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# Aggregation-induced emission and working mechanism of 1benzoyl and 1-benzyl pyrene derivatives

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Over the past decade, the researches on solid-state luminescent materials featuring aggregation-induced emission (AIE) have achieved great success. It has been proved that lots of planar ACQ (aggregation-caused quenching) chromophores can be turned to AIE luminogens (AIEgens) by combination of other AIE-active unit such as tetraphenylethene (TPE). In this work, we present a new method to create AIE luminogens just by introducing benzoyl or benzyl to a planar chromophore, pyrene. The generated 1-benzoyl and 1-benzyl pyrene derivatives exhibit weak emission when molecularly dissolved in good solvents but strong emission from pyrene dimers when aggregated in poor solvent or solid state. The crystal structure analysis and theoretical calculation are performed to depict the working mechanism of these new AIEgens. The results show that the structural rigidification of these 1-benzoyl pyrene derivatives is the major cause for their AIE effect. This new AIE system along with clear working mechanism will contribute to the development of AIE-related functional materials and theory.

### Introduction

Traditional fluorescent materials may experience weakened emission in the aggregated state due to the formation of detrimental species. This phenomenon is commonly referred to aggregation-caused quenching (ACQ).<sup>1</sup> However, strong emission in the aggregated state plays a vital role in practical applications, such as organic light-emitting diode (OLED),<sup>2</sup> bioimaging,<sup>3</sup> optical waveguide,<sup>4</sup> and so on. Obviously, most ACQ materials can't meet the demand, although various chemical, physical and engineering approaches may alleviate the ACQ effect to some extent. On the contrary, aggregationinduced emission (AIE) materials are weakly fluorescent or non-fluorescent in solutions, but show greatly enhanced emission in the aggregated state, opening a new path to solving the ACQ problem and developing highly efficient solidstate luminescent materials.<sup>5</sup>

Pyrene is a popular traditional chromophore with a big, planar  $\pi$ -conjugated system with intriguing merits, such as long fluorescence lifetime and pure blue fluorescence.

quenching,<sup>6</sup> and highly efficient solid-state emitters based on pyrene are much desired. Actually, researches have shown that the ACQ property of pyrene is not immutable in some cases. With the aid of certain molecular structure modulation or utilization of excimer emission, pyrene derivatives can be successfully utilized in optical sensors,<sup>7</sup> field effect transistors,<sup>8</sup> OLEDs,<sup>9</sup> etc. Particularly, introducing AIE unit to ACQ chromophores has been proved as a powerful strategy to create efficient solid-state emitters.<sup>5d-h</sup> For example, by grafting AIE-active tetraphenylethene (TPE) onto the peripheries of pyrene, the generated pyrene derivatives are typical AIE luminogens (AIEgens), and have been applied to fabricate highly efficient OLED devices.<sup>9c</sup> Other AIE-active pyrene derivatives are also emerging in recent years.<sup>10</sup> And the enhanced emission may result from suppression of intramolecular rotation, photoinduced electron transfer (PET), charge transfer (CT), or even certain excimer species. Even so, AIE-active pyrene systems are still very limited, leaving much space for further improvements of functional materials based on pyrene and deeper investigations on AIE mechanisms. In this work, we report a new series of AIE-active 1-benzoyl and1benzyl pyrene derivatives, which were readily prepared by Friedel-Crafts reactions, and their photophysical properties had been systematically studied. Single crystal and theoretical analyses were also conducted to understand the working mechanism of emission enhancement in the aggregated state in comparison with the solution state.

However, it is subjected to self-aggregation and fluorescence

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Electronic Supplementary Information (ESI) available: Synthetic routes; PL spectra in THF/water mixtures with different water fractions; transient PL decay curves; PL spectra in films and crystal, molecular packing manners in crystals; PL spectra of compound **6** in different solvents; HRMS and NMR spectra.



Scheme 1. Chemical structures of compounds 1-8

## **Results and discussion**

#### Synthesis

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The molecular structures of the new 1-benzoyl and 1-benzyl pyrene derivatives are illustrated in Scheme 1, and their synthetic routes are shown in Scheme S1 in the Electronic Supplementary Information (ESI). In brief, the Friedel-Crafts acylation reactions of pyrene with corresponding acyl chloride compounds generated desired 1-benzoyl pyrene derivatives (1, 2, 4, 6 and 7) in moderate yields of 46–78% at room temperature. Compound 8, which was used as a control, was obtained by Friedel-Crafts alkylation reaction of pyrene with benzyl bromide with a lower yield of 36%, even if at 80 °C for 4 hours. The Suzuki-Miyaura couplings of 1 and 4 with phenylboronic acid furnished 3 and 5, respectively. These 1-benzoyl and 1-benzyl pyrene derivatives had been fully characterized by NMR and mass spectroscopies, and the



**Fig. 1** Absorption spectra of the new 1-benzoyl and 1-benzyl pyrene derivatives in THF solutions (10<sup>-5</sup> M).

results were in good agreement with their structures (the detailed characterization data are given in the Experimental section and the raw spectra are supplied in ESI). All the 1-benzoyl and 1-benzyl pyrene derivatives were soluble in common organic solvents, including THF, chloroform, dichloromethane, etc., but almost insoluble in water.

#### **Optical property**

The absorption spectra of 1-benzoyl and 1-benzyl pyrene derivatives in THF solutions  $(10^{-5} \text{ M})$  are shown in Fig. 1. Compounds **1–6** exhibited similar spectral profiles along with maximum absorptions locating at 385–395 nm (Table 1). However, compound **7** shown a greatly red-shifted absorption maximum at 409 nm, which was owing to the strong electron-withdrawing effect of perfluorophenyl group, and thus strong intramolecular charge transfer (ICT) effect. As for compound **8**, the maximum absorption peak was apparently blue-shifted to 339 nm, due to its poor conjugation in the presence of sp<sup>3</sup> hybridization carbon linkage between pyrene and benzene.

The photoluminescence (PL) properties of the 1-benzoyl and 1-benzyl pyrene derivatives in different states were fully studied. As shown in Table 1 and Fig. S1, compounds 1-6 exhibited weak blue PL emissions in the range of 428-447 nm in THF solution, with low fluorescence quantum yields ( $\phi_{FS}$ ) of 0.2-0.6%. disclosing that they were weak emitters in the solution state. Compound 7 exhibited stronger PL emission peaking at 434 nm and a higher  $\Phi_{\rm F}$  of 9.3%. Compound **8**, however, had a bluest PL emission at 395 nm with a  $\Phi_{\rm F}$  of 2.9%, due to the weakest molecular conjugation. These emissions were associated with the single-molecule state of these compound in dilute solution. In the aggregated state, these 1benzoyl and 1-benzyl pyrene derivatives showed enhanced and red-shifted emissions. By adding a large amount of water into the THF solution, the nearly nonfluorescent compound 1 showed clearly increased emission with a red-shifted peak (Fig. 2A). Similar emission behaviors could also be observed for compounds 2-8. As a matter of fact, the addition of water should have resulted in aggregate formation because of their inherent hydrophobicity characteristics of the compounds,

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**Fig. 2** PL spectra of (A) **1** and (C) **8** in THF/water mixtures with different water fractions; (B) Plots of the relative PL intensity ( $I/I_0$ ) versus  $f_w$  for **1**, **2**, **3**, **4**, **5**, **6** and **7**.  $I_0$  = intensity in pure THF. Inset: Fluorescence photos taken under a UV lamp (365 nm).

thus the enhanced and red-shifted emissions came from the aggregates, demonstrating the AIE characteristics.

As shown in Fig. S1 and Table 1, the emissions of aggregates in THF/H<sub>2</sub>O mixtures with a water fraction of 99% and films of compounds 1-7, as well as crystals of compounds 1, 2, and 4-7 were obviously red-shifted in comparison with those in solutions. And the corresponding peak emission wavelengths were 498-544, 449-525, and 462-553 nm for the aggregates, films and crystals, respectively. The  $\Phi_{\rm FS}$  of the aggregates for compounds 1-7 were higher (1.7-12.8%) than those of solutions, and could be further enhanced to 4.7-36.1% in films, suggesting that these 1-benzoyl pyrene derivatives were new AlEgens indeed. It is worth mentioning that compound 7 showed stronger emission than compounds **1–6**. no matter in aggregates or films. Compound **8** possessed even higher  $\Phi_{\rm F}$ s in aggregates and films (42.5% and 55.4%, respectively) than those of 1-benzoyl pyrene derivatives, which was consistent with the tendency of their fluorescence lifetimes (Table 1). Furthermore, the large red-shifts in the excitation spectra compared to absorption spectra (Fig. S2) indicated interactions

Table 1. Optical properties of new pyrene derivatives.

between neighbouring pyrene rings in the ground state, that is												
to say, dimer-emission took place in these 1-benzoyl and 1-												
benzyl pyrene derivatives. The apparently higher emission												
efficiencies and longer lifetimes of compound 8 in the												
aggregated state than compounds 1–7 should be attributed to												
the absence of carbonyl group, which could lead to vibrational												
motion, strong dipole-dipole interaction, fluorescence-												
quenching $n-\pi^*$ transition and intersystem crossing (ISC)												
process, and thus accelerate nonradiative decay of the excited state. <sup>11</sup>												

#### Single crystal structure

It has been well known that solid-state emission is closely associated with the packing arrangement of the luminogen.<sup>11,12</sup> We obtained single crystals of compounds **1**, **2**, and **4–7** and used them to further study and understand the emission behaviors of these 1-benzoyl pyrene derivatives. The single crystals were grown from dichloromethane/*n*-hexane mixtures, and analyzed by X-ray diffraction crystallography. The crystal structures and the

		$\lambda_{ m em}$ (nm)				$arPhi_{ extsf{F}}$ (%)				ফ (ns)			
	$\lambda_{abs}$												
	(nm)	solnª	$aggr^b$	film <sup>c</sup>	cryt <sup>d</sup>	solnª	aggr <sup>b</sup>	film <sup>c</sup>	cryt <sup>d</sup>	soln <sup>a</sup>	aggr <sup>b</sup>	film <sup>c</sup>	cryt <sup>d</sup>
1	395	428	520	517	540	0.5	6.7	8.1	11.8	1.5	9.7	15.4	19.7
2	395	447	518	509	553	0.4	1.7	5.0	3.0	0.3	3.1	2.9	3.5
3	391	428	513	502	-	0.6	4.0	6.2	-	1.6	10.7	10.1	-
4	388	437	505	481	483	0.3	8.2	13.9	13.4	0.4	7.8	3.1	1.6
5	386	434	498	449	462	0.2	2.3	4.7	2.8	0.9	5.3	5.2	0.6
6	385	430	509	500	509	0.4	2.0	6.1	4.6	1.4	3.1	0.4	2.2
7	409	434	544	525	543	9.3	12.8	36.1	43.2	0.4	16.1	19.4	4.0
8	339	395	478	470	-	2.9	42.5	55.4	-	19.3	43.3	38.4	-

<sup>a</sup> THF solution (10<sup>-5</sup> M); <sup>b</sup> THF/H<sub>2</sub>O mixed solution ( $f_W$  = 99%); <sup>c</sup> Drop-casted on a quartz plate; <sup>d</sup> Single crystal. The fluorescence quantum yield ( $\Phi_F$ ) was measured by a calibrated integrating sphere.

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corresponding dihedral angles ( $\vartheta$ ) between the pyrene and benzene rings linked to the carbonyl group are illustrated in Table S1. In compounds **1** and **2**, the  $\vartheta$  values were 87.1° and 86.0°, respectively, revealing the almost perpendicular bonding manners of the pyrene and benzene rings, and thus the highly twisted structures. The  $\vartheta$ values of compounds 1 and 2 were much bigger than those of compounds **4** (62.2°), **5** (68.6°), **6** (66.3°), and **7** (66.0°), which might be attributed to the stronger steric hindrance of 2-positioned substitution. On the whole, certain free rotation of the rings could lead to fluorescence quenching in solutions to some extent.

Moreover, the molecular packing models and intermolecular interactions were investigated to further understand the emission properties of the aggregates (Fig. 3, Fig. S5-S10). As shown in Fig. 3, various intermolecular interactions could be clearly found in all the crystals, including  $\pi$ - $\pi$ , C-H··· $\pi$ , C-X··· $\pi$  (X denotes halogen atoms), C-H...O, C-H...X interactions, and even H-/F-bonding interactions, which were undoubtedly conducive to rigidifying molecular structures and restraining non-radiative dissipations in the aggregated state, rendering enhanced emission in aggregates. Meanwhile, diversities exist when having a thorough look at them. Both compounds 1 and 2 had anti-parallel-packed and partially overlapped dimeric pyrene pairs (Table S1), and the dimeric pairs turned to be 2D herringbone-like packing arrangements (Fig. S5 and

S6). And the shortest C-C distances between the two neighboring pyrene rings were 3.545 and 3.554 Å for compounds 1 and 2, respectively, indicative of typical intermolecular  $\pi - \pi$  stacking interactions. Similar anti-parallel slipped packing patterns and  $\pi$ - $\pi$ interactions for pyrene dimers could be observed in compounds 4 and 6 (Table S1). In addition, pyrene dimerization could be affected by certain substituents. That is to say, in compound 7, the perfluoro-substitution altered the parallel stacking manner to an edge-to-face one. In addition, the anti-parallel packing manner was changed to a parallel one for compound 5, in which the biphenyl units interacted through typical C-H $\cdots\pi$  interactions (Fig. 3d). It is worthy of mentioning that, for compound 7, stacked pyrene pairs were more likely to be a 3D network stacking, unlike 2D ones of others, and it became more apparent as observed from the c-axis (Fig. S10), deducing that molecular motions were restricted more effectively in compound 7 than in other 1-benzoyl pyrene derivatives. And this explained why compound 7 possessed the highest  $\Phi_{\rm F}$  among 1-benzoyl pyrene derivatives. In a word,  $\pi$ overlapped pyrene pairs existed and contributed to the dimer emission in all the 1-benzoyl pyrene derivatives. All of the weak intermolecular interactions were beneficial to rigidifying the molecular packing systems, suppressing the nonradiative relaxation, and thus resulting in solid-state emission enhancement.<sup>13</sup> Besides,



Fig. 3 Packing patterns and intermolecular interactions of (a) 1, (b) 2, (c) 4, (d) 5, (e) 6 and (f) 7 in crystals.

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Fig. 4 Calculated molecular orbital amplitude plots of HOMOs and LUMOs of compound 6 in gas and solid phases.

the 3D arrangement seemed to be more effective to enhance the emission than 2D arrangement.

#### **Electronic structure**

In order to better understand the enhanced emission in the aggregated state of 1-benzoyl pyrene derivatives, theoretical calculation was conducted on compound 6 as an example. Considering the aggregation effect, we also calculated the geometric and electronic structures of a large cluster cut from the crystal structure by using a combined quantum mechanics/molecular-mechanics (QM/MM) approach.<sup>14</sup> The QM part chose the Turbomole 6.5 quantum chemistry package, and the MM part chose the DL-POLY molecular mechanics package. For compound 6, the ground state and excited states configurations in both gas and solid states were optimized by density functional theory (DFT) and time dependent density functional theory (TDDFT), respectively. As shown in Fig. 4, the electron clouds of HOMO and LUMO of compound 6 were mainly centered on the pyrene and benzene units, respectively, in gas and solid phases. The carbonyl group contributed to both HOMO and LUMO. The separated distribution of HOMO and LUMO and twisted geometrical structure revealed that compound 6 would readily experience ICT effect, which had been further confirmed by solvatochromic effect studies. Obvious PL variations of compound 6 in nonpolar and highpolar solvents could be observed (Fig. S11), and the emission peak in toluene was 414 nm and moved to 463 nm in DMSO.





Fig. 5 The calculated reorganization energies versus the normal mode wavenumber for compound 6 in gas and solid phases.







**Fig. 7** Optimized overlapped  $S_0$  and  $S_1$  geometric structures of compound **6** in gas and solid phases. Color codes for structures:  $S_1$ , red carbonyl oxygen and cyan hydrogen;  $S_0$ , yellow carbonyl oxygen and purple hydrogen.

depends on the competition between the radiative and nonradiative decays. In other words, if the excited molecules return to the ground state in a dominative radiation transition, they fluoresce. For these AIE-active luminogens, their radiative and nonradiative reorganization energies were calculated and compared to have a thorough understanding of the emission behaviors in gas and solid phases. Fig. 5 shows the calculated reorganization energies of compound 6 in gas and solid phases, and the reorganization energy ratios of bond length, bond angle and dihedral angle are illustrated in Fig. 6. It can be seen that the high frequency bond stretching and bond angle openclose motions consumed large amounts of reorganization energy in both gas and solid phases, with proportions up to 64% and 78%, respectively. In solution, intramolecular bond stretching, angle changing and rotation dissipated most of the excited-state energy, and led to faint emission. While in solid state, the low frequency dihedral angle variation could be restricted by physical constraint, resulting in emission enhancement. These results further validated that restriction of intramolecular motion (RIM)<sup>5b,15</sup> accounted for the emission enhancement in the aggregated state. Another thing to be mentioned is that, the high frequency bond stretching and bond angle open-close motions were the intrinsic characteristics, and relatively difficult to be confined by intermolecular stacking. This is one of the reasons why the PL efficiency of compound 6 is lower than that of compound 8 in the aggregated state.

In order to gain deeper insight into the conformational changes from  $S_0$  (gas) to  $S_1$  (solid) state, the overlap of their geometries was also studied. As illustrated in Fig. 7, the  $S_1$  and  $S_0$  geometries of compound **6** were almost perfectly overlapped in solid phase, demonstrating negligible conformation variations in the excited state. But it was not the

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case in gas phase, namely, the  $S_1$  geometry distinctively changed compared with the  $S_0$  geometry, in terms of conformational twisting and rotation. These changes undoubtedly consumed much excited state energy, and thus caused weak solution-state emission. In a word, the larger changes of  $S_1$  geometry in gas phase than those in solid phase gave rise to weak emission in solutions, while the minimized changes of  $S_1$  geometry in solid phase accounted for the enhanced emission.

## Conclusion

In conclusion, a series of 1-benzoyl and 1-benzyl pyrene derivatives were readily synthesized and characterized. They were weak emitters with monomer emission of pyrene moiety in solutions, but showed apparently enhanced emissions with contributions from dimer emission of pyrene moieties in the aggregated state. Crystal analyses of 1-benzoyl pyrene derivatives revealed that they had highly twisted molecular conformations, and various intermolecular interactions were formed among molecules, which was conducive to molecular structure rigidification and thus emission enhancement in the aggregated states. Theoretical calculation results showed that the inhibited intramolecular motions, along with smaller  $S_1$  geometric changes of aggregates resulted in enhanced emission in the aggregated state. This instructive work had surely provided an effective and feasible way for turning the ACQ materials to AIE ones, and further validated the RIM mechanism of AIE.

# Experimental

#### Synthesis and characterization

(2-Bromophenyl)(pyren-1-yl)methanone (1): Anhydrous AlCl<sub>3</sub> (2.67 g, 20 mmol), 2-bromobenzoyl chloride (1.57 mL, 12 mmol) and pyrene (2.02 g, 10 mmol) were dissolved in 80 mL dry dichloromethane at 0 °C. After stirring for 3 hours at room temperature, the reaction mixture was poured into dilute hydrochloric acid solution and extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using petroleum/dichloromethane as the eluent. The yellow solid of compound 1 was obtained in 62% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 9.17 (d, J = 9.35 Hz, 1H), 8.26–8.20 (m, 3H), 8.13 (d, J = 8.85 Hz, 1H), 8.04-7.96 (m, 4H), 7.66-7.64 (m, 1H), 7.53–7.52 (m, 1H), 7.43–7.40 (m, 1H), 7.37–7.34 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), δ (TMS, ppm): 197.1, 141.4, 133.6, 132.5, 130.5, 130.0, 129.9, 129.6, 129.4, 129.22, 129.17, 129.13, 128.7, 126.3, 126.2, 125.6, 125.5, 125.4, 124.05, 123.97, 123.2, 122.8, 119.4. HRMS ( $C_{23}H_{13}BrO$ ): m/z 384.0156 ( $[M^+]$ , calcd 384.0150).

(2-Iodophenyl)(pyren-1-yl)methanone (2): The synthesis was analogous to that described for compound 1. Yellow powder, yield 46%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 9.17 (d, *J* = 9.35 Hz, 2H), 8.31–8.27 (m, 3H), 8.21 (d, *J* = 8.90 Hz, 1H), 8.10–8.06 (m, 3H), 7.99–7.97 (m, 2H), 7.50–7.46 (m, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$ 

(TMS, ppm): 198.4, 144.7, 139.1, 133.6, 130.5, 130.3, 130.0, 129.6, 129.2, 129.1, 128.94, 128.89, 128.8, 126.9, 126.2, 125.6, 125.5, 125.4, 124.10, 124.06, 123.2, 122.8. HRMS ( $C_{23}H_{13}IO$ ): m/z 432.0040 ([ $M^{+}$ ], calcd 432.0011).

[1,1'-Biphenyl]-2-yl(pyren-1-yl)methanone (3): A mixture of 1 (1.54 g, 4 mmol), phenylboronic acid (0.59 g, 4.8 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.23 g, 0.20 mmol) and K<sub>2</sub>CO<sub>3</sub> (2.21 g, 16 mmol) in toluene/ethanol/water (100 mL, 8/1/1 v/v/v) were heated to reflux for 12 h under nitrogen. After cooling to room temperature, the reaction mixture was poured into water, and extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silica-gel column chromatography using petroleumether/dichloromethane as the eluent. Light yellow powder, yield 64%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 8.91 (d, J = 9.30 Hz, 1H), 8.23–8.16 (m, 3H), 8.08 (d, J = 8.90 Hz, 1H), 8.03-8.00 (m, 1H), 7.92 (d, J = 9.00 Hz, 1H), 7.87 (s, 2H), 7.75 (d, J = 7.55 Hz, 1H), 7.63-7.60 (m, 1H), 7.52-7.46 (m, 2H), 7.24-7.22 (m, 2H), 6.92–6.89 (m, 2H), 6.76–6.73 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), δ (TMS, ppm): 200.6, 142.1, 140.9, 140.2, 133.7, 132.3, 130.9, 130.8, 130.5, 130.48, 130.40, 130.3, 130.0, 129.4, 129.3, 128.9, 128.7, 127.8, 127.2, 127.0, 126.8, 126.2, 126.1, 126.0, 125.0, 124.6, 124.1, 123.3. HRMS (C<sub>29</sub>H<sub>18</sub>O): *m/z* 382.1384 ([M<sup>+</sup>], calcd 382.1358)

**(4-Bromophenyl)(pyren-1-yl)methanone (4):** The synthesis was analogous to that described for compound **1**. Yellow powder, yield 64%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 8.32 (d, J = 9.25 Hz, 1H), 8.28–8.24 (m, 2H), 8.21–8.19 (m, 2H), 8.13–8.11 (m, 2H), 8.08–8.04 (m, 2H), 7.77–7.74 (m, 2H), 7.63–7.60 (m, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 196.3, 136.5, 132.3, 131.4, 131.0, 130.8, 130.1, 129.6, 128.7, 128.3, 128.1, 127.4, 126.2, 125.9, 125.5, 125.2, 125.0, 123.8, 123.5, 123.4, 122.8. HRMS (C<sub>23</sub>H<sub>13</sub>BrO): m/z 384.0182 ([M<sup>+</sup>], calcd 384.0150).

**[1,1'-Biphenyl]-4-yl(pyren-1-yl)methanone (5):** The synthesis was analogous to that described for compound **3.** Yellow powder, yield 68%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 8.36 (d, J = 9.25 Hz, 1H), 8.26–8.17 (m, 4H), 8.13–8.10 (m,3H), 8.07–8.04 (m, 1H), 7.97–7.95 (m, 2H), 7.70–7.68 (m, 2H), 7.65–7.64 (m, 2H), 7.48–7.45 (m, 2H), 7.42–7.38 (m, 1H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 198.0, 145.9, 139.9, 137.4, 133.3, 133.0, 131.24, 131.2, 130.7, 129.7, 129.1, 129.0, 128.9, 128.3, 127.3, 127.2, 127.3, 126.9, 126.4, 126.1, 125.9, 124.84, 124.78, 124.5, 123.8. HRMS (C<sub>29</sub>H<sub>18</sub>O): m/z 382.1319 ([M<sup>+</sup>], calcd 382.1358).

**Phenyl(pyren-1-yl)methanone (6):** The synthesis was analogous to that described for compound **1.** Yellow powder, yield 78%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>), *δ* (TMS, ppm): 8.35 (d, *J* = 7.25 Hz, 1H), 8.26–8.17 (m, 4H), 8.12–8.03 (m, 4H), 7.90–7.89 (m, 2H), 7.63–7.59 (m, 7.95 Hz, 1H), 7.49–7.46 (m, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>), *δ* (TMS, ppm): 197.4, 137.7, 132.14, 132.10, 132.0, 130.1, 129.65, 129.58, 128.7, 128.1, 127.8, 127.4, 126.2, 125.9, 125.4, 125.0, 124.9, 123.8, 123.7, 123.4, 122.7. HRMS ( $C_{23}H_{14}O$ ): *m/z* 329.0935 ([M<sup>+</sup> + Na], calcd 329.0937).

(Perfluorophenyl)(pyren-1-yl)methanone (7): The synthesis was analogous to that described for compound 1. Orange powder, yield 72%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 9.40 (d, *J* = 9.35 Hz, 1H), 8.39–8.32 (m, 3H), 8.27 (d, *J* = 8.90 Hz, 1H), 8.16–8.09 (m, 4H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 185.8, 134.8, 130.4, 130.2,

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130.1, 129.9, 129.5, 129.0, 127.6, 126.4, 126.1, 126.0, 125.8, 124.0, 123.4, 123.1, 122.9. HRMS ( $C_{23}H_9F_5O$ ): *m/z* 396.0612 ([M<sup>+</sup>], calcd 396.0574).

**1-Benzylpyrene (8):** Anhydrous AlCl<sub>3</sub> (2.67 g, 20 mmol) and benzyl bromide (2.40 mL, 20 mmol) were added to pyrene (2.02 g, 10 mmol) dissolved in 80 mL dry dichloromethane at 0 °C. The reaction mixture was heated to 80 °C and stirred for 4 h. Then the reaction mixture was cooled to room temperature, poured into water, and extracted with dichloromethane for three times. The combined organic layers were dried over anhydrous magnesium sulfate. After filtration and solvent evaporation, the residue was purified by silicagel column chromatography using petroleum as the eluent. The white solid product was obtained in 36% yield. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 8.11 (d, *J* = 2.60 Hz, 2H,), 8.00–7.91 (m, 7H), 7.31–7.26 (m, 4H), 7.22–7.18 (m, 1H), 4.38 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>),  $\delta$  (TMS, ppm): 140.3, 137.8, 130.3, 129.9, 128.0, 127.5, 126.4, 126.1, 125.1, 124.52, 124.49, 123.9, 123.5, 122.2, 41.4. HRMS (C<sub>23</sub>H<sub>16</sub>): *m/z* 292.1289 ([M<sup>†</sup>], calcd 292.1252).

## X-Ray crystallography

**Crystal data for 1 (CCDC 1533087):**  $C_{23}H_{13}$ BrO,  $M_W = 385.24$ , monoclinic, P2(1)/c, a = 9.7948(7), b = 21.5595(13), c = 7.9044(5) Å,  $\beta = 104.573(7)^{\circ}$ , V = 1615.48(19) Å<sup>3</sup>, Z = 4,  $D_c = 1.584$  g cm<sup>-3</sup>,  $\mu = 2.552$  mm<sup>-1</sup> (MoKα,  $\lambda = 0.71073$ ), F(000) = 776.0, T = 170 K,  $2\vartheta_{max} = 25.350$  (99.8%)<sup>o</sup>, 2945 measured reflections, 2440 independent reflections ( $R_{int} = 0.0290$ ), GOF on  $F^2 = 1.049$ ,  $R_1 = 0.0446$ , w $R_2 = 0.0745$  (all data),  $\Delta e 0.750$  and -0.470 eÅ<sup>3</sup>.

**Crystal data for 2 (CCDC 1533086):** C<sub>23</sub>H<sub>13</sub>IO,  $M_w$  = 432.23, monoclinic, P2(1)/c, *a* = 9.8713(5), *b* = 21.9189(11), *c* = 8.0295(4) Å, *b* = 105.165(2)<sup>o</sup>, *V* = 1676.83(15) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.712 g cm<sup>-3</sup>, *μ* = 1.917 mm<sup>-1</sup> (MoKα,  $\lambda$  = 0.71073), *F* (000) = 848.0, *T* = 172 K, 2 $\vartheta_{max}$  = 25.310 (98.9%)<sup>o</sup>, 3024 measured reflections, 2421 independent reflections ( $R_{int}$  = 0.0353), GOF on *F*<sup>2</sup> = 1.021, *R*<sub>1</sub> = 0.0503, w*R*<sub>2</sub> = 0.0797 (all data),  $\Delta$ e 0.781 and -0.372 eÅ<sup>3</sup>.

**Crystal data for 4 (CCDC 1533084):** C<sub>23</sub>H<sub>13</sub>BrO, *M*<sub>w</sub> = 385.24, triclinic, P-1, *a* = 7.9050(5), *b* = 9.5802(5), *c* = 10.6200(6) Å, *α* = 94.977(2)°, *β* = 101.008(2)°, *γ* = 93.532(2)°, *V* = 783.98(8) Å<sup>3</sup>, *Z* = 2, *D*<sub>c</sub> = 1.632 g cm<sup>-3</sup>, *μ* = 2.629 mm<sup>-1</sup> (MoKα, *λ* = 0.71073), *F* (000) = 388.0, *T* = 173 K, 2 $\vartheta_{max}$  = 25.380 (98.4%)°, 2852 measured reflections, 2365 independent reflections (*R*<sub>int</sub> = 0.0491), GOF on *F*<sup>2</sup> = 1.045, *R*<sub>1</sub> = 0.0549, *wR*<sub>2</sub> = 0.0774 (all data), *Δ*e 0.738 and -0.329 eÅ<sup>3</sup>.

**Crystal data for 5 (CCDC 1533088):**  $C_{23}H_{18}O$ ,  $M_W = 382.43$ , orthorhombic, P2(1)2(1)2(1), a = 5.2858(7), b = 8.2060(11), c = 42.862(6) Å, V = 1859.2(4) Å<sup>3</sup>, Z = 4,  $D_c = 1.366$  g cm<sup>-3</sup>,  $\mu = 0.081$  mm<sup>-1</sup> (MoK $\alpha$ ,  $\lambda = 0.71073$ ), F (000) = 800.0, T = 173 K,  $2\vartheta_{max} = 24.500$  (99.0%)<sup>o</sup>, 1847 measured reflections, 1559 independent reflections ( $R_{int} = 0.0412$ ), GOF on  $F^2 = 1.096$ ,  $R_1 = 0.0726$ , w $R_2 = 0.1953$  (all data),  $\Delta e 0.562$  and -0.287 eÅ<sup>3</sup>.

**Crystal data for 6 (CCDC 1533089):** C<sub>23</sub>H<sub>14</sub>O, *M*<sub>W</sub> = 306.34, triclinic, P-1, *a* = 8.6959(10), *b* = 8.9304(10), *c* = 11.2041(13) Å, *α* = 69.755(4)°, *b* = 80.944(4)°, *γ* = 69.789(4)°, *V* = 765.36(15) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.329 g cm<sup>-3</sup>, *μ* = 0.080 mm<sup>-1</sup> (MoKα, *λ* = 0.71073), *F* (000) = 320.0, *T* = 173 K, 2 $\vartheta$ <sub>max</sub> = 25.550 (98.0%)°, 2815 measured reflections, 1823 independent reflections (*R*<sub>int</sub> = 0.0334), GOF on *F*<sup>2</sup> = 1.020, *R*<sub>1</sub> = 0.0829, w*R*<sub>2</sub> = 0.1196 (all data), Δe 0.328 and -0.159 eÅ<sup>3</sup>. **Crystal data for 7 (CCDC 1533090):** C<sub>23</sub>H<sub>9</sub>F<sub>5</sub>O,  $M_W$  = 396.30, orthorhombic, P2(1)2(1)2(1), *a* = 7.9511(5), *b* = 8.4125(7), *c* = 24.0545(18) Å, *V* = 1609.0(2) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.636 g cm<sup>-3</sup>, *μ* = 0.139 mm<sup>-1</sup> (MoKα,  $\lambda$  = 0.71073), *F* (000) = 800.0, *T* = 173 K, 2ϑ<sub>max</sub> = 25.350 (99.0%)<sup>0</sup>, 2903 measured reflections, 2157 independent reflections (*R*<sub>int</sub> = 0.0530), GOF on *F*<sup>2</sup> = 1.065, *R*<sub>1</sub> = 0.0878, w*R*<sub>2</sub> = 0.1202 (all data),  $\Delta$ e 0.459 and -0.260 eÅ<sup>3</sup>.

# **Conflicts of interest**

There are no conflicts to declare.

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Apparent AIE phenomenon was observed for 1-benzoyl and 1-benzyl pyrene derivatives, and the working mechanism was elucidated.