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Effects of different substituted positions on the photophysical properties of pyrene-based sulfides



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ABSTRACT

A series of new pyrene-based sulfides were synthesized by the reaction between 4-methylbenzenethiol and R-bromopyrene (R = 1(1), 4(2), 2(3)). These compounds were structurally characterized and their properties were analyzed by spectroscopy, single crystal X-ray diffraction, electrochemistry and theoretical studies. Significant effect of substituted positions on photophysical properties were observed. The *p*-methylphenylthio group in 1- and 4-position significantly increases the absolute fluorescence quantum yield (Φ_F) in solid state, decreases the Φ_F in solution and almost does not change the Φ_F in film state compared to that of pyrene. However, this substituent in 2-position keeps the high Φ_F in solution, almost does not contribute to the Φ_F in solid state and significantly decreases the Φ_F in film state compared to that of pyrene. Moreover, compounds **1**, **2** and **3** exhibit typical aggregation-induced emission (AIE) properties that were proved by time-resolved photoluminescence.

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1. Introduction

Pyrene, the well-known polycyclic aromatic hydrocarbon chromophore discovered by Laurent in 1837, has attracted extensive attention of researchers from various scientific areas [1-9]. In the past decades, pyrene-based derivatives have been widely applied in the fields of organic light emitting diodes (OLEDs), organic photovoltaic cells (OPV), organic field-effect transistors (OFETs), fluorescent probe and so on [10-17].

To date, most reported pyrene-based fluorescent materials are functionalized by introducing substituents at the 1-, 3-, 6-, and 8-positions known as the most active sites for electrophilic substitution reactions [18–20]. The easy preparation and relatively simple purification of 1-substituted and 1-, 3-, 6-, and 8-tetrasubstituted pyrene provide possibility of introducing pyrene into interesting functional materials, which has attracted many researchers' interests. In addition, the development of 2- and 7-substituted pyrene are generally challenging because the 2- and 7-positions of pyrene are known as the molecular node sites [21–24]. The nodal plane in HOMO and LUMO passes through the 2- and 7-positions and is perpendicular to the molecule (Scheme 1). Consequently, little studies were carried out on the photophysical

properties of 2- and 7- substituted pyrene due to the difficulty of their synthesis. The 4-, 5-, 9-, and 10-positions of pyrene are defined as the K-regions that are very interesting and important for the preparation of extended aromatic systems [1,25–28]. However, these positions are generally difficult to be functionalized just as in the case of the 2- and 7-substituted pyrene. Although much efforts have been devoted to the functionalization of pyrene, the systemic studies about the effects of different substituted positions on the photophysical properties of pyrene are rarely reported.

Moreover, compounds exhibiting AIE property have drawn extensive interesting since AIE phenomenon was discovered by Tang's group in 2001 [29,30]. The parent nucleus of most AIE compounds are non-fluorescent or weak fluorescent in dilute solution or low water content solution, which will emit strong fluorescence in aggregation sate. On the contrary, traditional luminophores exhibit strong emission and suffer from the aggregation-caused quenching (ACQ) in aggregation state. Therefore, it is an interesting and important work to transform traditional ACQ luminophores into AIE compounds. In order to realize this transformation, understanding the effects of different substituted position on their photophysical properties in both solution and solid state is of very importance. In addition, in recent years, thioether linked compounds exhibiting AIE property have received great attention [31]. However, the interesting effects of thioether linked compounds on their own AIE phenomena have rarely reported.



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Scheme 1. Structure, HOMO and LUMO of pyrene (B3LYP).

In this work, a series of pyrene-based sulfide derivatives with different substituted position were synthesized, which exhibit obviously different photophysical properties. In solution, 1- and 4substituted pyrene-based sulfides (1 and 2) exhibit similar spectral properties. Both of them exhibit very weak emission ($\Phi_{\rm F}$, 7% and 3%) in dichloromethane (DCM) and relatively large red-shift in absorption and photoluminescence (PL) spectra compared to that of pyrene. However, 2-substituted pyrene-based sulfide (3) shows similar spectral properties to pyrene in solution, which exhibits very strong blue emission ($\Phi_{\rm F}$ 29%). In solid state, compounds 1 and **2** (Φ_{F} 75% and 79%) exhibit stronger emission than compound **3** (Φ_{F} , 69%). These results indicate that *p*-methylphenylthio substituent in 1- and 4-position significantly increases the solid state Φ_F and decreases the solution state Φ_F . However, *p*-methylphenylthio substituent in 2-position almost does not contribute to the Φ_F in solid state. In film state, *p*-methylphenylthio substituent in 1- and 4-position keeps a high $\Phi_F(\Phi_F, 41\% \text{ and } 44\%)$ compared to that of pyrene, but this substituent in 2-position significantly quenches the $\Phi_F(\Phi_F, 22\%)$. In addition, compounds **1**, **2** and **3** show obvious AIE properties,. These results will provide important guidance to relative studies and contribute to design and synthesis of functionalized pyrene-based derivatives.

2. Experimental section

2.1. Materials and instrumentation

Tetrahydrofuran (THF) was distilled from sodium and benzophenone in a nitrogen atmosphere. All other reagents and solvents were purchased commercially (AR grade) and used without further purification unless otherwise noted. The THF/water mixtures with different water fractions were prepared by slowly adding distilled water into the THF solution of samples under ultrasound at room temperature. The single crystals suitable for X-ray diffraction analysis were obtained by the slow evaporation of dichloromethane/methyl alcohol. ¹H NMR and ¹³C NMR spectra were collected on a Bruker-400 MHz spectrometer in CDCl₃ solution with TMS as an internal standard. Mass spectra were obtained on a MALDI-TOF MS. UV-vis spectra were recorded on Shimadzu UV-3600 with a UV-VIS-NIR spectrophotometer. Emission spectra were performed by a HITACHI fluorescence spectrometer (F-4600). Crystal data of compounds 1, 2 and 3 were collected on a Bruker APEX II CCDC diffractometer with graphite monochromated Mo-Ka radiation ($\lambda = 0.71073$ Å) at 296 K using the ω -scan technique. The Φ_F was measured by a FS5 spectrofluorometer. Their crystal structures were solved by direct methods with the SHELXS-2014 computer program, and refined by full matrix least-squares methods (SHELXL-2014) on F^2 . Images were created by using DIA-MOND program. CCDC number for compounds 1, 2 and 3 is 1898238, 1898241 and 1898242, respectively, and the data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) or at www.ccdc.cam.ac.uk/conts/retrieving.html. The ground state geometries of all molecules were fully optimized using density functional theory (DFT) at the B3LYP/6-31G (d, p) level, as implemented in Gaussian 09W software package.

2.2. Synthesis

2.2.1. Synthesis of pyren-1-yl(p-tolyl)sulfide (1)

1.69 g (12 mmol) 4-methylbenzenethiol, 2.81 g (10 mmol) 1bromopyrene and 50 mL DMF were added into a 100 ml round bottom flask. The above mixture was stirred for 10 min in an ice bath under the protection of N₂. Then, 0.48 g (12 mmol) NaH (60%) was slowly added into the above flask in batches and the mixture was stirred for another 10 min. After all the generated hydrogen was discharged, the mixture was refluxed for 10 h, poured into water, extracted with DCM and washed with water for three times. The organic phase was dried over MgSO₄, filtered, and concentrated. The concentrated product was purified by silica gel flash column chromatography using hexane as the eluent. Yield: 2.60 g, 80%. Melting point, 101–102 °C. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm):8.70-8.68 (d, 1H, J = 8.69 Hz), 8.24-8.22 (d, 2H, J = 8.23 Hz), 8.17-8.03 (m, 6H), 7.21-7.18 (m, 2H), 7.10-7.07 (m, 2H), 2.33 (s, 3H). ¹³C NMR (400 MHz, CDCl₃), δ (TMS, ppm): 136.41, 133.49, 131.69, 131.37, 131.27, 131.20, 131.00, 129.98, 129.76, 129.44, 128.35, 127.89, 127.26, 126.26, 125.51, 125.50, 125.34, 125.15, 124.73, 124.47, 21.04. MALDI-TOF MS (m/z): calcd for C₂₃H₁₆S 324.4, found 324.1. Elemental analysis: anal. calcd for C₂₃H₁₆S: C, 85.15; H, 4.97; S, 9.88%. Found: C, 85.09; H, 4.99; S, 9.82%.

2.2.2. Synthesis of pyren-4-yl(p-tolyl)sulfide (2)

The synthetic steps of **2** are the same as to the synthetic process of **1**. Yield: 2.49 g, 77%. Melting point, 116–117 °C. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 8.73–8.71 (dd, 1H, J = 8.72 Hz), 8.25–8.21 (m, 3H), 8.14–8.09 (m, 3H), 8.06–7.99 (dt, 2H, J = 8.03 Hz), 7.34–7.31 (m, 2H), 7.14–7.11 (m, 2H), 2.35 (s, 3H). ¹³C NMR (400 MHz, CDCl₃), δ (TMS, ppm): 136.78, 132.30, 132.03, 132.01, 131.44, 131.06, 130.88, 130.49, 130.34, 130.06, 127.64, 127.21, 126.19, 126.18, 125.77, 125.56, 125.27, 124.98, 124.21, 123.30, 21.10. MALDI-TOF MS(m/z): calcd for C₂₃H₁₆S 324.4, found 324.1. Elemental analysis: anal. calcd for C₂₃H₁₆S: C, 85.15; H, 4.97; S, 9.88%. Found: C, 85.09; H, 4.99; S, 9.86%.

2.2.3. Synthesis of pyren-2-yl(p-tolyl) sulfide (3)

The synthetic steps of **3** are the same as to the synthetic process of **1**. Yield: 1.39 g, 43%. Melting point, $103-104 \,^{\circ}$ C. ¹H NMR (400 MHz, CDCl₃), δ (TMS, ppm): 8.24–8.17 (d, 2H, *J*=8.19 Hz), 8.10–8.05 (m, 4H), 8.03–7.95 (m, 3H), 7.44–7.35 (m, 2H), 7.22–7.08

(m, 2H), 2.41 (s, 3H). ¹³C NMR (400 MHz, CDCl₃), δ (TMS, ppm):137.69, 134.66, 132.20, 131.83, 130.93, 130.21, 128.10, 126.80, 126.07, 125.95, 125.36, 124.45, 123.39, 21.20. MALDI-TOF MS (*m*/*z*): calcd for C₂₃H₁₆S 324.4, found 324.1. Elemental analysis: anal. calcd for C₂₃H₁₆S: C, 85.15; H, 4.97; S, 9.88%. Found: C, 85.09; H, 4.99; S, 9.90%.

3. Results and discussion

3.1. Synthesis and characterization

The synthetic routs for compounds **1**, **2** and **3** are illustrated in Scheme 2. Compounds **1**, **2** and **3** were structurally characterized by ¹H NMR, ¹³C NMR, single crystal X-ray diffraction and mass spectrometer techniques.

3.2. Photophysical properties in solution

The UV-vis absorption and photoluminescence (PL) spectra of compounds 1, 2 and 3 in DCM are shown in Fig. 1. As illustrated in Fig. 1A, compared to that of pyrene, the maximum absorption of 1, 2 and 3 red shifted 16, 10 and 6 nm, respectively. In addition, the absorption peaks of the compounds 1 and 2 become wide and the fine structures become unobvious. However, the absorption peak of compound **3** is relatively sharp and the distinct fine structures are observed, which is very similar to that of pyrene. This phenomenon is obviously resulted from the difference of substituted position. The electron cloud density of the 1-position and the 4-position of pyrene are abundant and the electron-rich *p*-methylphenylthio group can form an effective conjugate with the pyrene ring, which will increase the degree of conjugation of the whole system. The increased degree of conjugation thus results the red-shifted absorption. However, the electrons of *p*-methylphenylthio substituent in 2-position is difficult to efficiently conjugate with the pyrene ring due to the scarce electron cloud density of the 2-position. Therefore, the absorption of the compound **3** is basically derived from the pyrene ring, which may account for the similar absorption to pyrene. As can be seen from Fig. 1B, the maximum emission peak of compounds 1, 2 and 3 are observed at 415, 416 and 405 nm, respectively. Their emission peaks exhibit slight red shift compared to the emission peak of pyrene, which is consistent with the red



Scheme 2. Synthetic routes to compounds 1, 2 and 3.

shift of UV absorption. It is worth noting that the emission intensities of compounds **1** and **2** are very weak, their Φ_F are only 7% and 2% in DCM, respectively. However, the emission intensity of compound **3** is almost as strong as intensity of pyrene, the Φ_F reaches up to 30%. This phenomenon can be explained by the theory of restriction of intramolecular motion (RIM) proposed by Tang et al. [29,30] As described above, 1- and 4-substituted pyrene are effectively conjugate with abundant electron cloud density. In dilute solution, molecules are isolated and pyrene ring and the benzene ring can freely rotate around a single bond connected to the sulfur atom, which will largely consume the excited state energy. Therefore, compounds 1 and 2 emit weak fluorescence. However, 2-substituted pyrene is less conjugation and the luminescence behavior of the whole molecule is basically determined by the pyrene ring. The energy of the excited state is all located on pyrene ring and cannot be consumed by intramolecular rotation, which may account for the strong emission of compound 3.

3.3. Photophysical properties in crystal, solid and film state

Fig. 2 presents the PL spectra of pyrene, 1, 2 and 3. The relevant data are shown in Table 1. The crystal and powder of the compound **1** emit strong blue-green fluorescence with high Φ_F (75% and 74%), while its film emits green fluorescence with a relative low $\Phi_F(41\%)$. The crystal emission peak of compound 1 at 468 nm almost coincides with the emission peak of its powder state, but the emission peak of its film is red shifted to 489 nm. The large red-shifted emission of its film may be caused by stronger π - π interaction between molecules in the amorphous state due to the lack of lattice constraints. The luminescence phenomena of compounds 2 and 3 are similar to compound 1. Both crystals and powders of compounds 2 and 3 emit blue-green fluorescence and the emission peaks in both states almost coincide. The emission peaks of compounds 2 and 3 exhibit little change compare to that of compound **1**. However, their $\Phi_{\rm F}$ exhibit obvious difference. It is worth noting that the $\Phi_{\rm F}$ of compound **2** (79% and 78%) is higher than compounds 1 and 3. The Φ_F of compound 3 is lowest (68% and 69%) and Φ_F of its film state is only 22%. These results indicate that pmethylphenylthio substituent in 1- and 4-position may significantly increase the Φ_F in solid state. However, *p*-methylphenylthio substituent in 2-position almost does not contribute to the Φ_F in solid state.

3.4. Crystal structure

The white crystals of 1, 2 and 3 were obtained by slow evaporation of DCM/MeOH solution and the selected suitable single crystals were analyzed by single crystal X-ray diffraction technique. The crystal data are given in Table S1 and the crystal structures of 1, 2 and 3 are shown in Fig. S1. Fig. 3 presents the packing model of 1, 2 and 3. As illustrate, the pyrene rings in the molecule of compounds 1, 2 and 3 are stacked in parallel with each other. Different degrees of slip are observed for the two parallel pyrene rings. In compound 1, the two parallel pyrene rings exhibit the least slip, and the slip of compound 2 is larger than that of compound 1. The distance between the parallel pyrene rings in **1** and **2** is 3.417 and 3.510 Å indicating strong π - π interaction. Therefore, the π - π interaction in compound **1** is stronger than that in compound **2**, which may account for the lower Φ_F of compound **1** than compound 2. In compound 3, the two parallel pyrene rings are almost stagger and only a very small fraction of them overlap, which suggests the absence of π - π interaction. However, the Φ_F of **3** is still low and close to Φ_F of pyrene. This phenomenon may result from the scarce electron cloud density of the 2-position described above. In addition, there exist affluent intermolecular C–H \cdots π interaction



Fig. 1. (A) Absorption spectra of pyrene, **1**, **2** and **3** in DCM. (B) PL spectra of pyrene, **1**, **2** and **3** in DCM. Insets of (B): the emission images of **1**, **2** and **3** DCM taken under 365 nm UV illumination. For Absorption measurement, pyrene, **1**, **2** and **3** concentrations: 10⁻⁵ M. For PL measurement, pyrene, **1**, **2** and **3** concentrations: 10⁻⁴ M, excitation wavelength: 340 nm.



Fig. 2. PL spectra of pyrene, 1(A), 2 (B) and 3 (C) in crystal, powder and film state. (D): the emission images of 1, 2, 3 and pyrene. From left to right: crystal in daylight, crystal in 365 UV, powder in 365 UV, film in 365 UV. For PL measurement, excitation wavelength: 340 nm.

Table 1
Data of UV-vis absorption and PL emission of compounds 1–3 and pyrene. ($\lambda_{abs,max} = absorption maximum; \lambda_{em,max} = emission maximum; Cry = Crystal; Pow = Powder.$)

Compound	$\lambda_{abs,max}/nm$	λ _{em,max} /nm			Stokes-shift/nm	$\Phi_F(\%)$	$\Phi_F(\%)$			
		DCM	Cry	Pow	Film		DCM	Cry	Pow	Film
1	352	415	468	470	489	63	7	75	74	41
2	346	416	469	469	480	70	3	79	78	44
3	342	405	466	467	480	63	29	69	68	22
ру	336	390	449	449	449	54	32	68	67	44



Fig. 3. Orthogonal projection of two parallel molecules in crystals (top) and crystal packing model of 1, 2 and 3 (bottom).

(from 2.649 to 2.854 Å) in the crystal structures of compounds 1-3, which stabilizes the conformation of molecules and reduces the non-radiative transition to some extent. Therefore, the Φ_F of solid phase is higher than that in solution.

3.5. AIE property

The AIE properties of compounds 1 and 2 have further investigated by dissolving them in THF and then adding water as bad solvent. As is shown, compounds 1 and 2 are typical AIE-active compounds (Fig. 4). As illustrated, when the water content is less than 80%, only a weak emission peak around 400 nm is observed for compound 1, which decreases with the increase of water content in a whole. However, when the water content reaches 80%, a new emission peak appears at about 490 nm and the emission peak at 400 nm is disappeared completely. With further increasing the water content, the intensity of emission peak at 409 nm gradually increases. Similar phenomenon is observed for compound 2. However, the intensity of emission peak at 400 nm is lower than that of compound 1, which is consistent with results in Table 1. Interestingly, for compound **3**, strong emission is observed both in low and high water content solutions, which is obviously different from that of compounds 1 and 2. This interesting phenomenon

exhibits obvious effects of different substituted positions on photophysical properties.

In order to confirm the AIE nature, time-resolved single-photon counting (TCSPC) technique was carried out (Fig. S2). As can be seen from Fig. S3A-S3C, the luminescence decay curves of compounds 1, 2 and 3 in pure THF solution are well fitted with two-ordered exponential decays. For compound 1, a shorter component with lifetime (τ) of 0.51 ns and a longer species with a lifetime of 4.18 ns were observed in THF solution. For compound 2 and 3, the lifetime of shorter components are 0.77 ns and 0.51 ns, the lifetime of longer whereas are 4.18 ns and 7.89 ns, respectively. According to previous reports, the above longer components were explained by excimer emission lifetime [32,33]. In addition, the emission lifetime of aggregated state (water content = 95%) of compounds 1, 2 and 3 are 22.62 ns (95.17%), 23.29 ns (96.49%) and 14.73 ns (96.24%), respectively, which are longer than that of compounds 1, 2 and 3 in THF. Therefore, the longer lifetime (22.62 ns, 23.29 ns and 14.73 ns) are not resulted from excimer, which can be attributed to the emission lifetime of aggregates.

3.6. Theoretical calculation

To further understand the relationship between structure and



Fig. 4. PL spectra of compound **1** (A), **2** (B) and **3** (C) in H₂O/THF mixtures with different water fractions. Insets: the emission images of **1**, **2** and **3** in H₂O/THF mixtures with different water fractions taken under 365 nm UV and daylight illumination. For PL measurement, **1**, **2** and **3** concentrations: 10⁻⁴ M, excitation wavelength: 365 nm.

physical properties, quantum mechanical computations on their energy levels based on DFT/B3LYP/6-31G (d,p) using Gaussian 09 software were performed. The diagrams of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of 1, 2 and 3 are shown in Fig. 5. The HOMO of compound 1 is distributed on the molecule and LUMO is mainly located on pyrene ring. The pyrene ring, sulfur atom and the benzene ring are very effective conjugated indicating that the spectral properties of compound **1** are determined by the electronic behavior of the entire molecule. The HOMO and LUMO levels and energy gaps of compound 1 are -5.675 eV, -2.070 eV and 3.605 eV, respectively, to that of pyrene which is decreased compared (-5.338 eV, -1.497 eV and 3.841 eV). These results are consistent with red-shifted spectral of compound 1 compared to that of pyrene. The range of HOMO distribution of compound 2 is reduced compared to that of compound **1** and the LUMO distribution is similar to that of compound **1**. The HOMO and LUMO levels and energy gaps are -5.708 eV, -1.970 eV and 3.738 eV, respectively. Compared to that of compound **1**, the HOMO level of compound **2** is reduced but the LUMO level is increased, therefore, the energy gap is increased. However, the energy gap of compound **2** is still smaller than that of pyrene. Consequently, the wavelength of compound **2** is red-shifted than pyrene but degree of red-shifted wavelength is smaller than compound **1**. The HOMO and LUMO of compound **3** are all distributed on the pyrene ring suggesting that its spectral properties are completely determined by pyrene ring and substituent group at 2-position has a negligible effect on spectral properties. These results well explain the similar spectral properties of compound **3** and pyrene.



Fig. 5. Molecular orbital energy levels of the HOMO and LUMO of 1, 2 and 3 calculated by using the B3LYP/6-31G basis set.

3.7. Electrochemical studies

The electrochemical properties of compounds 1, 2 and 3 were investigated using cyclic voltammetry (CV) method in anhydrous DCM with the concentration of 1.0×10^{-3} M. Cyclic voltammetry curves are illustrated in Fig. 6 and the obtained data are summarized in Table 2. On the basis of the onset potentials of oxidation (Eox onset), the HOMO energy levels of compounds 1, 2 and 3 were calculated with the values of -5.09, -5.11 and -5.13 eV, respectively, using the equation HOMO = $-eE_{onset}$ –4.37 eV. These results are slightly higher than that of pyrene (-4.92 eV). The band gaps of compounds 1, 2 and 3 were derived from the absorption edge in the absorption spectra with the values of 3.25, 3.46 and 3.56 eV respectively. Although the calculated values are slightly higher than the values estimated by CV, the trend is consistent with the order of maximum absorption wavelength. The LUMO values of compounds **1**, **2** and **3** can be estimated by subtraction of the optical band gap energies from the HOMO energy levels (LUMO = HOMO - Eg), the obtained value is -1.84 for 1, -1.65 and -2.68 and -1.57 eV, respectively.

4. Conclusions

In conclusion, we have designed and synthesized a new series of pyrene-based sulfides **1**, **2** and **3**. In solution, compounds **1** and **2** (1and 4-substituted pyrene-based sulfides) exhibit very weak emission (Φ_F , 7% and 3%) and relatively large red-shift in absorption and PL spectra compared to that of pyrene. However, compound **3** (2substituted pyrene-based sulfide) exhibits very strong blue emission (Φ_F , 29%) in solution. In solid state, compound **3** (Φ_F , 69%).



Fig. 6. Plot of cyclic voltammetry for compounds 1–3 and pyrene.

Table 2

Electrochemica	l properties	of compounds	s 1, 2 and 3
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Compounds	Eox onset(V)	HOMO (eV)		LUMO (eV)		Eg (eV)	
		Exptl ^a	Calc ^b	Exptl	Calc.	Exptl	Calc.
1	0.72	-5.09		-1.84	-2.070	3.25	3.605
2	0.74	-5.11	-5.708	-1.65	-1.970	3.46	3.738
3	0.76	-5.13	-5.621	-1.57	-1.834	3.56	3.787
Ру	0.55	-4.92	-5.338	-1.27	-1.497	3.65	3.841

^a Experimental value.

^b Calculated value.

These results indicate that *p*-methylphenylthio substituent in 1and 4-position significantly increases the Φ_F of pyrene-based derivate in solid state and decreases the Φ_F in solution. However, *p*-methylphenylthio substituent in 2-position almost does not contribute to Φ_F in solid state. In film state, the *p*-methylphenylthio substituent in 1- and 4-position keeps a high Φ_F (Φ_F , 41% and 44%) compared to that of pyrene, but this substituent in 2-position significantly quenches the Φ_F (Φ_F , 22%). Besides, compounds 1, 2 and 3 exhibit typical AIE properties. The theoretical calculation values agree well with the experimental data. These results will provide important guidance to relative studies and contribute to design and synthesis of functionalized pyrene-based derivatives.

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Appendix A. Supplementary data

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