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# Pyrene-based deep-blue fluorophores with narrow-

# band emission

Yiwei Liu,<sup>†, ‡</sup> Jianyu Zhang,<sup>‡, ‡</sup> Xiaohui Wang,<sup>†</sup> Zhixin Xie,<sup>†</sup> Heng Zheng,<sup>†</sup> Sheng Zhang,<sup>†</sup> Xumin Cai,<sup>§</sup> Yu Zhao,<sup>†</sup>

Carl Redshaw,§ Yonggang Min,  $^{\dagger}*$  Xing Feng $^{\dagger}*$ 

<sup>†</sup>Guangdong Provincial Key Laboratory of Information Photonics Technology, School of Material and Energy, Guangdong University of Technology, Guangzhou, 510006, P. R. China

<sup>4</sup>Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, and GuangdongHong Kong-Macau Joint Laboratory of Optoelectronic and Magnetic Functional Materials, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong 999077, China

<sup>8</sup>Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, International Innovation Center for Forest Chemicals and Materials, College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China

<sup>§</sup>Chemistry, School of Natural Sciences, University of Hull, Hull, Yorkshire HU6 7RX, UK

<sup>‡</sup>Y. Liu and J. Zhang contributed equally to this work

\*Corresponding authors

Email: hyxhn@sina.com (X. Feng), ygmin@gdut.edu.cn (Y. Min)



**ABSTRACT**: High-efficiency narrow-band luminescent materials have attracted intense interest, resulting in their great colorimetric purity. This has led to a variety of high-tech applications in high-definition displays, spectral analysis, and biomedicine. In this study, a rigid pyrene core was employed as the molecular backbone, and four narrow-band pyrene-based blue emitters were synthesized using various synthetic methods (such as Lewis-acid catalyzed cyclization domino, Pd-catalyzed coupling reactions like Suzuki-Miyaura and Sonogashira). Due to the steric effect of the hydroxy group at the 2-position, the target compounds show deep blue emission (< 429 nm, CIE: x = 0.14, Y < 0.08) with full width at half maximum (FWHM) less than 33 nm both in solution and when solidified. The experimental and theoretical results indicated that the substituents at the 1- and 3-positions exhibit a large dihedral angle with the pyrene core, and the molecular motion is almost fixed by multiple intra- and intermolecular hydrogen bonding interactions in the crystallized state, leading to a suppression of the vibrational relaxation of the molecular structure. Moreover, we observed that the suppression of the vibrational relaxation in the molecular structures and the construction of rigid conjugated structures can help to develop narrow-band organic light-emitting materials.

**KEYWORDS:** pyrene, narrow-band emission, deep-blue materials, structure-properties properties, vibrational relaxation

# **1. INTRODUCTION**

Organic luminescent materials, as the key components in organic light-emitting diode (OLED) devices, have garnered significant interest in both academic research and industrial communities. This is attributed to their diverse molecular types, controllable molecular functionalization with

tunable optical properties, and relatively low cost.<sup>1,2</sup> The photophysical properties of organic luminescent materials have played a crucial role in influencing the performance of optoelectronic devices. With the development of display technology, ultra-high-definition displays are becoming a hot research topic and one of the most important next-generation display technologies.<sup>3-7</sup> Among them, the color purity of organic luminescent materials is one of the main factors that affect the ultra-high-definition displays.<sup>8</sup> In general, most organic materials exhibit bright emissive properties with wide full width at half-maximum (FWHM) under irradiation, leading to low color purity, This is attributed to the complex vibrational coupling of luminescent molecules in the ground state and the corresponding structural relaxation in the excited states.<sup>9</sup> On the other hand, despite organic materials with red and green emission colors in commercial products, the development of high-performance (deep) blue emitters remains a great challenge.<sup>10</sup> This challenge arises from drawbacks such as a large energy gap and low stability. Therefore, from the molecular design perspective, developing high-efficiency (deep) blue organic luminescence materials with narrow-band emission emerges as one of the most critical strategies to address the issue of insufficient color purity in blue OLED materials and devices for ultra-high-definition displays.<sup>11</sup>

Pyrene is an important member of the polycyclic aromatic hydrocarbon family and exhibits deep blue fluorescence, a high quantum yield, good thermal stability, and high carrier mobility.<sup>12-15</sup> On the other hand, pyrene with a large  $\pi$ -conjugation, and a planar molecular backbone, prefers to form  $\pi$ - $\pi$  stacking interactions, resulting in a red-shifted emission with quenched fluorescence. Much effort has been devoted to functionalizing the pyrene core not only at the active sites (1-, 3-, 6-, and 8-positions) and K-region (4-, 5-, 9-, and 10-positions), but also at the nodal sites (2- and 7-positions). These position-dependent pyrene derivatives exert good control over the electronic transitions and ultimately lead to different optical behavior.<sup>12,16,17</sup> In the case of substituents at the nodal sites of pyrene, the 2,7-substituted pyrenes display different absorption behavior, and the S<sub>2</sub>  $\leftarrow$ S<sub>0</sub> and S<sub>1</sub> $\leftarrow$ S<sub>0</sub> excitation mainly involves the HOMO and LUMO orbitals, and the HOMO-1 and LUMO+1 orbitals, respectively.<sup>18-20</sup> Meanwhile, both the S<sub>2</sub> $\leftarrow$ S<sub>0</sub> and S<sub>1</sub> $\leftarrow$ S<sub>0</sub> excitations have been strongly influenced by substituents at the 1-position of the pyrene core. Moreover, the 2,7substituted pyrenes exhibit "pyrene-like" absorption behavior with a larger fluorescence lifetime compared to 1-position substituted pyrenes. <sup>18,21</sup>

Due to their excellent photophysical properties, pyrene-based luminescent materials are widely used in the field of organic electronics. Wang and Müllen developed a direct C-H borylation strategy for  $\pi$ -extension at the non-K-region of pyrene via functionalization at the 2- and 2,7- positions to achieve rigid planar molecules. Such molecules displayed narrowband emission and good fluorescence quantum yield (> 0.7) in solution, as well as *p*-type charge transport properties with hole mobility up to1.5×10<sup>-3</sup> cm<sup>2</sup> V<sup>-1</sup> S<sup>-1</sup> and an on/off ratio of 5×10<sup>4</sup>.<sup>22</sup> The 1,3-substituted pyrenes exhibit excellent electroluminescence properties, blue emission (456-482 nm), lower turn-on voltage ( $\leq$  3.1 V),) and highly efficient exciton utilization efficiency (77.3%), as well as low-efficiency roll-off.<sup>23</sup> Recently, our group synthesized several multi-substituted pyrene-based chemical intermediate<sup>24</sup> to achieve a series of pyrene-based luminescent materials with narrow-band emission (less than 55 nm) properties.<sup>24,25</sup>

It is noteworthy that molecular conformations can broaden the FWHM emission of organic luminescence materials.<sup>26</sup> The key point to achieve narrow-band emission is to suppress the molecular motion (such as vibration and rotation) and to reduce the vibrational coupling between the ground and excited states of the molecule, *i.e.*, to reduce the number of vibrational levels involved in the separation of vibrational frequencies.<sup>9,27,28</sup> Alternatively, it is possible to keep the

vibrational energy level of the excited state constant concerning the ground state, *i.e.*, by 1) increasing the molecular rigidity, 2) reducing the geometrical configuration change of the excited state concerning the ground state, 3) reducing the nuclear coordinate change between the respective equilibrium states of the ground state and the excited state, and 4) increasing the overlap of the hole/particle distribution in the excited state.<sup>29,30</sup> Following the above methods, many instances of small Stokes shifts and narrow-band emissions have been reported.<sup>31-36</sup>

Inspired by the advantage of the deep blue emission in 1,3-disubstituted compound and pyrenebased emitters containing hydroxy group, herein, we attempted to prepare narrow-band emission of pyrene-based blue emitter by introducing the hydroxy group into the pyrene-core. A set of pyrene-based emitters **3-5** and **6b** have been prepared via functionalizing the pyrene at both active sites (1-, and 3-position) and node plane (2-position). Moreover, the impact of the number of substituents, spatial effects, molecular packing, and the expansion of the  $\pi$ -conjugated rigid molecular skeleton on the pyrene-based emission behavior have been fully investigated. This article highlights new bromopyrene chemical intermediates for constructing novel pyrene-based fluorophores with fantastic photophysical properties. As expected, the target compounds exhibit deep blue fluorescence (CIEy < 0.08) with narrow-band emission (FWHM < 33 nm) both in solution and in the film state, which is one of the narrowest FWHM emission of pyrene-based blue-emitters reported to date. On the other hand, although the products are asymmetric, expanded  $\pi$ -conjugated compounds with a more planar structure, they still exhibit a relatively narrow FWHM emission (less than 48 nm). The compounds 3 and 4 represent some of the narrowest FWHM values among pyrene-based luminescent materials. Thus, this study opens a new avenue for designing pyrene-based blue emitters with narrow FWHM for potential ultra-high-definition display applications.

# 2. RESULTS AND DISCUSSIONS

## 2.1 Synthesis and Characterization

The synthetic strategy for the pyrene-based compounds **3-6** is presented in Scheme 1. According to our previous reports, bromination of 7-tert-butyl-2-hydroxylpyrene (1)<sup>37</sup> affords the new pyrene-based chemical intermediates 2a and 2b in good yield, respectively, depending on the stoichiometric ratio employed for the brominating agent of benzyltrimethylammonium tribromide (BTMABr<sub>3</sub>). <sup>25,38,39</sup> These intermediates were involved in a Suzuki-Miyaura coupling reaction using 4-methoxylphenyl units as substituents, resulting in compounds 3 and 4 in 86% and 65% yields, respectively. To investigate the effect of the rigid, expanding  $\pi$ -conjugated molecular skeleton on the optical behavior, compound 4 underwent a bromination reaction to yield an insoluble intermediate (1-bromo-7-(*tert*-butyl)-3-(4-methoxyphenyl)pyren-2-ol). bromide Subsequently, a one-pot Pd-catalyzed coupling reaction afforded the target compound pyreno[2,1b]furan 5 in a 29% yield. Generally, such a classical approach achieves a high yield under common experimental conditions.<sup>25</sup> However, according to our speculation, the one-pot Pd-catalyzed coupling reaction involves two continuous reaction processes: the Pd-catalyzed Sonogashira coupling reaction and cycloaddition reaction, resulting in a relatively low yield of compound 5. Furthermore, envision a Lewis-acid-catalyzed, one-step cyclization domino-type reaction to prepare a new pyrene-based Aggregation-Induced Emission (AIE) molecule with AIE characteristics for thermal energy storage application.<sup>37</sup> As a comparison, we attempted to synthesize methoxy-substituted chromene molecules containing six rings under the same experimental conditions. Unexpectedly, compound 6a was not formed, even upon changing the experimental conditions, such as stoichiometric ratio, reaction temperature, and reaction time. However, a new 1-substituted pyrene-based system containing olefin bonds (C=C) (6b) was

synthesized in 39% yield via a ZnCl<sub>2</sub>-catalyzed one-step reaction. We infer that the relatively low electron-donating ability of the methoxyl group cannot further trigger the cyclization reaction to form a stable pyrene-based chromene compound (**6a**).<sup>40</sup> All target compounds demonstrated good solubility in common organic solvents (such as CH<sub>2</sub>Cl<sub>2</sub>, THF, and DMSO), which is beneficial for further characterization of their molecular structures and purity. Indeed, all compounds were fully characterized by <sup>1</sup>H/<sup>13</sup>C NMR spectroscopy and high-resolution mass spectrometry (HRMS) (Figures S1-S18), as well as by single crystal X-ray diffraction.



Scheme 1. Synthetic routes for the pyrene-based compounds 3-6. Conditions: (a) BTMABr<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 40 °C, 12h; (b) 4-methoxyphenylboronic acid, K<sub>2</sub>CO<sub>3</sub>, Pd(PPh<sub>3</sub>)<sub>4</sub>, toluene, ethanol, H<sub>2</sub>O, 90 °C, 24 h; (c) 1-ethynyl-4-methoxybenzene, PPh<sub>3</sub>, CuI, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, DMF, Et<sub>3</sub>N, 100 °C, 36 h; (d) 1-ethynyl-4-methoxybenzene, ZnCl<sub>2</sub>, toluene, 80 °C, 24h.

# 2.2 Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) of compounds **3-5** and **6b** was conducted to understand the effects of the molecular structures, the number of substituents, and the length of  $\pi$ -conjugation on the thermal stability. As shown in Figure 1, an increase in molecular weight (achieved by increasing the number of substituents or expanding the  $\pi$ -conjugation) contributes to higher thermal decomposition temperatures (T<sub>d</sub>). The thermal stabilities (with 5% weight loss) of compounds **3** (399 °C) and **5** (405 °C) are higher compared to those of **4** (340 °C) and **6b** (350 °C), respectively. Moreover, the pyreno[2,1-b]furan **5** exhibits a higher T<sub>d</sub> compared to compound **3**. As the temperature was raised above 600 °C, molecules **3** and **5** still had a char yield of 12 wt.% and 22 wt.%, respectively, indicating that **3** and **5** have more aromatic substituents or larger carbon skeletons.<sup>41,42</sup>



Figure 1. TGA curve of compounds 3-5 and 6b.

# 2.3 Single Crystal X-ray Diffraction.

Suitable single crystals of **3**, **4**, and **6b** for X-ray diffraction analysis were grown from a mixture of CH<sub>2</sub>Cl<sub>2</sub> (or CHCl<sub>3</sub>) and hexane by slow evaporation at ambient temperature; the key crystal

parameter data are summarized in Table S1 and S2. Both compounds 3 and 6b crystallized in the monoclinic system with space groups  $P_{21/n}$  for **3**, and  $P_{21/c}$  for **6b**, respectively. Crystal **4** belongs to the triclinic system with space group P-1 and its unit cell contains two molecules. In the three sets of crystals, the C-O bond distance (the C at the 2-position of pyrene and the O from the OH group) is in the range of 1.366-1.380 Å with an angle in the range of 121.25-122.22°. The distance of the C-O (H) is almost equal to 2,7- dihydroxypyrene (1.387 (17) Å) and 2- hydroxypyrene (1.384 (15) Å). <sup>43</sup> The length of the C-O single bonds in the ground state is shorter than typical C-O bonds (1.426±0.005 Å), indicating that the lone pair electrons of the oxygen atom couples with the pyrene ring.<sup>44</sup> Moreover, the twist angle between the pyrene ring and the phenyl ring is 68.31° and 89.77° for 3, and 67.98° for 4, respectively. For compound 6b, the phenyl ring at the 1-position is almost perpendicular to the pyrene ring with a dihedral angle of 83.26°. Clearly, due to the presence of the -OH group at the 2-position, the twist angle is larger than 1,3-disubstituted pyrenes (the twist angles between the pyrene ring and the phenyl ring are less than 56.6°),<sup>38</sup> indicating that the -OH group can play a significant role in increasing the stereoscopic effect, leading to a larger twist angle between the terminal group and the pyrene core (Figures 2, S19-S23).



Figure 2. Molecular structures of compounds 3, 4, and 6b, the ellipsoid probability is 30%.

In the packing of the crystal structure, crystal **3** adopts a herringbone packing motif via several pairs of C-H··· $\pi$  and hydrogen bonds (Figure 3A). No obvious  $\pi$ - $\pi$  stacking was observed between the pyrene rings, and the pyrene core was connected to the neighboring pyrene via several short C-H··· $\pi$  interactions with distances in the range of 2.804-2.897 Å. Moreover, the centroid-to-centroid distance between two parallel pyrene moieties is 7.492 Å with a dihedral angle of 9.08° (Figures 3B and 3D). On the other hand, the two pyrenes in a plane were connected by hydrogen bonding interactions (O5-H5A···O3, C30-H30B···O5, O2-H2···O4, C63-H63···O2) with distances of 2.223-2.697 Å. These complex weak intermolecular interactions are beneficial for fixing the molecular motion via close packing in the crystal structure (Figure 3).



Figure 3. (A) Packing structure of crystal 3 with (B-D) three types of molecular patterns via intramolecular interactions.



**Figure 4**. Packing structure of crystal **4** (A) side view (B) top view and (C) molecular packing via hydrogen-bonding interactions. Packing structure of (D) and (E) for crystal **6b**.

By contrast, compound 4 adopts a head-to-tail packing pattern halfway between  $\pi$ - $\pi$  stacking and C-H… $\pi$  interactions, and the distance between two parallel rings is 3.416 Å, while the centroid-tocentroid distance between the two parallel pyrene moieties is 4.275 Å. According to the McRaés theory, when the aligned angle between transitional moments and the center-to-center axis of two molecules is smaller than 54.7, it can be regarded as *J*-aggregates; in contrast, the H-aggregate has an aligned angle larger than 54.7. In this case, the calculated aligned angle value for crystal **4** is 53.0° which is smaller than 54.7°. Thus, crystal **4** is arranged in a *J*-aggregation.<sup>45</sup> Similarly, crystal **4** in the plane is also connected by hydrogen bonds (O2-H2…O1, C14-H14…O2) with distances of 2.270 Å and 3.170 Å (Figure 4A-C). On the other hand, crystal **6b** adopts a herringbone structural arrangement, and the dominant intermolecular interactions are C-H··· $\pi$  interactions and hydrogen bonds, where the oxygen atom in the methoxy (O-CH<sub>3</sub>) forms hydrogen bonding (C-H···O) interactions with the proton atoms at the 4-, 5- positions of the pyrene core with distances of 2.593 Å and 2.697 Å. The methyl group in the methoxy in **6b** also forms a C-H··· $\pi$  interaction with the pyrene center at a distance of 2.904Å. Due to the steric effect of the *tert*-butyl and -OH groups at the 2- and 7-position, the  $\pi$ - $\pi$  stacking interaction is inhibited in **6b** (Figure 4D and 4E), and the centroid-to-centroid distance between the two parallel pyrene moieties is 8.965 Å.

## **2.4 Photophysical Properties**

The UV-vis absorption and emission spectra of **3**-**5** and **6b** were measured in dilute tetrahydrofuran solution (10<sup>-5</sup> M) and are shown in Figure 5A; key parameters are summarized in Table 1. Compounds **3**, **4**, and **6b** exhibit similar absorption behavior in the UV-vis absorption spectra with three different absorption bands in the ranges 220-307 nm, 319-375 nm, and 375-420 nm, respectively, likely due to the similar pyrene cores. The longwave absorption band of **5** is red-shifted to 413 nm, compared to **3**, **4**, and **6b**, caused by the extension of the  $\pi$ -conjugation of the pyreno[2,1-b]furan core.<sup>25</sup> Due to their similar molecular structures, compounds **3** and **4** exhibit a similar molar extinction coefficient ( $\varepsilon$ ). Still, the long-wavelength absorption band of compound **6b** was hyperchromic-shifted by about 10 nm, with an enhanced  $\varepsilon$  from 35300 (**4**) to 45900 (**6b**), attributed to the presence of C=C bonds lowering the coplanar structure between the pyrene ring and the phenyl ring, indicating the improvement of bonding strength during the C atoms.<sup>46</sup> On the other hand, compound **5** exhibits a relatively low  $\varepsilon$  both in the short-wavelength and the long-wavelength absorption band.



Figure 5. (A) UV-vis absorption and normalized PL spectra of 3-5 and 6b in (B) THF (~  $10^{-5}$  M) solution, (C) in the film state, insert: fluorescence photographs of 3-5 and 6b were taken under daylight (up) and 365 nm UV irradiation (down) in the solid state, (D) summary of the FWHM of emission spectra of pyrene-based molecules in the film state; the stars in red and blue represent 3-5 and 6b, the corresponding pyrene-based luminescent molecular structures (A)-(I) are summarized in Table S3.

To understand the effect of the molecular structure on the electronic structure of the four compounds 3-5, and 6b, density functional theory (DFT) calculations using the B3LYP/6-311G (d, p) and CAM-B3LYP/6-311G(d,p) function level with the Gaussian 16 program were conducted. As shown in Figure S30, the electronic distribution at the ground state for the HOMO and LUMO levels of compounds **3-5**, and **6b** are similar. The HOMO and LUMO of **3** and **4** are mainly located over the entire pyrene core and partial substituents. Despite the presence of the vinyl group in compound **6b**, the HOMO energy levels of the **4** and **6b** molecules are almost the same, and the LUMO energy levels are only slightly different, indicating that the introduction of the vinyl group exerts only a slight influence on the electronic distribution. Due to the expanded  $\pi$ -conjugation, it was found that the HOMO and LUMO energy levels of compound 5 are mainly located at the pyrene and pyreno[2,1-b]furan core, which exhibits very low LUMO and high HOMO, resulting in a small energy gap compared to the other three compounds. This indicates that the formation of the pyreno[2,1-b]furan backbone has a strong influence on the electron cloud distribution in the pyrene system.<sup>25</sup> Furthermore, DFT calculations were also performed using the CAM-B3LYP/6-311G(d,p) basis set, as shown in Figure S31. The most significant difference is that the calculated results based on CAM-B3LYP/6-311G(d,p) basis set show a larger HOMO and lower LUMO energy level, resulting in a larger energy gap.

Generally, pyrene exhibits four absorption bands at 372 nm, 334, 272, and 243 nm, which are assigned to the  $S_1 \leftarrow S_0$ ,  $S_2 \leftarrow S_0$ ,  $S_3 \leftarrow S_0$  and  $S_4 \leftarrow S_0$  transitions, respectively.<sup>21</sup> Thus, to understand the effect of the hydroxy group at the 2-position on the energies of the  $S_n \leftarrow S_0$  transition in this series of pyrenes, the vertical excitation energies for compounds **3-5**, and **6b** were also determined using both B3LYP and CAM-B3LYP functionals. Taking compound **3** as an example, based on the B3LYP functionals, the predicted  $S_1 \leftarrow S_0$ ,  $S_2 \leftarrow S_0$ , and  $S_3 \leftarrow S_0$  excitations are at 427 nm, 385

nm, and 335 nm with oscillator strengths of 0.5847, 0.146, and 0.0395, respectively. When using CAM-B3LYP, the predicted excitation energies for the  $S_1 \leftarrow S_0$ ,  $S_2 \leftarrow S_0$ , and  $S_3 \leftarrow S_0$  excitations are at 388 nm (f = 0.7624), 350 nm (f = 0.0994) and 287 nm (f = 0.0001), respectively; the latter is more consistent with its absorption spectral results. The main reason is that the CAM functional could improve the accuracy of the excited states in the TD-DFT calculations in large  $\pi$ -conjugated polycyclic aromatic hydrocarbon systems.<sup>21,47</sup> Thus, by combining the theoretical calculations, it is easy to assign the  $S_1 \leftarrow S_0$ ,  $S_2 \leftarrow S_0$ , and  $S_3 \leftarrow S_0$  excitations for compounds **3**, **4** and **6b** according to the absorption band. Moreover, for both these functionals, the  $S_1 \leftarrow S_0$  and  $S_2 \leftarrow S_0$  excitations are mainly described by a HOMO→LUMO and HOMO-1→LUMO transition, respectively. In addition, due to the expanding  $\pi$ -conjugated molecular backbone in compound **5**, it is difficult to identify the  $S_1 \leftarrow S_0$  and  $S_2 \leftarrow S_0$  excitations, instead of a broad absorption band with a maximum absorption peak at 412 nm with molar absorption coefficient ( $\epsilon$ ) of 26300 M<sup>-1</sup> cm<sup>-1</sup>.

Table 1. The photophysical properties of the pyrene-based compounds 3-5 and 6b.

Comd.	$\lambda_{(S1 \leftarrow S0)}$ [nm] <sup>a</sup>	$\epsilon$ $M^{-1} cm^{-1}$	$\lambda(s_{2}-s_{0})$ [nm] <sup>a</sup>	$\epsilon$ $M^{-1}$ $cm^{-1}$	$\lambda_{maxPL}$ (nm) solns <sup>b</sup> /films <sup>c</sup>	$arPhi_f$ solns <sup>b</sup> /films <sup>c</sup>	τ (ns) solns <sup>b</sup> /films <sup>c</sup>	FWHM[cm <sup>-1</sup> (nm)] <sup>e</sup> solns <sup>b</sup> /films <sup>c</sup>
3	394	6600	355	35400	408/427	0.52/0.09	10.08/3.14	1801(33)/1251(25)
4	392	5000	332	21200	405/429	0.56/0.04	8.89/4.91	1915(33)/1011(20)
5	412	26300	$\mathbf{nd}^{\mathrm{d}}$	$\mathbf{nd}^{\mathrm{d}}$	429/504	0.70/0.25	1.57/8.82	2226(43)/1847(48)
6b	390	6500	345	45900	399/420	0.10/nd.	3.23/1.70	1804(30)/1527(31)

<sup>a</sup> Maximum absorption wavelength; <sup>b</sup> Measured in THF solution at room temperature; <sup>c</sup> Measured in the film state. nd: less than 0.01. <sup>d</sup> nd: cannot identify the  $S_1 \leftarrow S_0$  and  $S_2 \leftarrow S_0$  excitations. <sup>e</sup>

Upon excitation, the fluorescence spectra of 3-5 and 6b emit deep blue fluorescence with maximum emission peaks at 408, 405, 429, and 399 nm in THF solution with CIE coordinates of (0.16, 0.02), (0.16, 0.02), (0.15, 0.05) and (0.16, 0.01), respectively. Compared to in solution, the emission peaks of the three compounds in the film state were red-shifted to 427, 429, and 420 nm, respectively, while for compound 5, a larger red-shifted emission of about 75 nm to 504 nm was observed (Figures 5B and C). The former may contribute to the molecular aggregation via intramolecular interactions (such as C-H $\cdots\pi$  and hydrogen-bonding interactions), and the latter may be ascribed to the J-aggregation between the pyreno[2,1-b]furan core,<sup>48</sup> resulting in an excimer emission. This is why compounds 3, 4, and 6b emit deep-blue light upon UV excitation, while compound 5 emits green light (Figure 5C). The CIE coordinates of compounds 3-5 and 6b in the film state are (0.14, 0.08), (0.14, 0.05), (0.19, 0.06), and (0.15,0.05), respectively (Figure S24), meeting the B.T. 2020 blue light standard. More importantly, the four compounds exhibit narrow-band emission with a FWHM of  $1801 \text{ cm}^{-1}$  (33 nm) for 3, 1915 cm<sup>-1</sup> (33 nm) for 4, 2226 cm<sup>-1</sup> (43) for **5**, and 1804 cm<sup>-1</sup> (30 nm) for **6b** in solution, respectively. The FWHM trend becomes narrower with a value of 1251 cm<sup>-1</sup> (25nm) for **3** and 1011 cm<sup>-1</sup> (20 nm) for **4** in molecular aggregation, respectively, (Table 1) (Notes: the wavenumber is the linear energy units, and the nanometer is not, a few nanometer at the blue end of the spectrum represents much more energy than a few nanometer at the red end of the spectrum.). The emission of FWHM values of these compounds are relatively narrow in pyrene-based luminescent materials (Figure 5D and Table S3).<sup>38,49-51</sup> This is mainly attributed to the presence of the -OH group at the 2-position acting as a steric hindrance group, which enhances the rigidity of molecular scaffolds and suppresses vibrational coupling via a steric effect and strong hydrogen bonding, facilitating the lower FWHM both in solution and in the film state. On the other hand, the increased FWHM for 5 may be ascribed

to the molecular aggregation of the large  $\pi$ -conjugated planar molecules. Although the photophysical properties of these compounds (such as quantum yield and the FWHM) are falling short of the value of the high-quality of multi-resonance thermally activated delayed fluorescence (MR-TADF) emitters,<sup>[51]</sup> the target compounds of the narrow-band emission of pyrene-based emitter still exhibit some advantages in the aspect of mild synthetic condition, easy functionalizable and good air/thermal-stability, etc. Moreover, the intermolecular interaction is also can regulated by a molecular tailoring. Thus, this present provides a feasible molecular strategy to high-performance narrow-band emission of pyrene-based blue emitters.

Furthermore, the fluorescence quantum yield ( $\Phi_f$ ) of compounds **3-5** and **6b** were measured in THF solution and thin film. As shown in Table 1, compounds **3-5** display a considerable  $\Phi_f$  in the range of 0.52~0.70, while the compound **6b** shows a low  $\Phi_f$  with a value of 0.1. However, the  $\Phi_f$ decreases to 0.09 for **3**, 0.04 for **4**, and 0.25 for **5** in the film state, respectively. Moreover, compound **6b** is almost non-emissive in the film state. Compared to the molecules without a -OH group reported in previous work,<sup>38</sup> these compounds containing a hydroxyl group with low quantum yield may be not only ascribed to the introduction of the hydroxyl groups increasing the number of intermolecular hydrogen bonds, but also due to the presence of the strong intermolecular interactions (such as  $\pi$ -stacking, according to their corresponding crystal packing.), leading to leading to enhanced intermolecular interactions and thus suppressing emission, as well as the low quantum yield in the solid state (Table 1). Thus, the synergetic effect of the hydrogen bond and the  $\pi$ -stacking can assist the exciton transition via the non-radiation decay channels.

The concentration-dependent fluorescence spectra of **3-5** and **6b** were measured in THF solution over the concentration range from  $10^{-7}$  to  $10^{-3}$  M, and all data are summarized in Figure S25 and Table S4. The compounds emit bright blue fluorescence with maximum emission peaks at 407 nm,

405 nm, 428 nm, and 399 nm, with a shoulder peak at 426 nm, 423 nm, 454 nm, and 419 nm, respectively. As the concentration increased, the shoulder emission for each compound gradually enhanced to be a dominant emission peak. This may be ascribed to the distance between the two pyrenes becoming closer in the excited state at high concentration.<sup>48,52</sup> Moreover, no clear excimer emission was observed in the solution, and the presence of the bulky group may plays a vital role in suppressing molecular aggregation in the solution, which is consistent with their crystal packing.

Furthermore, on increasing the solvent polarity from the nonpolar solvent cyclohexane (Cy) to the highly polar dimethyl sulfoxide (DMSO), compounds **3-5** and **6b** showed similar absorption behavior with a slightly red-shifted absorption peak. The maximum emission peaks were red-shifted in the range of 6~13 nm in the six different polar solvents, indicating that the electronic structure of the ground state compound is independent of the polarity of the solvent (Figures S26-S29 and Table S5).<sup>53</sup> The Lippert-Mataga plots for the compounds **3-5** and **6b** were applied to evaluate the relationship between the Stokes shifts ( $\Delta v$ :  $v_a$ - $v_f$ , cm<sup>-1</sup>) and the solvent orientation polarization  $f(\varepsilon, n)$  (Figure S30),<sup>54</sup> according to the equation (1)

$$hc(v_a - v_f) = hc(v_a^0 - v_f^0) - \frac{2(\mu_e - \mu_g)^2}{a^3}f(\varepsilon, n) \quad (1)$$

where *c* is the speed of light, *h* is Planck's constant, *f* is the orientational polarizability of the solvent;  $v_a^0 - v_f^0$  corresponds to the Stokes shift when *f* is zero;  $\mu_e - \mu_g (\Delta \mu)$  is the difference between the dipole moments of the excited and ground states, where  $\mu_e$  is the excited-state dipole moment and  $\mu_g$  is the ground-state dipole moment; *a* is the solvent cavity (Onsager) radius, derived from the Avogadro number (*N*), molecular weight (*M*), and density ( $d = 1.0 \text{ g/cm}^3$ );  $\varepsilon$  and *n* are the solvent dielectric and the solvent refractive index, respectively; and  $f(\varepsilon, n)$  and *a* can be calculated, respectively, as follows:

$$f(\varepsilon,n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

Table S6 lists the Stokes shift of compounds **3-5** and **6b** in various solvents with a range of f values. It was found that all molecules exhibited good linear correlations with regression coefficient ( $\mathbb{R}^2$ ) values of 0.59117, 0.75648, 0.84693, and 0.01548, respectively. This indicates that fluorescence depended on the polarity of solvents. The relatively low slope values (731, 728, 1167, and -50) of the plots suggest that the excited state nature of S<sub>1</sub> changes slightly when compared to their ground state in different solvents. This implies that there is no clear charge transfer process property in this system.

#### 2.5 The relationship between the reorganization energy and the molecular structure

Polycyclic aromatic hydrocarbon (PAH) materials, such as anthracene, phenanthrene, and pyrene, usually exhibit relatively small structural relaxation due to their rigid structures. Intramolecular charge transfer (ICT) interactions can intensify the stretching vibrations between the donor and acceptor when the electron-donating auxochromophores are connected to the PAH units, resulting in a widening of the emission spectrum.<sup>55</sup> According to the Franck-Condon theory,<sup>56</sup> the excited molecules could occur via a deformation of the molecular geometry process and the resultant vibrational relaxation and internal conversion. The reorganization energy ( $\lambda$ ) is a key parameter for understanding the effect of the molecular structural deformation on the emission spectra, the reorganization energy of the four molecules at different wavenumbers in the isolated state was calculated based on Marcus' theory.<sup>57,58</sup> The recombination energies of compounds **3**, **4**, and **6b** in the solid state were calculated based on their crystal structures via quantum mechanics (QM) and molecular mechanics (MM; QM/MM) calculations.<sup>59</sup> Based on the

reorganization energy decomposition results, it can be seen that the representative vibrational modes with the largest contribution to the reorganization energy are mainly located in the highfrequency region (1300-1800 cm<sup>-1</sup>) for the stretching vibrations of the molecular bond lengths in this system.<sup>55</sup> As show in Figures 6A, 6C and S33A, S33C, S34A, and S34C, the compounds exhibited a  $\lambda$  value of 2163 cm<sup>-1</sup> for **3**, 1131 cm<sup>-1</sup> for **4** and 1212 for **6b** in the crystallized state, respectively. According to the results, compounds 3, 4, and 6b have the lowest proportion of the phenyl rotation with twisting vibrations energy (in the low-frequency region) <200 cm<sup>-1.28</sup> Compared to in solution, the contribution of the dihedral angle declined to 15.11% for 3, 7.47% for 4, and 9.22% for 6b, respectively, which was attributed to the rotation of the phenyl ring, which has been restricted in the crystallized state, resulting in a rigid molecular backbone. Meanwhile, the contribution of the bond length increased to 84.06% for 3, 86.05% for 4, and 83.3% for 6b, respectively, which arises from the increased stretching vibrations of the bond. In general, the stretching vibrations in the high-frequency mode may lead to shoulder peaks in the emission spectra,<sup>56,60,61</sup> and the presence of the -OH group at the 2-position not only acts as a steric group but also can strengthen the intermolecular interaction using hydrogen bonding. The synergistic effect can effectively decrease molecular motion and improve the rigidity of molecular scaffolds in the aggregated state and reduce vibrational coupling, leading to a narrower FWHM emission peak in the solid state; this result is in good agreement with the emission spectra.

Furthermore, the four-point method based on the Jablonski diagram was performed to calculate the reorganization energy ( $\lambda$ ), which reflects the changes in electronic configuration in the electronic ground and the excited state. The  $\lambda$  is calculated using the equation:  $\lambda = E_0(R_+) - E_0(R_0)$ +  $E_+(R_0) - E_+(R_+)$  with  $\lambda$  value of 0.583 eV for **3**, 0.459 eV for **4** and 0.361 eV for **6b** in the isolated state,<sup>62</sup> respectively. These values have decreased to 0.499 eV for **3**, 0.273 eV for **4** and 0.288 eV for **6** in the crystallized state, respectively. Both theoretical calculation methods are consistent with the spectroscopic experimental results. (Figures 6B, 6D, S33B, S33D, S34B and S34D).



**Figure 6**. Plots of reorganization energies *versus* the normal mode wavenumber of compounds **3** in (A) the isolated state and (C) the crystallized state calculated by TD-DFT at the CAM-B3LYP 6-311G (d,p) level of Gaussian 16 program. (B) Potential energy surfaces of compound **3** in (B) the isolated state and (D) the crystallized state.

#### **3. CONCLUSIONS**

In this study, a set of new pyrene-based emitters, namely **3-5**, and **6b**, were successfully synthesized from novel pyrene-based intermediates. Importantly, the compounds **3**, **4**, and **6b** exhibit deep blue fluorescence with a narrow-band emission both in solution and in the crystallized state, with FWHM of less than 33 nm. This result represents one of the narrowest FWHM reported to date in the field of pyrene-based luminescent materials. Single X-ray crystal diffraction analysis

and the theoretical calculations revealed that the presence of a hydroxy group not only plays a vital role in increasing the dihedra angle at the *ortho*-position of the phenyl ring via steric effects but also strengthens intermolecular interactions between adjacent pyrenes. This synergistic effect is beneficial for suppressing the  $\pi$ - $\pi$  stacking, restricting molecular motion by hydrogen bonding, and reducing reorganization energy, ultimately narrowing the FWHM of the target materials. Thus, this article opens a new avenue for the preparation of a new type of narrow-band deep blue pyrene-based emitters for practical applications in OLED devices.

# **4. EXPERIMENTAL SECTION**

### 4.1 Materials

Unless otherwise stated, all reagents used were purchased from commercial sources and were used without further purification. 7-(*tert*-Butyl)pyren-2-ol (1) was prepared according to the method of Marder.<sup>21,43,63-65</sup>

**Preparation of the thin film**: the solution with a concentration of  $10^{-5}$  M was dropped on a quartz plate, which was rapidly accelerated to a spin-coating speed (2000 rpm) to form a thin film. Subsequently, the quartz plate containing the compounds was heated to 80 °C for solvent removal.

## 4.2 Characterization

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AVANCE III 400M spectrometer using CDCl<sub>3</sub>- and DMSO-*d6* as the solvent (CDCl<sub>3</sub>, <sup>1</sup>H:  $\delta = 7.26$  ppm, <sup>13</sup>C:  $\delta = 77.06$  ppm. DMSO-*d6*, <sup>1</sup>H:  $\delta = 2.50$  ppm, <sup>13</sup>C:  $\delta = 39.53$  ppm). Coupling constant (*J*) values are given in hertz (Hz). High-resolution mass spectra (HRMS) were recorded using an LC/MS/MS, which consisted of a High-Performance Liquid Chromatography (HPLC) system (Ultimate 3000 RSLC, Thermo Scientific,

USA) and a Q Exactive Orbitrap (QE orbitrap type) mass spectrometer. UV-Vis absorption spectra and photoluminescence (PL) spectra were recorded on a Shimadzu UV-2600 and a Hitachi F-4700 fluorescence spectrometer. PL quantum yields were measured using absolute methods using a Hamamatsu C11347-11 Quantaurus-QY Analyzer. Thermogravimetric analysis was carried out on a TA TGA Q5500 under dry nitrogen at a heating rate of 10 °C min<sup>-1</sup>. The quantum chemistry calculations were performed using the Gaussian 09W (RB3LYP/6-311G(d,p) basis set) software package.<sup>66</sup>

# 4.3 X-ray Crystallography

Crystallographic data for compounds **3**, **4**, and **6b** was collected on a Bruker APEX 2 CCD diffractometer with graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) in the  $\omega$  scan mode or on a Rigaku AFC12 diffractometer equipped with a HyPix detector and a rotating anode source, also with Mo K $\alpha$  radiation.<sup>67,68</sup> The structure was solved by charge flipping or direct methods algorithms and refined by full-matrix least-squares methods on  $F^{2}$ .<sup>69,70</sup> The *tert*-butyl groups in crystals **4** and **6b** are disordered and were refined fractionally. Further details are provided in Table S1 and S2. CCDC 2283682 for crystal **3**, 2283684 for crystal **4**, and 2291874 for crystal **6b**, respectively, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

#### **4.4 Synthetic Procedures**

*Synthesis of 1,3-dibromo-7-(tert-butyl)pyren-2-ol (2a):* A mixture of 7-(*tert*-butyl)pyren-2-ol (1) (500 mg, 1.82 mmol, 1.0 eq.) and benzyltrimethylammonium tribromide (2.50 g, 6.42 mmol, 3.5 eq.) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 ml). Then, the mixture was heated in an oil bath for 24 h at

40 °C under a nitrogen atmosphere. After cooling, filtration was performed to give pure 1,3dibromo-7-(*tert*-butyl)pyren-2-ol (**2a**) (620 mg, yield 79%) as a white color solid. <sup>1</sup>H NMR (400 MHz, DMSO-*d6*)  $\delta$  (ppm): 10.41 (s, 1H), 8.38 (s, 2H), 8.26 (d, *J* = 9.3 Hz, 2H), 8.23 (d, *J* = 9.2 Hz, 2H), 1.52 (s, 9H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d6*)  $\delta$  149.1, 149.1, 130.2, 129.4, 129.3, 124.9, 123.9, 120.8, 120.1, 109.6, 35.1, 31.7 ppm. HRMS (FTMS+p APCI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>20</sub>H<sub>17</sub>Br<sub>2</sub>O, 432.9625; found 432.9607; error 4.167 ppm.

Synthesis of 1-bromo-7-(tert-butyl)pyren-2-ol (2b): A mixture of 7-(tert-butyl)pyren-2-ol (1) (274 mg, 1.00 mmol, 1 eq.) and benzyltrimethylammonium tribromide (584 mg, 1.50 mmol, 1.5 eq.) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (20 ml). Then, the mixture was heated in an oil bath for 12 h at 40 °C under a nitrogen atmosphere. Upon completion of the reaction, the reaction solution was quenched with deionized water (50 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 50 mL). The organic layer was washed with water (2 × 40 mL) and saturated brine (50 mL), and then the solution was dried by MgSO<sub>4</sub> and condensed under reduced pressure. The residue was purified through column chromatography (SiO<sub>2</sub>, hexane/CH<sub>2</sub>Cl<sub>2</sub> = 4:1 (volume ratio)) to give 1-bromo-7-(*tert*-butyl)pyren-2-ol (2b) (237 mg, yield 67%) as a grey colored solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.24-8.22 (m, 3H), 8.12 (d, *J* = 9.2 Hz, 1H), 8.02 (d, *J* = 9.0 Hz, 1H), 7.87 (d, *J* = 9.0 Hz, 1H), 7.78 (s, 1H), 6.11 (s, 1H), 1.60 (s, 9H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 150.1, 148.7, 131.6, 130.2, 130.0, 129.8, 129.6, 128.7, 126.3, 124.9, 123.5, 123.1, 122.2, 120.7, 111.4, 107.8, 35.2, 32.0 ppm. HRMS (FTMS+p APCI) *m/z*: [M+H]<sup>-</sup> calcd for C<sub>20</sub>H<sub>18</sub>BrO, 351.0384; found 351.0391; error 1.9941 ppm.

*Synthesis of 7-(tert-butyl)-1,3-bis(4-methoxyphenyl)pyren-2-ol (3):* A mixture of 1,3-dibromo-7-(*tert*-butyl)pyren-2-ol (**2a**) (250 mg, 0.57 mmol, 1.0 eq.), (4-methoxyphenyl)boronic acid (262 mg,

1.73 mmol, 3.0 eq.) and K<sub>2</sub>CO<sub>3</sub> (400 mg, 2.89 mmol, 5.0 eq.) was dissolved in the mixture of toluene (7 ml), ethanol (2 ml) and H<sub>2</sub>O (1 ml) and was stirred at room temperature for 10 mins and then Pd(PPh<sub>3</sub>)<sub>4</sub> (100 mg, 0.08 mmol, 0.15 eq.) was added. The resulting mixture was refluxed in an oil bath for 24 h at 90 °C under a nitrogen atmosphere. After cooling, the reaction mixture was quenched with deionized water (50 mL) and extracted with  $CH_2Cl_2$  (2 × 50 mL). The organic layer was washed with water  $(2 \times 40 \text{ mL})$  and saturated brine (50 mL), and then the combined organic solution was dried by MgSO4 and condensed under reduced pressure. The residue was purified through column chromatography (SiO<sub>2</sub>, hexane/CH<sub>2</sub>Cl<sub>2</sub> = 1:1 (volume ratio)) to give 7-(*tert*butyl)-1,3-bis(4-methoxyphenyl)pyren-2-ol (3) as a white colored powder, which was further recrystallized in a mixture of  $CH_2Cl_2$  and hexane ( $V_{CH_2Cl_2}$ : Vhexane = 1:1) to achieve a white crystal solid (240 mg, yield 86%, melting point 276 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.17 (s, 2H), 7.96 (d, J = 9.2 Hz, 2H), 7.79 (d, J = 9.2 Hz, 2H), 7.52 (d, J = 8.5 Hz, 4H), 7.15 (d, J = 8.6 Hz, 4H), 5.44 (s, 1H), 3.93 (s, 6H), 1.58 (s, 9H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 159.4, 148.3, 148.1, 132.6, 130.1, 130.0, 128.0, 127.5, 124.8, 123.1, 122.5, 120.0, 114.5, 55.4, 35.1, 31.9 ppm. HRMS (FTMS+p APCI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>34</sub>H<sub>31</sub>O<sub>3</sub>, 487.2273; found 487.2267; error 1.2314 ppm.

Synthesis of 7-(tert-butyl)-1-(4-methoxyphenyl)pyren-2-ol (4): A mixture of 1-bromo-7-(tertbutyl)pyren-2-ol (2b) (200 mg, 0.56 mmol, 1.0 eq.), (4-methoxyphenyl)boronic acid (128 mg, 0.84 mmol, 1.5 eq.) and K<sub>2</sub>CO<sub>3</sub> (90 mg, 0.65 mmol, 1.1 eq.) was dissolved in the mixture solvent of toluene (7 ml), ethanol (2 ml) and H<sub>2</sub>O (1 ml) and was stirred at room temperature for 10 mins, and then Pd(PPh<sub>3</sub>)<sub>4</sub> (70 mg, 0.06 mmol, 0.1 eq.) was added. The resulting mixture was refluxed in an oil bath for 24 h at 90 °C under a nitrogen atmosphere. After cooling, the reaction mixture was quenched with deionized water (50 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 50 mL). The organic layer was washed with water (2 × 40 mL) and saturated brine (50 mL), and then the solution was dried by MgSO<sub>4</sub> and condensed under reduced pressure. The residue was purified through column chromatography (SiO<sub>2</sub>, hexane/CH<sub>2</sub>Cl<sub>2</sub> = 2:1 (volume ratio)) to give 7-(*tert*-butyl)-1-(4methoxyphenyl)pyren-2-ol (4) as a white powder, which was further recrystallized in a mixture of CHCl<sub>3</sub> and hexane (V<sub>CHCl3</sub>:Vhexane = 1:3) to achieve a white crystalline solid (140 mg, yield 65%, melting point: 227 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.20 (s, 1H), 8.16 (s, 1H), 8.04 (d, J = 9.0 Hz, 1H), 7.97 (d, J = 9.0 Hz, 1H), 7.94 (d, J = 9.2 Hz, 1H), 7.79 (s, 1H), 7.70 (d, J = 9.2Hz, 1H), 7.46 (d, J = 8.7 Hz, 2H), 7.18 (d, J = 8.6 Hz, 2H), 5.41 (s, 1H), 3.94 (s, 3H), 1.57 (s, 9H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 159.9, 151.0, 148.1, 132.6, 132.0, 130.6, 130.2, 129.7, 128.2, 126.6, 126.3, 124.6, 123.0, 122.9, 122.8, 122.4, 120.0, 115.1, 111.1, 55.5, 35.2, 32.0 ppm. HRMS (FTMS+p APCI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>25</sub>O<sub>2</sub>, 381.1855; found 381.1846; error 2.3610 ppm.

Synthesis of 2-(tert-butyl)-6,8-bis(4-methoxyphenyl)pyreno[2,1-b][furan (5): A mixture of 7-(tert-butyl)-1-(4-methoxyphenyl)pyren-2-ol (4) (190 mg, 0.50 mmol, 1.0 eq.) and benzyltrimethylammonium tribromide (234 mg, 0.60 mmol, 1.2 eq.) was dissolved in dry CH<sub>2</sub>Cl<sub>2</sub> (10 ml), and then the mixture was heated in an oil bath for 12 h at 40 °C under a nitrogen atmosphere. Upon completion of the reaction, the reaction solution was quenched with deionized water (50 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 50 mL). The organic layer was washed with water (2 × 40 mL) and saturated brine (50 mL), and then the solution was dried by MgSO4 and condensed under reduced pressure. The residue was washed by hot CH<sub>2</sub>Cl<sub>2</sub> to achieve 1-bromo-7-(*tert*-butyl)-3-(4-methoxyphenyl)pyren-2-ol as a grey-colored solid in quantitative yield, which was used for the next step without further purification. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.39 (d, *J* = 9.2 Hz, 1H), 8.25 (d, *J* = 1.6 Hz, 1H), 8.19 (d, *J* = 1.7 Hz, 1H), 8.17 (d, *J* = 9.2 Hz, 1H), 7.95 (d, *J* = 9.3 Hz,

1H), 7.72 (d, J = 9.2 Hz, 1H), 7.45 (d, J = 8.7 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 6.01 (s, 1H), 3.95 (s, 3H), 1.58 (s, 9H) ppm. Then, a mixture of 1-bromo-7-(tert-butyl)-3-(4-methoxyphenyl)pyren-2-ol (100 mg, 0.21 mmol, 1.0 eq.), 1-ethynyl-4-methoxybenzene (43 mg, 0.32 mmol, 1.5 eq.), triphenylphosphine (40 mg, 0.15 mmol, 0.71 eq.) and CuI (40 mg, 0.21 mmol, 1.0 eq.) was dissolved in a mixture of DMF (3 ml) and triethylamine (5 ml) and was stirred at room temperature for 10 min., and then PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (50 mg, 0.07 mmol, 0.33 eq.) was added. The resulting mixture was reacted for 36 h at 100 °C under a nitrogen atmosphere. After cooling, the reaction mixture was quenched with deionized water (50 mL) and extracted with  $CH_2Cl_2$  (2 × 50 mL). The organic layer was washed with water  $(2 \times 40 \text{ mL})$  and saturated brine (50 mL), and then the combined organic solution was dried by MgSO<sub>4</sub> and condensed under reduced pressure. The residue was purified through column chromatography (SiO<sub>2</sub>, hexane/CH<sub>2</sub>Cl<sub>2</sub> = 3:1 (volume ratio)) to give 2-(tert-butyl)-6,8-bis(4-methoxyphenyl)pyreno[2,1-b]furan (5) as a green powder, which was further recrystallized in a mixture of CH<sub>2</sub>Cl<sub>2</sub> and hexane ( $V_{CH_2Cl_2}$ :Vhexane = 1:2) to afford a green crystalline solid (31 mg, yield 29%, melting point 249 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), δ (ppm): 8.42 (d, J = 8.9 Hz, 1H), 8.23 (d, J = 1.7 Hz, 1H), 8.19 (d, J = 7.1 Hz, 1H), 8.18 (s, 1H), 8.16 (s, 1H), 7.93 (d, J = 9.4 Hz, 1H), 7.87 (d, J = 8.8 Hz, 2H), 7.75 (d, 2H), 7.66 (s, 1H), 7.21 (d, 2H), 6.99 (d, J = 8.8 Hz, 2H), 3.99 (s, 3H), 3.87 (s, 3H), 1.60 (s, 9H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>), δ (ppm): 160.1, 159.3, 157.1, 150.5, 148.3, 132.7, 131.1, 130.7, 127.5, 127.3, 126.7, 126.6, 126.3, 125.4, 125.0, 124.0, 123.5, 123.4, 122.9, 122.3, 122.1, 122.0, 120.6, 114.3, 114.0, 98.7, 55.5, 55.4, 35.2, 32.0 ppm. HRMS (FTMS+p APCI) m/z: [M+H]<sup>+</sup> calcd for C<sub>36</sub>H<sub>31</sub>O<sub>3</sub>, 511.2273; found 511.2260; error 2.5429 ppm.

*Synthesis of 7-(tert-butyl)-1-(1-(4-methoxyphenyl)vinyl)-2λ<sup>5</sup>-pyren-2-one (6b):* A mixture of 7-(*tert*-butyl)pyren-2-ol (1) (200 mg, 0.72 mmol, 1 eq.), 1-ethynyl-4-methoxybenzene (313 mg, 2.16 mmol, 3 eq.) and ZnCl<sub>2</sub> (98 mg, 0.72 mmol, 1 eq.) was dissolved in toluene (5 ml) and heated to 80 °C, and the system was stirred and refluxed in an oil bath for 24 h under a nitrogen atmosphere. After cooling, the reaction mixture was poured into water (50 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 50 mL). The organic layer was washed with water (2 × 40 mL) and saturated brine (50 mL), and then the solution was dried by MgSO<sub>4</sub> and condensed under reduced pressure. The residue was purified through column chromatography (SiO<sub>2</sub>, hexane/CH<sub>2</sub>Cl<sub>2</sub> = 8:1 (volume ratio)) to give 7-(*tert*-butyl)-1-(1-(4-methoxyphenyl)vinyl)-2 $\lambda$ <sup>5</sup>-pyren-2-one (**6b**) (155 mg, yield 39%, melting point 201 °C) as a white colored solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 8.20 (d, *J* = 1.6 Hz, 1H), 8.14 (d, *J* = 1.5 Hz, 1H), 8.04 (d, *J* = 9.0 Hz, 1H), 7.98 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.83 (d, *J* = 9.2 Hz, 1H), 7.81 (s, 1H), 7.29 (d, *J* = 8.9 Hz, 2H), 6.79 (d, *J* = 8.9 Hz, 2H), 6.36 (s, 1H), 5.83 (s, 1H), 5.51 (s, 1H), 3.76 (s, 3H), 1.56 (s, 9H) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>),  $\delta$  (ppm): 160.1, 150.9, 148.2, 142.1, 132.2, 131.6, 130.3, 130.2, 129.7, 128.4, 127.8, 126.6, 124.8, 122.9, 122.8, 122.6, 122.6, 120.0, 117.0, 114.2, 111.3, 55.3, 35.2, 32.0 ppm. HRMS (FTMS+p APCI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>2</sub>9H<sub>31</sub>O<sub>2</sub>, 407.2011; found 407.2001; error 2.4558 ppm.

# ASSOCIATED CONTENT

#### **Data Availability Statement**

The data underlying this study are available in the published article and its Supporting Information.

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website. Details of the experimental characterization, including <sup>1</sup>H/<sup>13</sup>C NMR spectra, HRMS. Results of UV–vis and fluorescence spectra, crystal parameters, and DFT calculations (PDF). Single crystal X-ray diffraction of **3**, **4**, and **6b** (CIFs)

#### **AUTHOR INFORMATION**

#### **Corresponding Author**

**Xing Feng -** Guangdong Provincial Key Laboratory of Information Photonics Technology, School of Material and Energy, Guangdong University of Technology, Guangzhou 510006, P. R. China, orcid.org/0000-0002-4273-979X; E-mail: <u>hyxhn@sina.com</u>.

**Yonggang Min** - Guangdong Provincial Key Laboratory of Information Photonics Technology, School of Material and Energy, Guangdong University of Technology, Guangzhou 510006, P. R. China; E-mail: ygmin@gdut.edu.cn.

## Authors

*Yiwei Liu* - Guangdong Provincial Key Laboratory of Information Photonics Technology, School of Material and Energy, Guangdong University of Technology, Guangzhou, 510006, P. R. China

Jianyu Zhang - Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, and GuangdongHong Kong-Macau Joint Laboratory of Optoelectronic and Magnetic Functional Materials, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong 999077, China

Xiaohui Wang - Guangdong Provincial Key Laboratory of Information Photonics Technology, School of Material and Energy, Guangdong University of Technology, Guangzhou, 510006, P. R. China

*Zhixin Xie* - Guangdong Provincial Key Laboratory of Information Photonics Technology, School of Material and Energy, Guangdong University of Technology, Guangzhou, 510006, P. R. China

Heng Zheng - Guangdong Provincial Key Laboratory of Information Photonics Technology, School of Material and Energy, Guangdong University of Technology, Guangzhou, 510006, P. R. China

*Sheng Zhang -* Guangdong Provincial Key Laboratory of Information Photonics Technology, School of Material and Energy, Guangdong University of Technology, Guangzhou, 510006, P. R. China

*Xumin Cai* - Jiangsu Co-Innovation Center of Efficient Processing and Utilization of Forest Resources, International Innovation Center for Forest Chemicals and Materials, College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, China

Yu Zhao - Guangdong Provincial Key Laboratory of Information Photonics Technology, School of Material and Energy, Guangdong University of Technology, Guangzhou, 510006, P. R. China.

Carl Redshaw - Chemistry, School of Natural Sciences, University of Hull, Hull, Yorkshire HU6 7RX, UK.

### **Author Contributions**

Yiwei Liu: Methodology, Data curation, Investigation, Writing-Original Draft. Jianyu Zhang: Data curation, Software, Investigation. Xiaohui Wang: Data curation, Investigation. Heng Zheng: Data curation. Sheng Zhang: Data curation. Xumin Cai: Investigation. Yu Zhao: Methodology, Writing
Review & Editing. Carl Redshaw: Writing - Review & Editing. Yonggang Min: Source, Writing
Review & Editing. Xing Feng: Supervision, Writing - Review & Editing, Funding acquisition.
<sup>‡</sup>Y. Liu and J. Zhang contributed equally to this work.

## Notes

The authors declare no competing financial interest.

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