentration quenching effect.[6] Other examples shown in Figure 1b including the diaryl-substituted ethylene decorated with ethoxy groups reported by Huang and co-works,[7] the Acceptor-Donor-Acceptor (A-D-A) type molecular structure proposed by Zheng and co-workers,[8] the organoboron architecture with adjacent imino-double bond constructed by Li's group.[9] These fascinating molecular designs share effective AIE characteristic with sacrifice of solution state emission. As efficient dispersion state emission is also pivotal for numerous procedures involving fluorescence sensing, tracing, *etc.*, obtaining luminogens with balanced photoluminescence emission in both dispersion and aggregation states is quite intriguing.

Fluoranthene is such a planar luminogen with active photoluminescence emission in both dispersion and aggregation states. The phenomenon of being immune to concentration quenching with it has been disclosed at 1968[10] while research on the fluoranthene derivatives and attached applications initiated since then.[11] Facilitated with its simple molecular structure, high chemical stability and diverse modification strategy, a series of novel devices and techniques spring up. High-efficient electroluminescent devices have been designed and fabricated with fluoranthene and its derivatives.[12] High-performance organic solar cell based on fluoranthene derivatives have been reported.[13] Besides, bio-imaging agents,[14]

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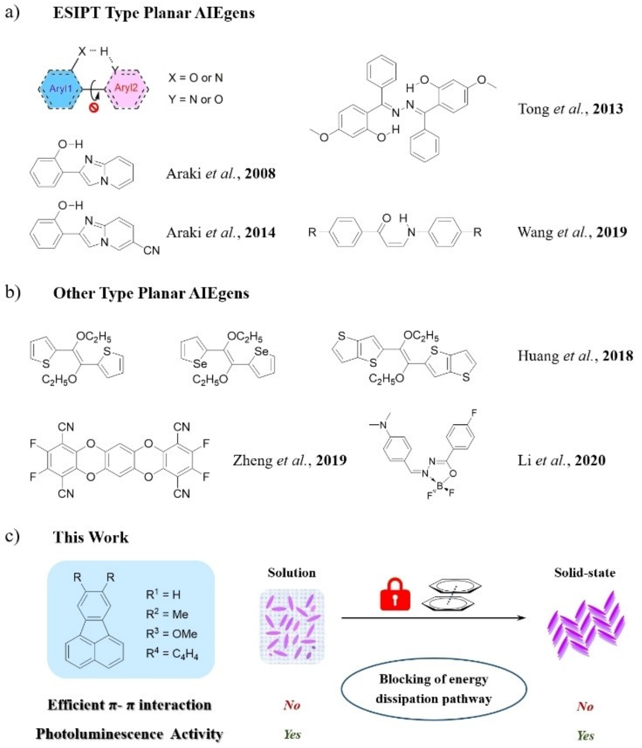

Figure 1. Illustration of (quasi-)planar luminogens with active solid-state emission. a) ESIPT type, b) other types, c) the fluoranthene-type luminogens within our work.

emissive nano-structures[15] and luminescent cocrystals[16] have been developed within fluoranthene scaffold. However, systematic summarization and illustration of their inherent photochemical properties under molecular level are scarcely carried out. In this work, we comprehensively investigate the abnormal photoluminescence behaviors within this family of fluoranthene derivative planar luminogens for the first time. Our results and illustrations might stimulate more research insights which facilitate construction of progressive luminescent devices and techniques. Four typical instances are picked and synthesized for discussion as shown in Figure 1c. Their counter-intuitive photochemical behaviors in the solid-state are displayed and thoroughly demonstrated with X-ray Crystallography and theoretical calculation. Naive live-cell imaging experiments are further conducted with encouraging results for potential applications.

Results and Discussion

In this work, we firstly obtained the target luminogens in high purity via elaborate procedures as supplied in the Supporting Information. ^{1}H-NMR, ^{13}C-NMR and MALDI-TOF-MS results were acquired to confirm the proposed molecular structures of these luminogens. Gradually extended conjugation length from **FA**, **DiMe-FA**, **DiOMe-FA** to **Naph-FA** was evidenced by bathochromic shifting of the maximum absorption wavelength in UV-Vis spectra as shown in Figure 2. Observation of fine structures in absorption curves indicates that plausible planar molecular geometry might be taken by these four luminogens.[7,17]

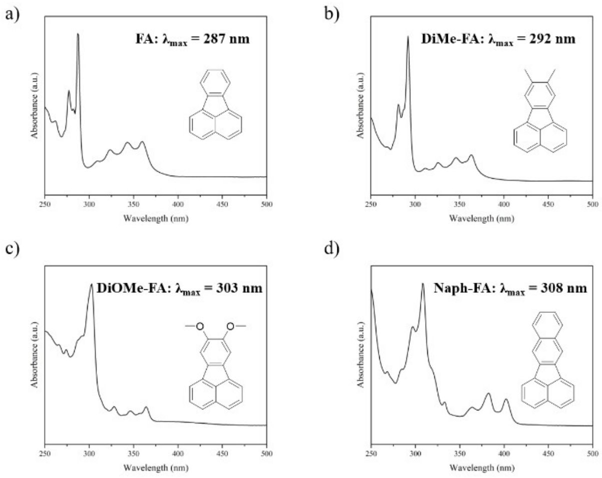

Figure 2. UV/Vis absorption spectral profiles of a) **FA**, b) **DiMe-FA**, c) **DiOMe-FA** and d) **Naph-FA**. (THF as solvent; concentration: 10 μM)

With the grasp of basic spectroscopic information at ground state, we carry out our investigation on the emissive behavior of these four luminogens under irradiation. As summarized in Table 1, maximum emission wavelength of **FA**, **DiMe-FA**, **DiOMe-FA** and **Naph-FA** ranges from 433 nm to 526 nm. It covers purple, blue, cyan and yellow within the visible range to be exact. Large stokes shift beyond 200 nm has been recorded which is scarcely observed among pristine organic molecules.[18] Solid-state fluorescence spectrum of four pressed powder samples present an increasing maximum emission wavelength from **FA** to **Naph-FA** in accordance with the absorption spectrum. Irradiating on the solid samples engenders brilliant emission which seems quite counter-intuitive for these planar molecules.[2–3] Photoluminescence quantum yield measurement shows that these four luminogens emit efficiently at both solution and solid-state under irradiation. A well accepted protocol is utilized to reveal the intrinsic aggregation-induced emission (AIE) property of this molecular skeleton (detailed procedure and results is illustrated in *Supporting Information*). And we could uncover that bright spot preserves as it transforms from solution state to solid-state in Figure 3b. This novel property endows our luminogens with huge potential in both solution and solid-state applications.

Abnormal photochemical behavior of this type of luminogen provokes our research interest in disclosing the fundamental working principle beyond molecular level. X-Ray diffraction method proves to be a powerful tool in analyzing structure and interaction at ensemble level. Thus, we attempt to grow single crystals via liquid/liquid diffusion method in $CHCl_3$-hexane solution. This protocol yields needle-like crystals for **FA** and **Naph-FA**. Prismatic single crystal is obtained for **DiMe-FA** while platelet one for **DiOMe-FA**. Planar geometrical configurations are confirmed with solid evidence through the well-solved crystal structures as shown in the left and middle column of

Table 1. Photochemical parameters of **FA** and its derivatives. Detailed spectral profile can be found in the Supporting Information.

Parameters	FA	DiMe-FA	DiOMe-FA	Naph-FA
$\lambda_{\text{abs max, sol}}$ [nm]	287	292	303	308
$\varepsilon_{\text{abs max, sol}}$ [$L \cdot mol^{-1} \cdot cm^{-1}$]	47884	48398	33672	26553
$\lambda_{\text{em max, sol}}$ [nm]	463	482	526	433
$PLQY_{sol}$ [%]	27.85	16.67	7.21	36.31
τ_{sol} [ns]	32.7	24.1	7.74	8.23
$\lambda_{\text{abs max, s}}$ [nm]	402	424	426	408
$\lambda_{\text{em max, s}}$ [nm]	460	494	514	512
$PLQY_{s}$ [%]	64.50	26.32	14.83	12.34
τ_{s} [ns]	44.2	35.7	13.9	14.9

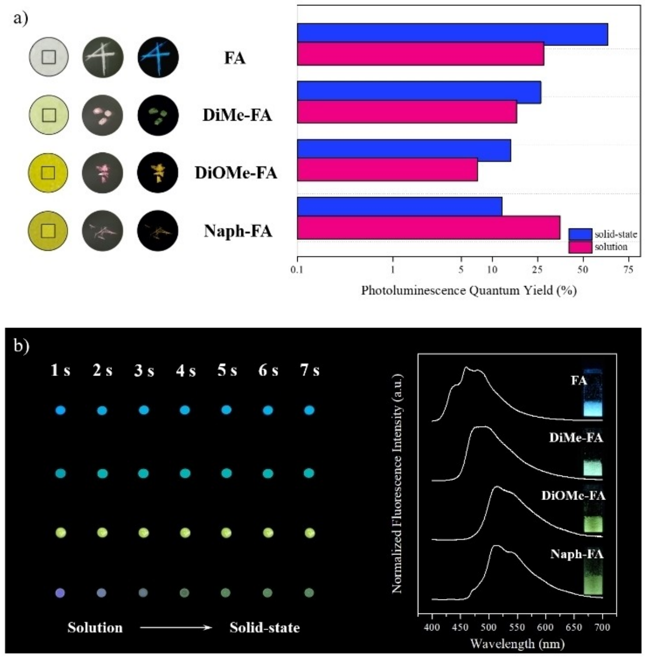

Figure 3. Four planar luminogens with active photoluminescence emission in both the dispersion and aggregation states. a) Crystalline samples under a fluorescence microscope and their corresponding PLQY values in solution and in the solid state. b) Direct observation of photoluminescence emission during the transformation from solution to the solid state and the solid-state fluorescence spectra of four luminogens. (PLQY of solution samples are measured at 1 mM in THF solution).

Figure 4 (CCDC Nos. 2108695, 2108697, 2108698 and 2108699). Analogously, these four molecules take the herringbone staking mode within their packing structures as shown in the right column of Figure 4. Parallel displacement spanning 5.309 Å, 5.675 Å and 5.372 Å is identified for **FA**, **DiOMe-FA** and **Naph-FA** crystal respectively. DiMe-FA molecule is observed to adopt anti-parallel alignment with the center of mass displacement as 3.278 Å.

Aiming at further understanding the basic chemical principles dominating this abnormal concentration quench immunity effect, we carry out theoretical calculations of four planar luminogens at both solution and solid phase. As shown in Figure 5, few differences could be tracked from their electronic structures including main frontier molecular orbitals, energy levels and transition properties within solution and solid-state. These results are in accordance with our experimental spectral profiles. To identify plausible aggregation effect, we calculate the exciton couplings of investigated systems as shown in Table S2. The exciton coupling is too small to induce an excitonic effect except **Naph-FA** presents a positive exciton coupling around 18–25 meV (see in Figure S13). It is a general phenomenon that most solid-state emission quenching luminogens experience strong π–π stacking interactions within their packing structures. We attempt to explore intermolecular interactions exhibiting in crystal structures of four planar luminogens. As shown in Table 2, the intermolecular dispersion predicted by XSAPT+MBD method[19] in nearest dimer of the all the investigated crystal structures and classical ACQ system perylene as comparison. It could be found that perylene bears larger absolute value of E_{disp}, which corresponds to a stronger π-stacking effect. Since the E_{disp} contributes to the major attractive forces, the larger absolute value of E_{disp} leads to a more attractive E_{tot} experienced by each π-electron.[20] Compare to perylene with strong π–π interaction, the FA derivates have smaller total interaction energy around −7.13 to −9.99 kcal·mol^{-1} between its nearest monomer. Due to the smaller interaction energy, excimers are not likely to form inside these materials and thus benefit active solid-state emission.

As an exploration of practicality, we conduct the living-cell imaging study on these four luminogens.[21] The most commonly researched *HeLa* cells are selected for our experiment and then short-time incubation with exact dyes is performed

Table 2. π–π interaction energies and dispersion energies of the investigated molecules. The nearest dimer in the crystal structure is chosen for calculation. All energetics are shown in the unit of kcal·mol^{-1}.

Molecule	E_{tot}	E_{disp}	E_{tot} per π-electron	ACQ
FA	−7.13	−9.84	−0.45	NO
DiMe-FA	−7.41	−11.06	−0.46	NO
DiOMe-FA	−9.99	−12.75	−0.62	NO
Naph-FA	−9.63	−14.41	−0.48	NO
Perylene	−14.41	−30.52	−0.72	YES

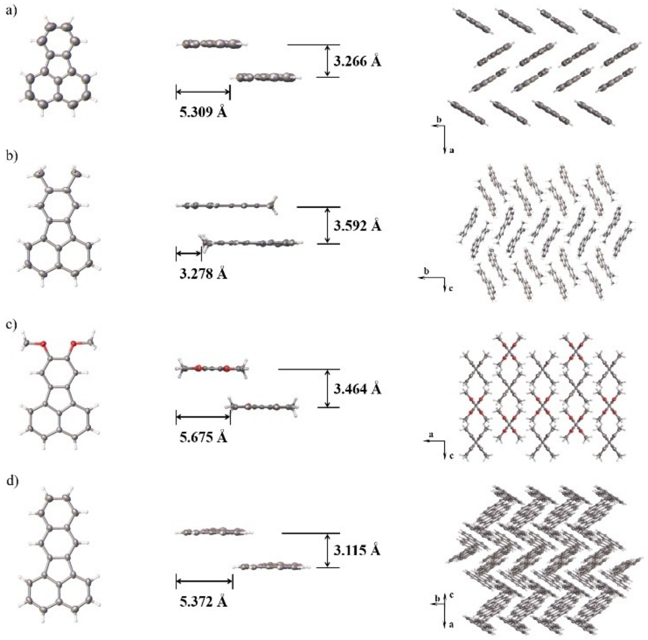

Figure 4. X-ray crystal structures including structural solutions, alignment analysis and the packing model of a) **FA**, b) **DiMe-FA**, c) **DiOMe-FA** and d) **Naph-FA**.

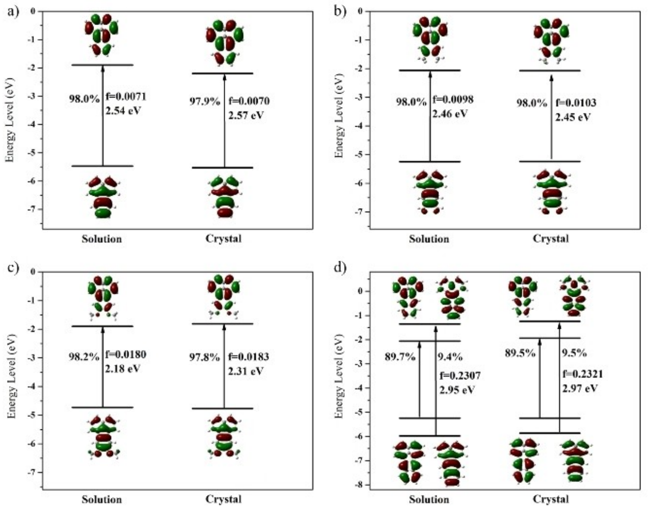

Figure 5. Selected frontier molecular orbitals and important transitions of the S1 state at optimized S1 geometries in solution and crystal of a) **FA**, b) **DiMe-FA**, c) **DiOMe-FA** and d) **Naph-FA**.

before confocal observation (*Hela* cells were purchased form Biorbyt and detailed experimental procedure could be found in Supporting Information). In Figure 6, we could notice the bright emission from stained cells with specific dyes. This modest living-cell imaging performance stimulates our vitalities towards further molecular engineering based on the fluoranthene scaffold according to our synthetic strategy. Introduction of targeted functional groups and diverse post-modification avenues offer huge potential in Biomedical applications. Relevant project is impelling in our laboratory and systematic results would be summarized in our future work.

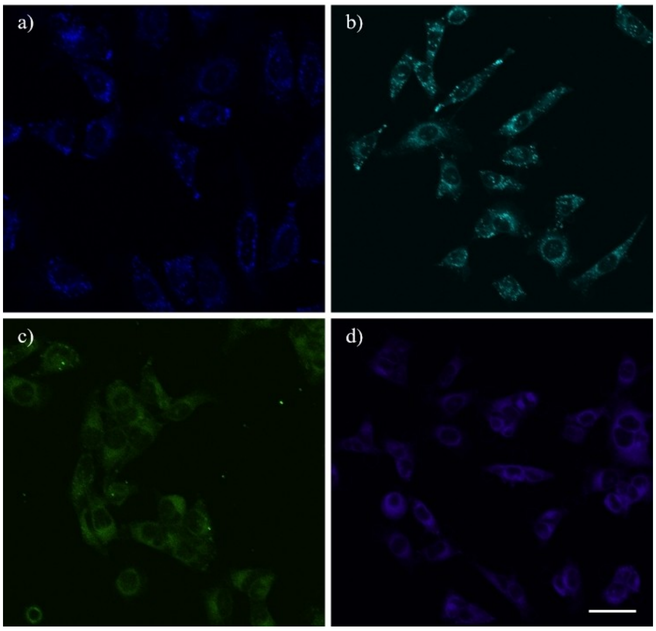

Figure 6. Confocal images of HeLa cells stained with a) **FA** (collected at 450–470 nm), b) **DiMe-FA** (collected at 470–490 nm), c) **DiOMe-FA** (collected at 515–525 nm) and d) **Naph-FA** (collected at 420–440 nm). (Concentration: 10 μM of each sample in MEM; excitation wavelength: 405 nm; all the images share the same scale bar of 20 μm.)

Conclusions

Novel family of planar luminogens with active photoluminescence emission at both dispersion and aggregation state have been systematically investigated for the first time. Spectral profiles and photochemical parameters at dispersion and aggregation state are determined and illustrated in-depth. We consider the herringbone stacking mode and the resultant weakened π–π interaction in their crystal structures as a universal phenomenon through this family of luminogens which facilitates the immunity of concentration quenching effect under aggregation state. And X-ray Crystallography and theoretical calculation results verify our speculation. Native cell imaging observation affords satisfactory outcomes and further applications within cytobiology and OLED devices based on this type of planar luminogens are in progress.

X-ray Crystallography

Deposition Number(s) 2108695, 2108697, 2108698, 2108699 and 2126743 contain(s) the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: fluoranthenes · imaging agents · pi interactions · planarity · solid-state emission

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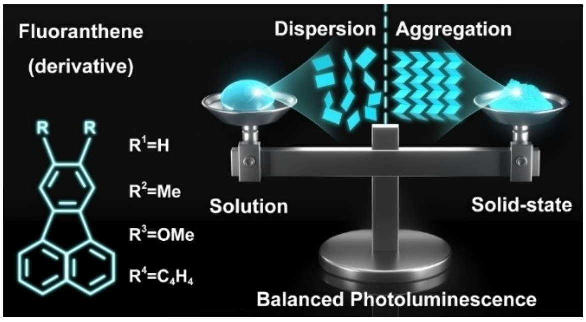

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A Family of Planar Luminogens with Active Photoluminescence in both Dispersion and Aggregation States

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