

## Supporting Information

### **Pyrene-based aggregation-induced emission luminogens with less color migration for Anti-counterfeiting Applications**

Xiaohui Wang,<sup>a</sup> Lirong Wang,<sup>b</sup>, Xiaoyu Mao,<sup>a</sup> Qingsong Wang,<sup>a</sup> Zhongfei Mu,<sup>a</sup> Li An,<sup>c</sup>

Wan Zhang,<sup>c</sup> Xing Feng,<sup>a\*</sup> Carl Redshaw,<sup>d</sup> Changyong Cao,<sup>e</sup> Anjun Qin,<sup>\*b</sup> Ben Zhong

Tang<sup>\*b,f</sup>

<sup>a</sup>School of Material and Energy, Guangdong University of Technology, Guangzhou 510006, P. R. China. Email: [hyxhn@sina.com](mailto:hyxhn@sina.com) (X. Feng.)

<sup>b</sup>NSFC Center for Luminescence from Molecular Aggregates, SCUT-HKUST Joint Research Laboratory, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China. Email: [msqinaj@scut.edu.cn](mailto:msqinaj@scut.edu.cn) (A. J. Qin)

<sup>c</sup>Beijing Institute of Graphic Communication, Beijing 102600, P.R. China.

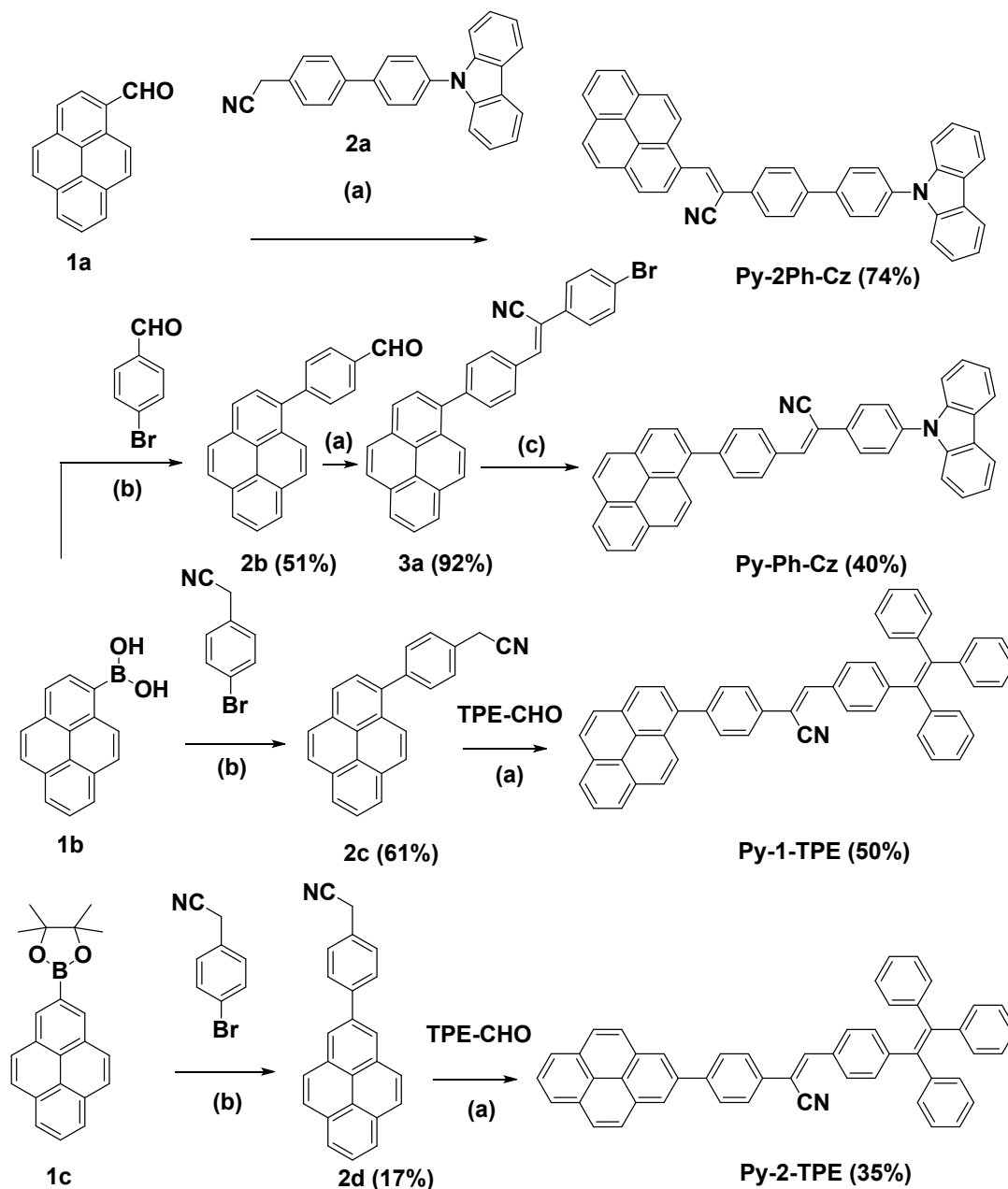
<sup>d</sup>Department of Chemistry, University of Hull, Cottingham Road, Hull, Yorkshire HU6

<sup>e</sup>Laboratory for Soft Machines & Electronics, Michigan State University, East Lansing 48824, MI

<sup>f</sup>Department of Chemistry and Hong Kong Branch of Chinese National Engineering Research Center for Tissue Restoration and Reconstruction, The Hong Kong University of Science & Technology, Kowloon, Hong Kong 999077, P. R. China; Shenzhen Institute of Molecular Aggregate Science and Engineering, School of Science and Engineering, The Chinese University of Hong Kong, Shenzhen 518172, China. Email: [tangbenz@ust.hk](mailto:tangbenz@ust.hk) (B. Z. Tang)

## Experimental section

### Synthesis



(a) dry ethanol, K<sub>2</sub>OtBu, reflux, (b) Pd(PPh<sub>4</sub>)<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub>, toluene, ethanol, H<sub>2</sub>O, (c) Pd(OAc)<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, P(tBu)<sub>3</sub>

**Scheme S1** Synthetic route to four pyrene-based AIEgens.

### Synthesis

#### 2.5. Synthesis of 2-Bpin-Pyrene (**1c**)<sup>[1]</sup>

A Schlenk tube was charged with pyrene (2.00 g, 9.88 mmol, 1.0 eq.), bis(pinacolato)diboron (2.79 g, 11.0mmol, 1.11 eq.), 4,4'-di-*tert*-butyl-2,2'-dipyridine

(0.20 g, 0.72 mmol, 0.73 eq.) and cyclohexane (50 mL). After stirring for 5 min., the  $[\text{Ir}(\mu\text{-OMe})\text{cod}]_2$  (0.20 g, 0.30 mmol, 0.03 eq) was added, the mixture was vigorously stirred and heated at 80°C for 16 h under a nitrogen atmosphere. Then, the reaction solution was poured into H<sub>2</sub>O (100 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic phase was washed with H<sub>2</sub>O and water and brine (50 mL), the organic phase was dried over MgSO<sub>4</sub> and evaporated. The crude product was further purified by column chromatography using hexane/ dichloromethane ( $V_{\text{hexane}}:V_{\text{CH}_2\text{Cl}_2} = 1:1$ ) as the eluent. A white solid of 2-Bpin-Pyrene was obtained (750 mg) in 23% yield and a white solid of 2,7-di-Bpin-Pyrene was obtained (1.0 g) in 22% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.63 (s, 2H), 8.16 (d,  $J = 7.6$  Hz, 2H), 8.10 (d,  $J = 9.0$  Hz, 2H), 8.05 (d,  $J = 9.0$  Hz, 2H), 8.03 – 7.96 (m, 1H), 1.46 (s, 12H). The NMR spectroscopic result is agreement with the previous reports.<sup>[1]</sup>

#### 2.6. Synthesis of 2-(4'-(8a,9a-dihydro-9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)acetonitrile (**2a**)<sup>[2]</sup>

A mixture of 2-(4-bromophenyl)acetonitrile (400 mg, 2.04 mmol, 1.00 eq.), 9H-carbazole-9-(4-phenyl) boronic acid (700 mg, 2.44 mmol, 1.20 eq.), sodium carbonate (500 mg, 4.71 mmol, 2.3 eq.) and tetrakis(triphenylphosphine) palladium (40 mg, 0.035 mmol, 0.02 eq.) in toluene (10 mL) and ethanol (3 mL) were refluxed overnight under a nitrogen atmosphere. After cooling to room temperature, the mixture was quenched with water, extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 100 mL), and washed with water and brine. The organic extracts were dried with MgSO<sub>4</sub> and evaporated. The residue was purified by column chromatography using a hexane/CH<sub>2</sub>Cl<sub>2</sub> mixture ( $V_{\text{hexane}}:V_{\text{CH}_2\text{Cl}_2} =$

1:1) as eluent to give compound **2a** as a light white powder (450 mg, yield 61%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, Figure S1) δ 8.16 (d, *J* = 7.8 Hz, 2H), 7.84 – 7.78 (m, 2H), 7.73 – 7.69 (m, 2H), 7.68 – 7.63 (m, 2H), 7.48 (d, *J* = 8.2 Hz, 4H), 7.43 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.34 – 7.28 (m, 2H), 3.84 (s, 2H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>, Figure S2) δ 140.8, 140.2, 139.2, 137.3, 129.3, 128.6, 128.5, 127.8, 127.4, 126.0, 123.5, 120.4, 120.1, 117.8, 109.8, 23.4.

### 2.7. Synthesis of 1-(4-formylphenyl) pyrene (**2b**)<sup>[3]</sup>

Under a nitrogen atmosphere, 1-bromopyrene (400 mg, 1.42 mmol, 1.0 eq.), 4-formylphenylboronic acid (256 mg, 1.71 mmol, 1.2 eq.) and K<sub>2</sub>CO<sub>3</sub> (800 mg, 5.80 mmol, 4.1 eq.) were dissolved in a mixture of toluene (16 mL)/ ethanol (4 mL) / H<sub>2</sub>O (4 mL) and stirred for 5 min. Then, Pd(PPh<sub>3</sub>)<sub>4</sub> (120 mg, 0.11 mmol, 0.06 eq.) was added, and the mixture was vigorously stirred at reflux for 24 h. After cooling to room temperature, the reaction mixture was washed with water (100 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> three times (3 × 50 mL). The combined organic layer was washed with water and brine (50 mL), dried over MgSO<sub>4</sub> and evaporated. The crude product was further purified by column chromatography using hexane/CH<sub>2</sub>Cl<sub>2</sub> (V<sub>hexane</sub>:V<sub>CH<sub>2</sub>Cl<sub>2</sub></sub> = 10:1) as the eluent to yield 1-(4-formylphenyl) pyrene (215 mg, 51%) as a green-yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 10.17 (s, 1H), 8.27 – 8.18 (m, 3H), 8.13 (d, *J* = 1.9 Hz, 2H), 8.10 (d, *J* = 3.8 Hz, 2H), 8.07 (d, *J* = 4.8 Hz, 2H), 8.04 (t, *J* = 5.1 Hz, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 2H). This NMR spectroscopic result is in agreement with the previous reports.<sup>[3]</sup>

### 2.8. Synthesis of 2-(4-(pyren-1-yl)phenyl)acetonitrile (**2c**)

Under a nitrogen atmosphere, 1-Py-Bpin (1.23 g, 5 mmol, 1 eq.), 4-bromophenylacetonitrile (1.078 g, 5.5 mmol, 1.1 eq.),  $K_2CO_3$  (1 g, 7.26 mmol, 1.45 eq.) were dissolved in a mixture of toluene (30 mL)/ ethanol (5 mL) /  $H_2O$  (5 mL) and stirred for 10 min. Then,  $Pd(PPh_3)_4$  (300 mg, 0.087 mmol, 0.017 eq.) was added and the mixture was heated at  $90^\circ C$  for 24 h. After cooling to room temperature, the mixture was poured into  $H_2O$  (100 mL) and extracted with  $CH_2Cl_2$  ( $3 \times 50$  mL). The combined organic layer was washed with water and brine (50 mL), and then the solution was dried over  $MgSO_4$  and evaporated. The crude product was further purified by column chromatography using hexane/ dichloromethane ( $V_{hexane}:V_{CH_2Cl_2} = 3:2$ ) as the eluent and eventually recrystallized from a mixture of hexane and dichloromethane to afford a yellow solid, namely 1-p-phenylacetonitrile-pyrene (Py-1-CN) (949 mg, 60%).  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.24 – 8.14 (m, 3H), 8.10 (d,  $J = 9.2$  Hz, 3H), 8.05 – 7.97 (m, 2H), 7.93 (d,  $J = 7.8$  Hz, 1H), 7.63 (d,  $J = 8.1$  Hz, 2H), 7.50 (d,  $J = 7.9$  Hz, 2H), 3.87 (s, 2H) ppm.  $^{13}C$  NMR (151 MHz,  $CDCl_3$ )  $\delta$  141.1, 136.5, 131.4, 131.2, 130.9, 130.7, 128.8, 128.4, 128.0, 127.7, 127.6, 127.4, 127.3, 126.1, 125.2, 124.9, 124.9, 124.8, 124.8, 124.6, 117.9, 53.4, 23.4 ppm. HRMS (FTMS+p APCI) m/z: found, 318.1268  $[M+H]^+$ ; calcd for  $C_{24}H_{15}N$  requires  $[M]^+$  317.1204.

### 2.9. Synthesis of 2-(4-(pyren-2-yl)phenyl)acetonitrile (**2d**)

Under a nitrogen atmosphere, 2-Bpin-pyrene (500 mg, 1.52 mmol, 1 eq.), 4-bromophenylacetonitrile (359 mg, 1.83 mmol, 1.20 eq.), and  $K_2CO_3$  (500 mg, 3.63 mmol, 2.4 eq.) were dissolved in a mixture of toluene (15 mL)/ ethanol (2 mL) /  $H_2O$  (2 mL) and stirred for 10 min. Then,  $Pd(PPh_3)_4$  (100 mg, 0.087 mmol, 0.06 eq.) was

added and the mixture was heated at 90°C for 24 h. After cooling to room temperature, the mixture was poured into H<sub>2</sub>O (100 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organic layer was washed with water and brine (50 mL), and then the solution was dried over MgSO<sub>4</sub> and evaporated. The crude product was further purified by column chromatography using hexane/ dichloromethane (V<sub>hexane</sub>:V<sub>CH<sub>2</sub>Cl<sub>2</sub></sub> = 3:1) as the eluent and eventually recrystallized from a mixture of hexane and dichloromethane to afford a white solid 2-(4-(pyren-2-yl)phenyl)acetonitrile(Py-2-Ph) (84 mg, 17 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.38 (s, 2H), 8.21 (d, *J* = 7.6 Hz, 2H), 8.18 – 8.09 (m, 4H), 8.06 – 7.99 (m, 1H), 7.91 (d, *J* = 8.1 Hz, 2H), 7.53 (d, *J* = 7.9 Hz, 2H), 3.87 (s, 2H) ppm. <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 141.5, 137.8, 131.7, 131.2, 129.0, 128.8, 128.6, 128.0, 127.5, 126.1, 125.3, 124.5, 124.1, 123.5, 117.9, 53.4, ppm. HRMS (FTMS+p APCI) *m/z*: found, 318.1271 [M+H]<sup>+</sup>; calcd for C<sub>24</sub>H<sub>15</sub>N requires [M]<sup>+</sup> 317.1204.

#### 2.10. Synthesis of (Z)-2-(4-bromophenyl)-3-(4-(pyren-1-yl)phenyl)acrylonitrile (**3a**)

To a 100 mL two-necked flask was added 1-(4-formylphenyl) pyrene (180 mg, 0.58 mmol, 1 eq.), 4-bromophenyl acetonitrile (137 mg, 0.70 mmol, 1.20 eq.), KO<sup>*t*</sup>Bu (150 mg, 1.4 mmol, 2.31 eq.) and dry ethanol (10 mL). The reaction mixture was degassed with nitrogen for 5 min., and then refluxed overnight. After cooling to room temperature, the reaction mixture was filtered and washed with ethanol. The residue was further recrystallized in a mixture of hexane and dichloromethane to yield (Z)-2-(4-bromophenyl)-3-(4-(pyren-1-yl)phenyl)acrylonitrile (260 mg, 92%) as a yellow solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.22 (ddd, *J* = 13.8, 9.6, 5.6 Hz, 4H), 8.10 (dd, *J* = 12.2, 4.1 Hz, 5H), 8.05 (d, *J* = 7.7 Hz, 1H), 8.01 (t, *J* = 5.5 Hz, 1H), 7.77 (d, *J* = 8.3

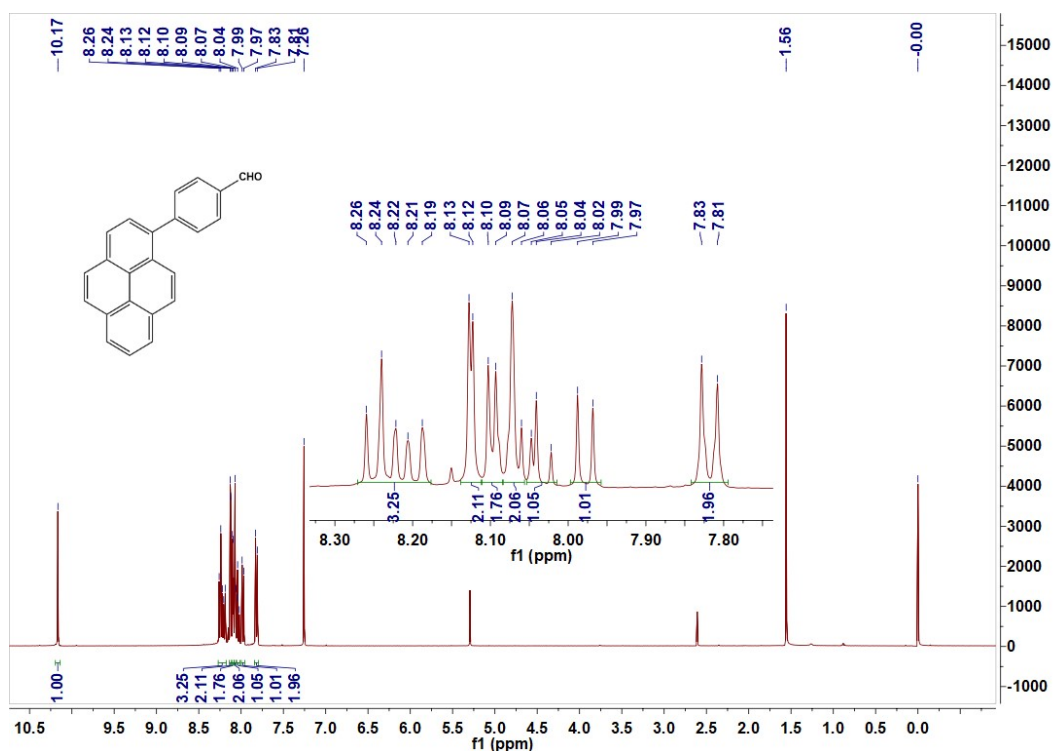
Hz, 2H), 7.63 (d,  $J = 15.2$  Hz, 5H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  149.0, 142.2, 136.4, 133.5, 132.4, 132.3, 131.5, 131.3, 131.0, 130.9, 129.5, 128.4, 127.9, 127.8, 127.5, 127.4, 126.2, 125.4, 125.1, 125.0, 124.9, 124.8, 124.8, 123.5, 117.8, 110.5, 53.4 ppm. HRMS (FTMS+p APCI)  $m/z$ : found, 484.0695  $[\text{M}+1]^+$ ; calcd for  $\text{C}_{31}\text{H}_{18}\text{BrN}$  requires  $[\text{M}]^+$  483.0623.

### References

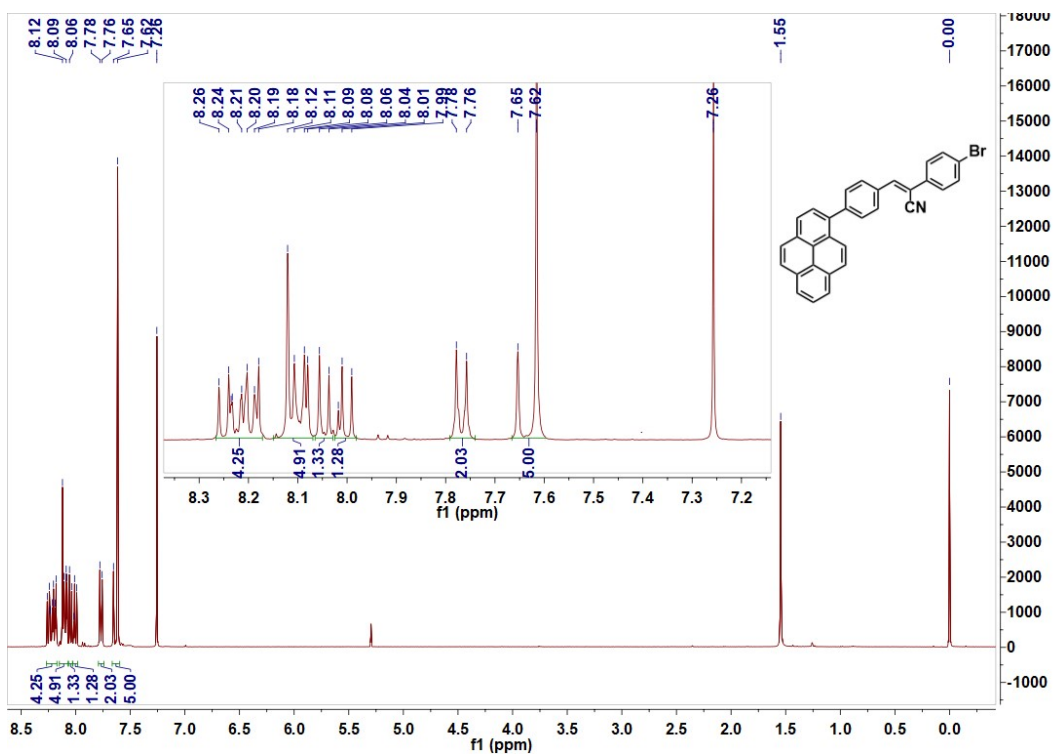
- [1] A. G. Crawford, A. D. Dwyer, Z. Liu, A. Steffen, A. Beeby, L. O. Palsson, D. J. Tozer and T. B. Marder, *J. Am. Chem. Soc.*, 2011, 133, 13349.
- [2] Z. Hu, Y. Li, M. Kang, M. M. Islam, M. Chen, J. Zhang, Y. Xiao, X. Feng, C. Redshaw, M. Zhang, Q. Chen, S. Xie J. W. Y. , Lam, B. Z. Tang, *EcoMat.*, 2020, 1.
- [3] A. Kathiravan, V. Srinivasan, T. Khamrang, M. Velusamy, M. Jaccob, N. Pavithra, S. Anandan, K. Velappan. *Phys. Chem. Chem. Phys.*, 2017, 19, 3125.

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## NMR spectroscopy

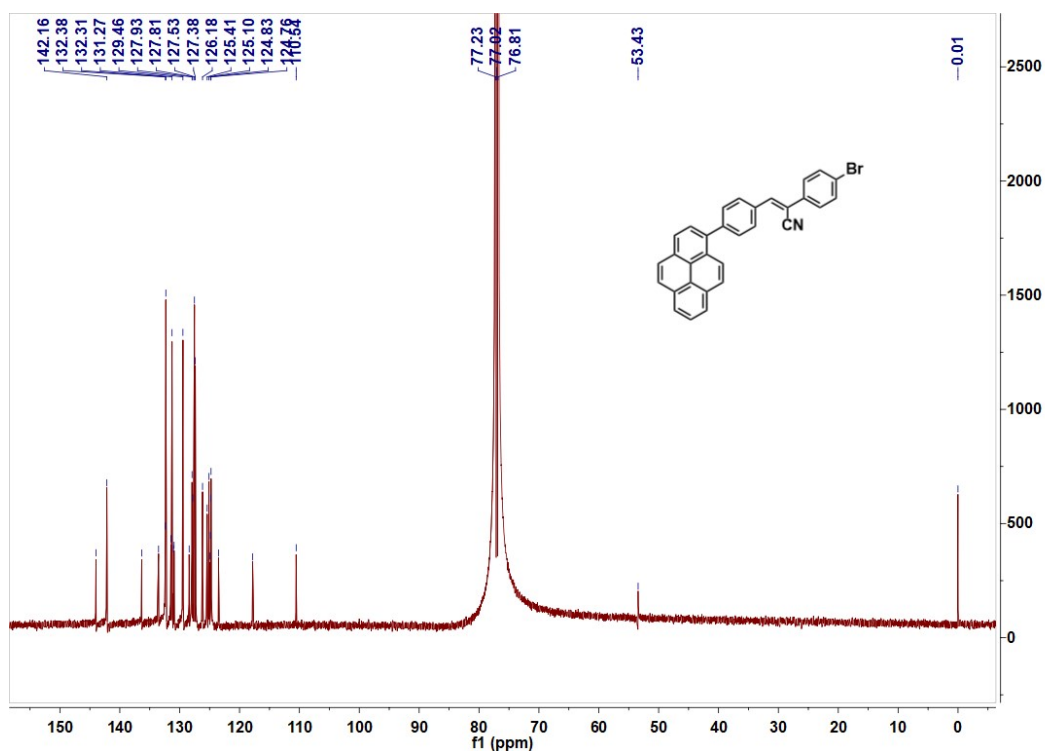


**Figure S1** <sup>1</sup>H-NMR spectrum (400 MHz, 293 K, \* CDCl<sub>3</sub>) for 1-(4-formylphenyl)pyrene

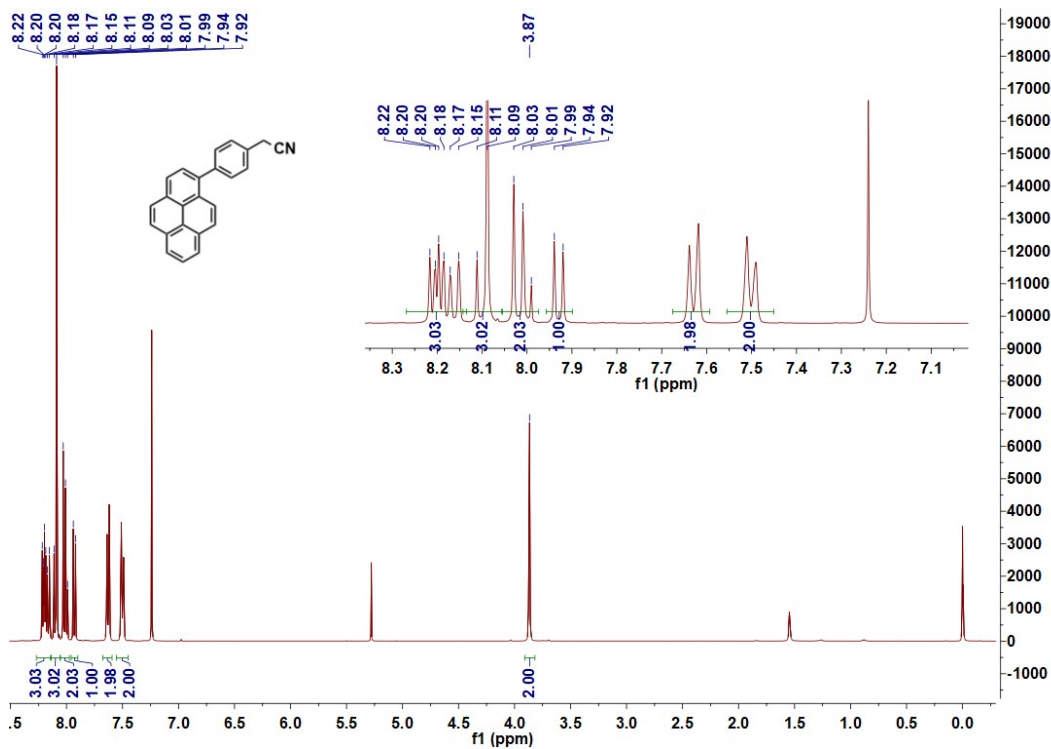


**Figure S2** <sup>1</sup>H-NMR spectrum (400 MHz, 293 K, \* CDCl<sub>3</sub>) for (Z)-2-(4-bromophenyl)-3-(4-(pyren-1-yl)phenyl)acrylonitrile

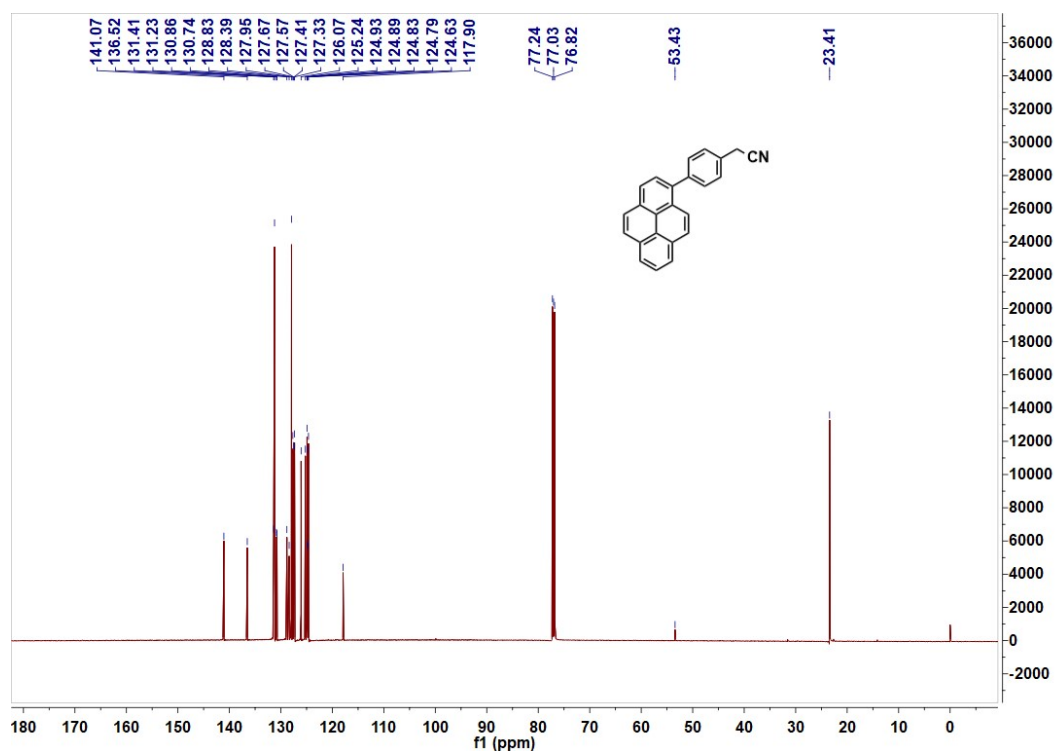




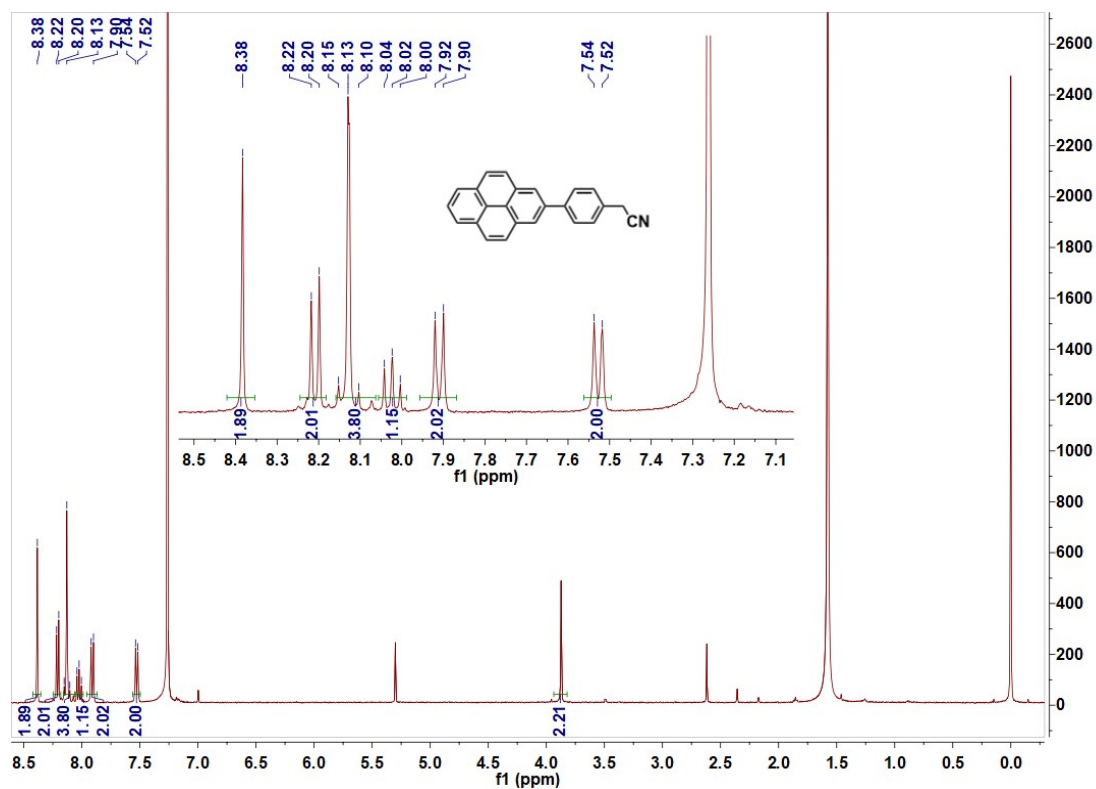
**Figure S3** <sup>13</sup>C-NMR spectrum (151 MHz, 293 K, \* CDCl<sub>3</sub>) for (Z)-2-(4-bromophenyl)-3-(4-(pyren-1-yl)phenyl)acrylonitrile



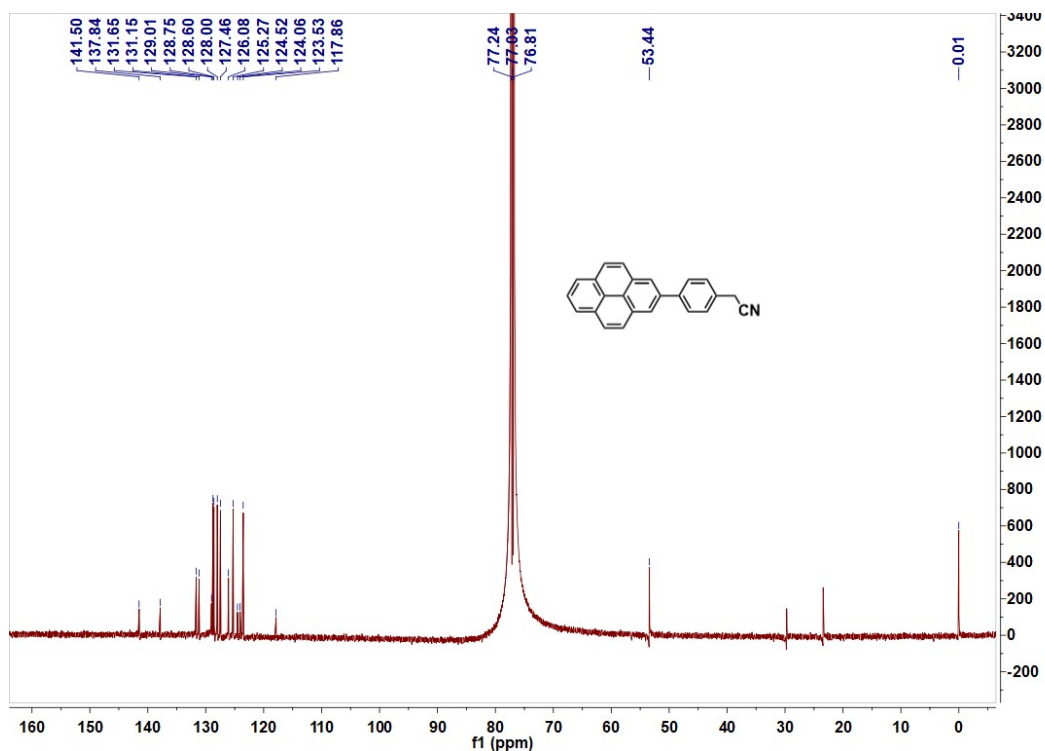
**Figure S4** <sup>1</sup>H-NMR spectrum (400 MHz, 293 K, \* CDCl<sub>3</sub>) for 2-(4-(pyren-1-yl)phenyl)acetonitrile



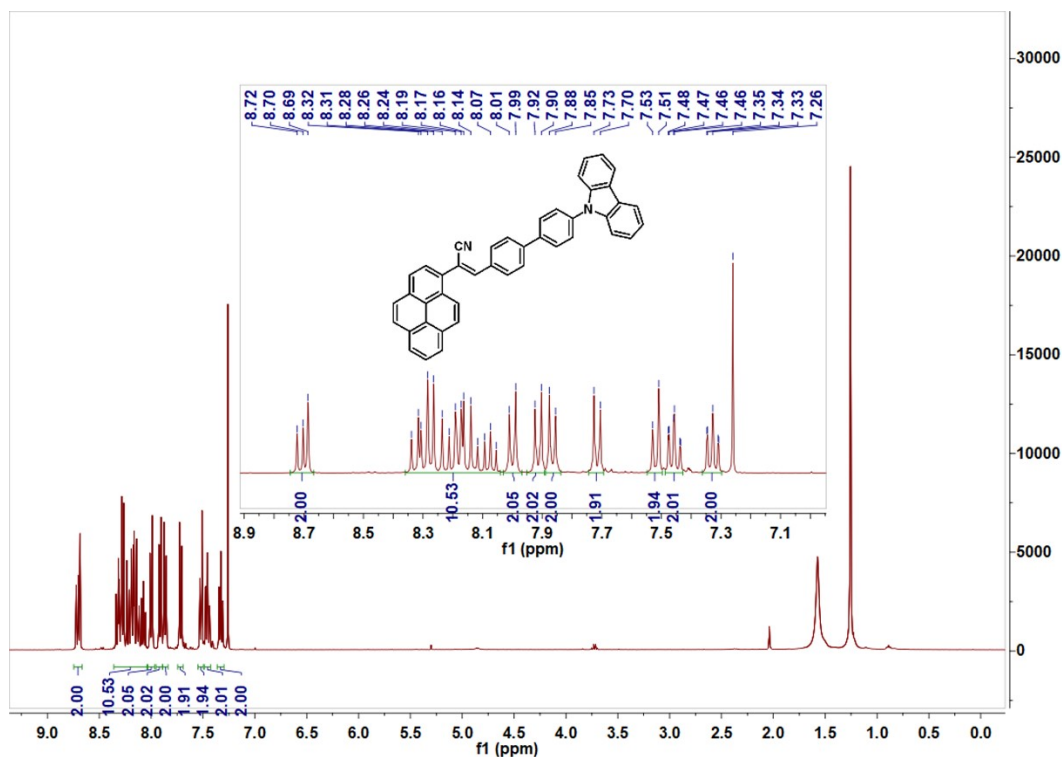
**Figure S5**  $^{13}\text{C}$ -NMR spectrum (151 MHz, 293 K, \*  $\text{CDCl}_3$ ) for 2-(4-(pyren-1-yl)phenyl)acetonitrile



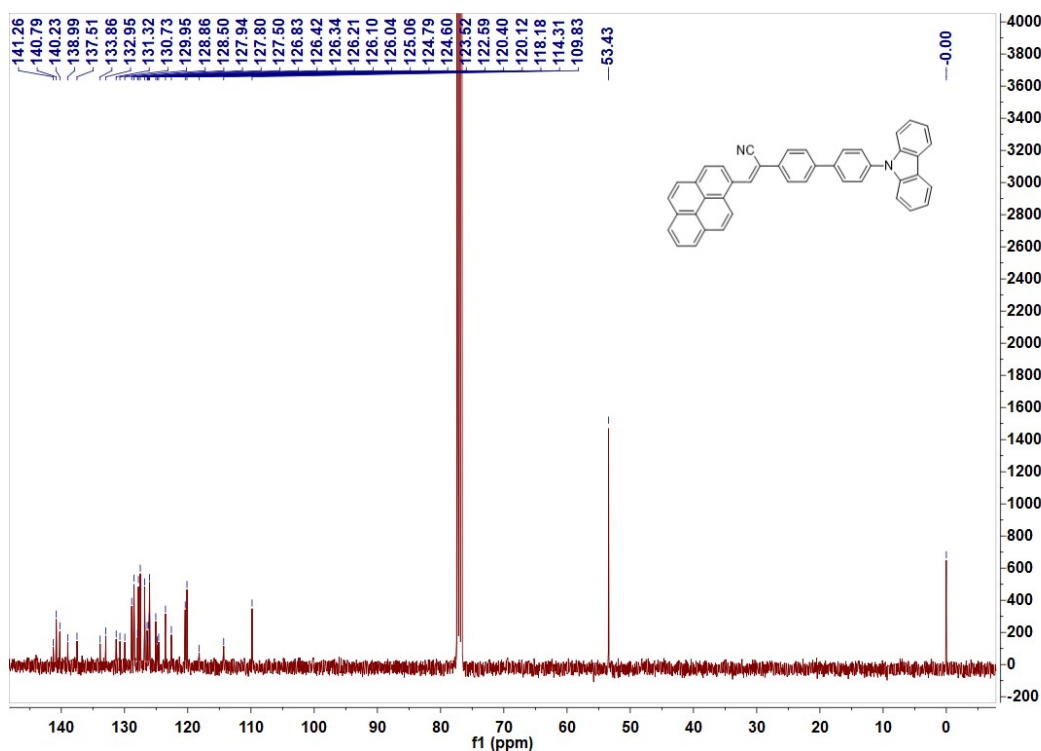
**Figure S6**  $^1\text{H}$ -NMR spectrum (400 MHz, 293 K, \*  $\text{CDCl}_3$ ) for 2-(4-(pyren-2-yl)phenyl)acetonitrile



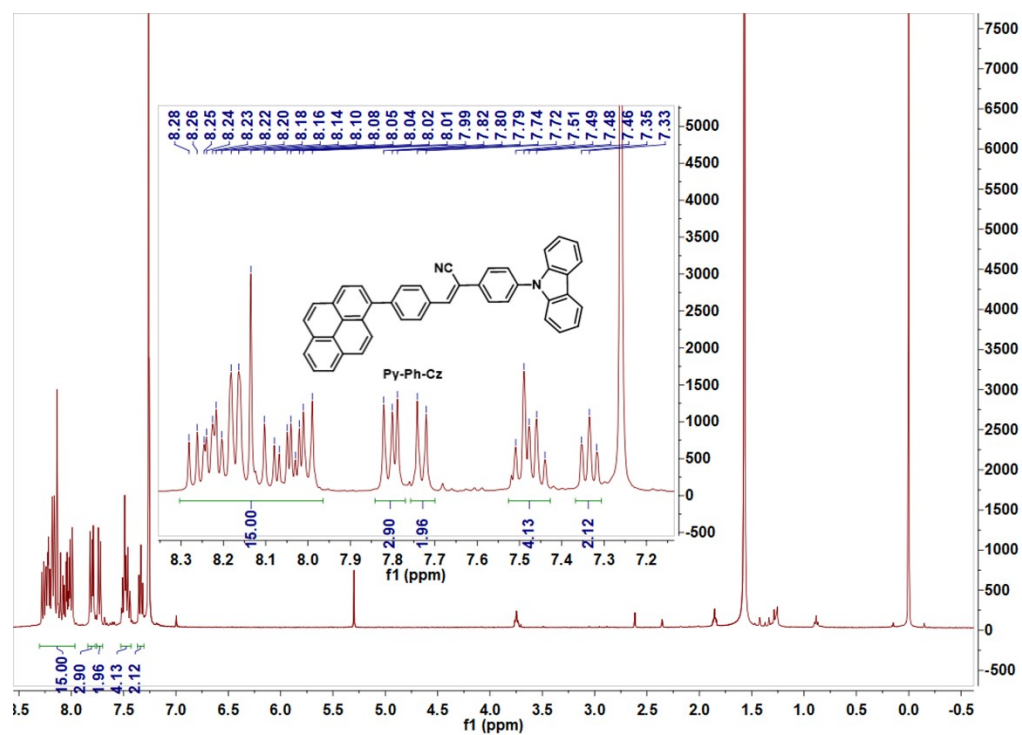
**Figure S7** <sup>13</sup>C-NMR spectrum (151 MHz, 293 K, \* CDCl<sub>3</sub>) for 2-(4-(pyren-2-yl)phenyl)acetonitrile



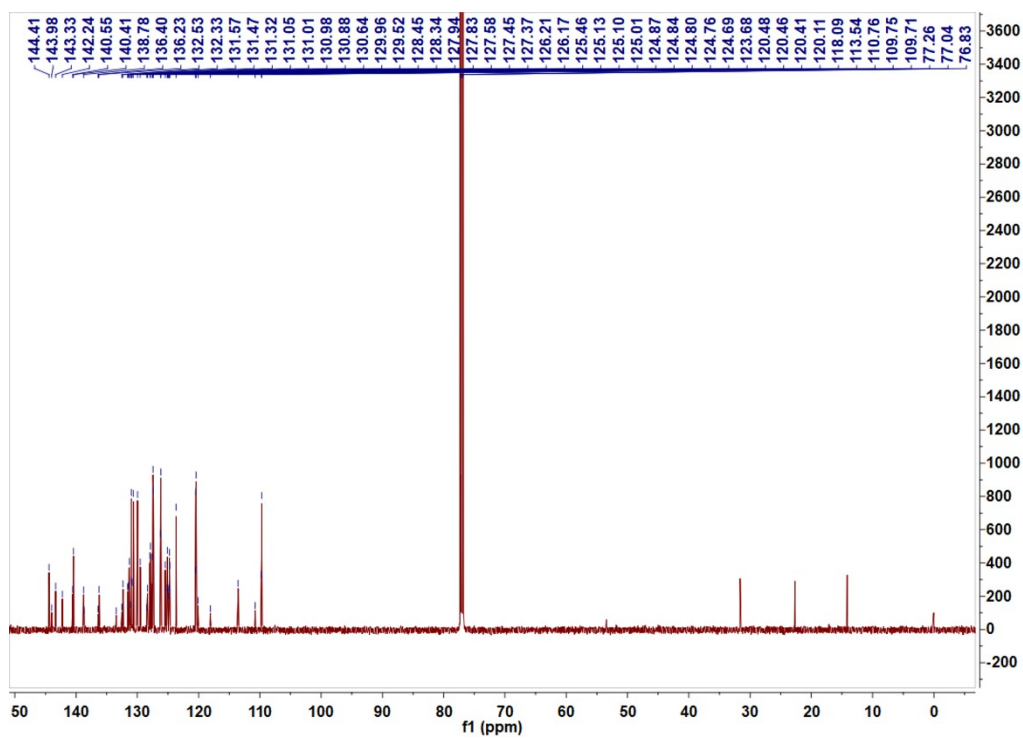
**Figure S8** <sup>1</sup>H-NMR spectrum (400 MHz, 293 K, \* CDCl<sub>3</sub>) for (Z)-2-(4'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)-3-(pyren-1-yl) acrylonitrile (**Py-2Ph-Cz**).



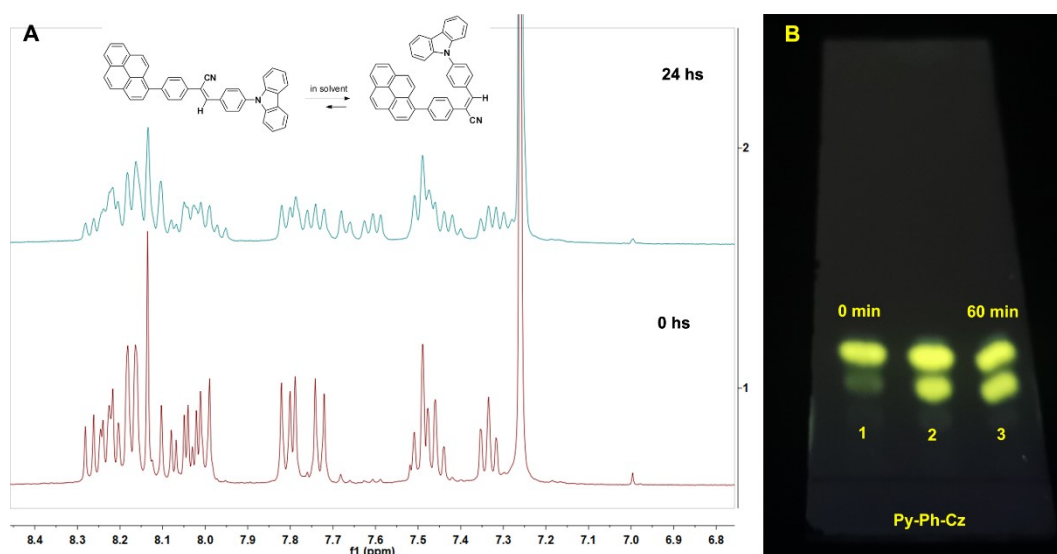
**Figure S9**  $^{13}\text{C-NMR}$  spectrum (101 MHz, 293 K,  $^*\text{CDCl}_3$ ) for (Z)-2-(4'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)-3-(pyren-1-yl)acrylonitrile (**Py-2Ph-Cz**).



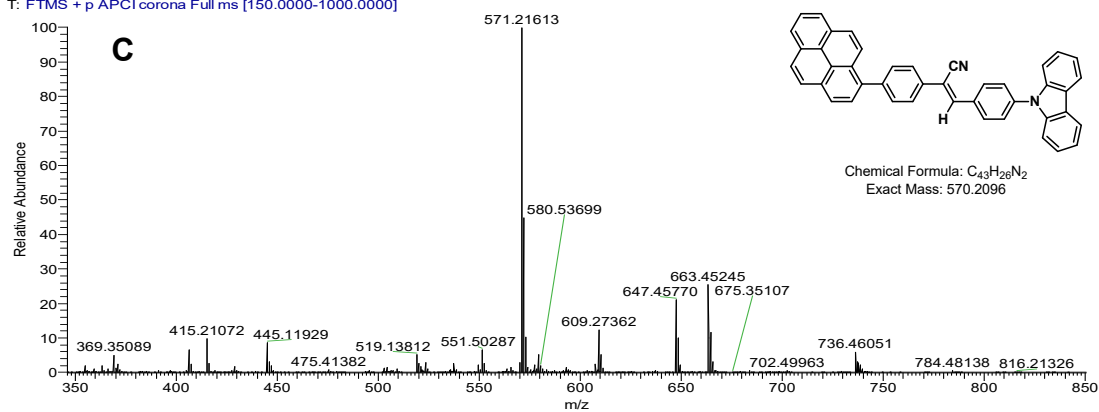
**Figure S10**  $^1\text{H-NMR}$  spectrum (400 MHz, 293 K,  $^*\text{CDCl}_3$ ) for (Z)-2-(4'-(9H-carbazol-9-yl)phenyl)-3-(4-(pyren-1-yl)phenyl)acrylonitrile (**Py-Ph-Cz**).



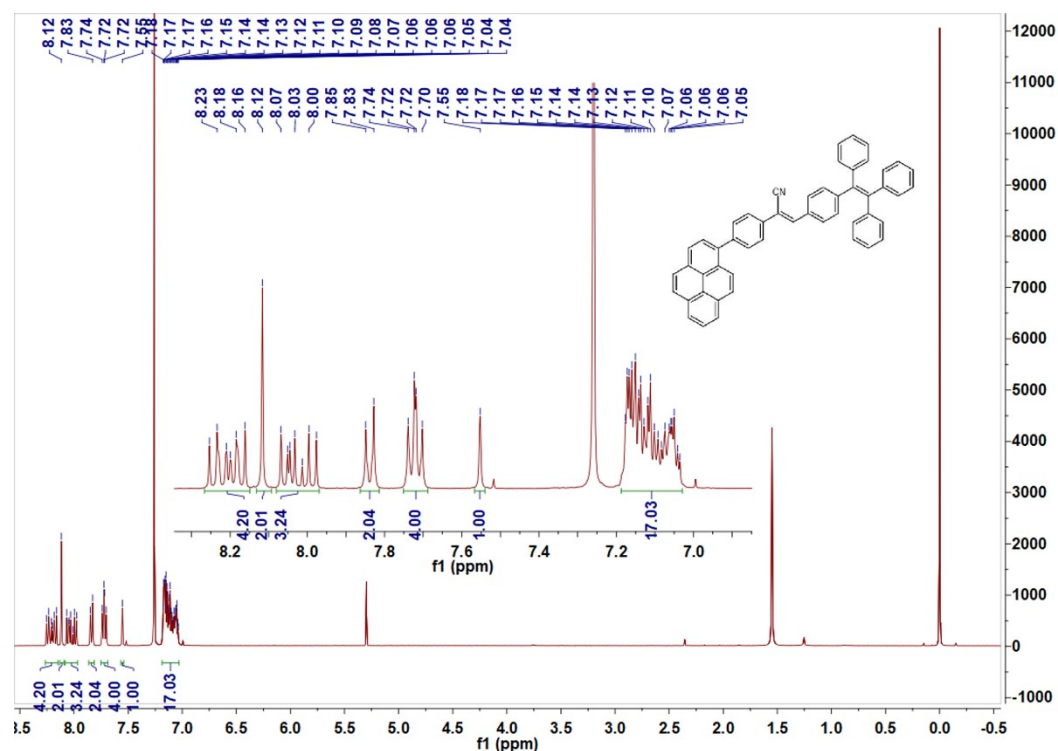
**Figure S11**  $^{13}\text{C}$ -NMR spectrum (151 MHz, 293 K,  $^*\text{CDCl}$ ) for (Z)-2-(4-(9H-carbazol-9-yl)phenyl)-3-(4-(pyren-1-yl)phenyl)acrylonitrile (**Py-Ph-Cz**).



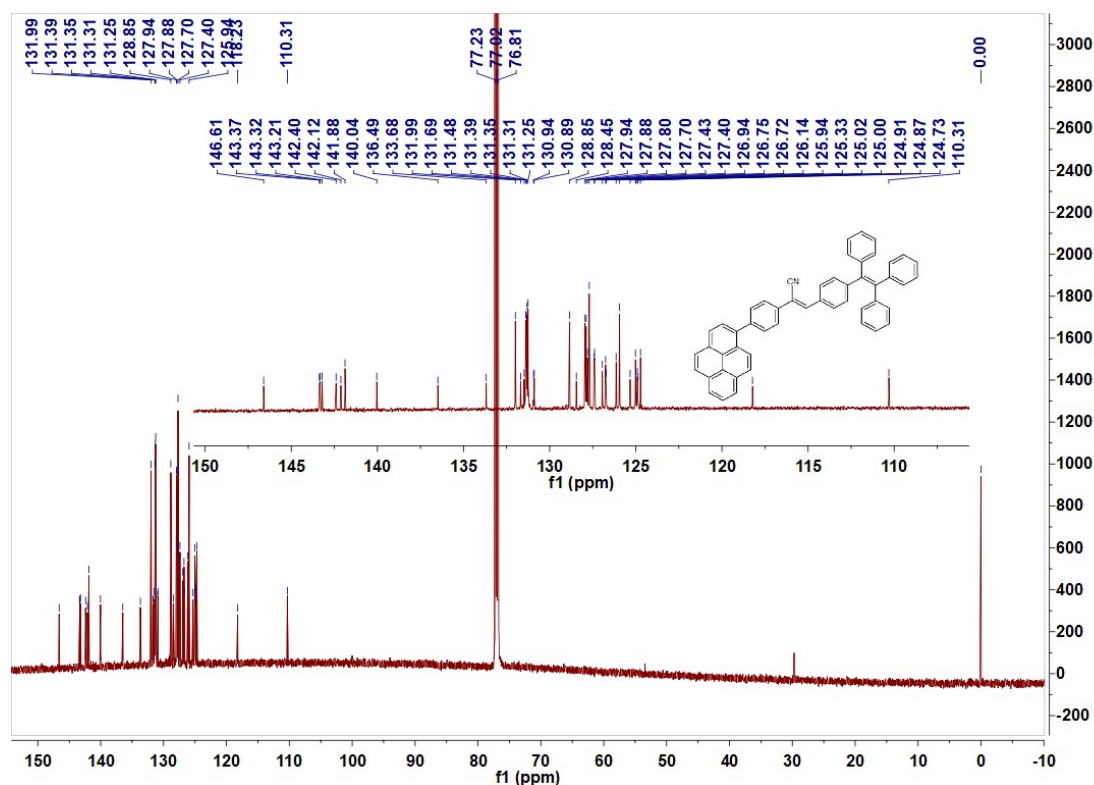
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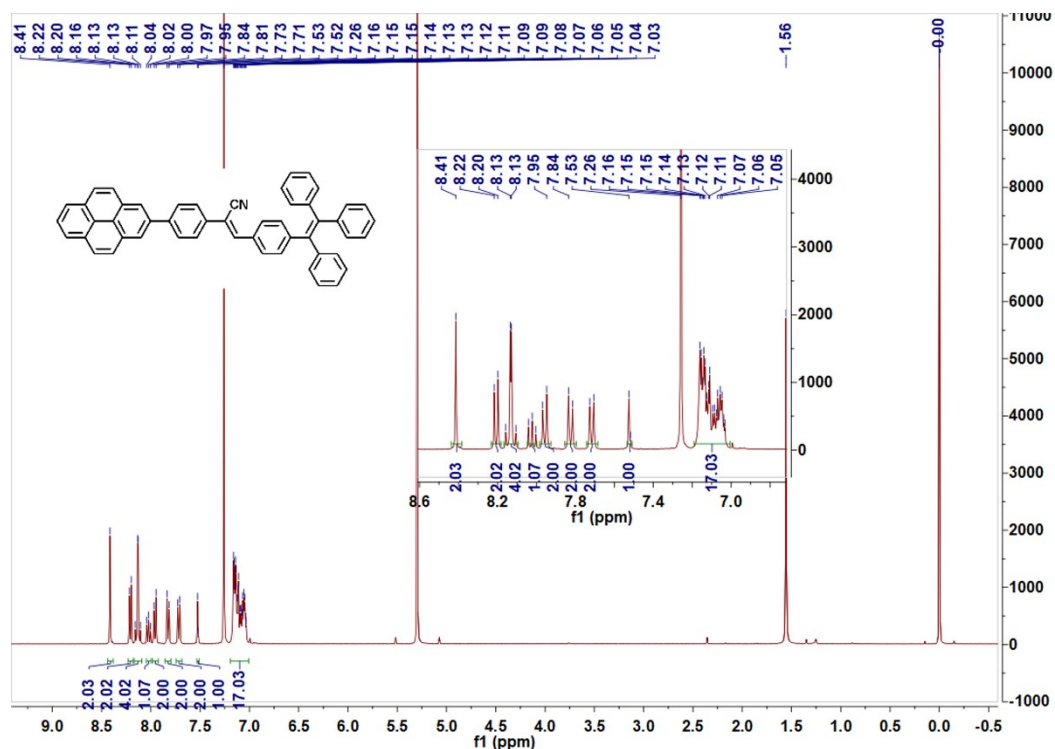
**Figure S12** A) The <sup>1</sup>H NMR spectrum (400 MHz, 293 K, \*CDCl<sub>3</sub>) for **Py-Ph-Cz** at 0 h and 24 h, B) Digital photographs of TLC for compound **Py-Ph-Cz** at 0 min. and 60 min., C) The mixture of E/Z-configurational isomers for **Py-Ph-Cz**.



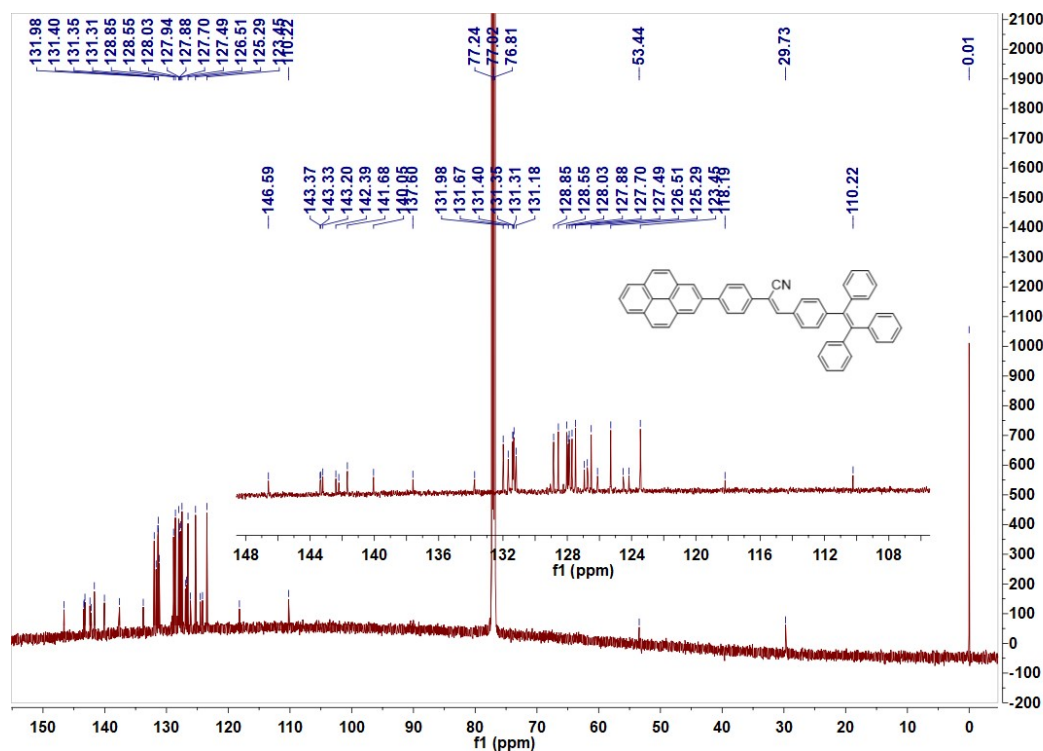
**Figure S13** <sup>1</sup>H-NMR spectrum (400 MHz, 293 K, \* CDCl<sub>3</sub>) for (Z)-2-(4-(pyren-1-yl)phenyl)-3-(4-(1,2,2-triphenylvinyl)phenyl)acrylonitrile (**Py-1-TPE**).



**Figure S14** <sup>13</sup>C-NMR spectrum (151 MHz, 293 K, \* CDCl<sub>3</sub>) for (Z)-2-(4-(pyren-1-yl)phenyl)-3-(4-(1,2,2-triphenylvinyl)phenyl)acrylonitrile (**Py-1-TPE**).



**Figure S15** <sup>1</sup>H-NMR spectrum (400 MHz, 293 K, \* CDCl<sub>3</sub>) for (Z)-2-(4-(pyren-2-yl)phenyl)-3-(4-(1,2,2-triphenylvinyl)phenyl)acrylonitrile (**Py-2-TPE**).



**Figure S16** <sup>13</sup>C-NMR spectrum (151 MHz, 293 K, \* CDCl<sub>3</sub>) for (Z)-2-(4-(pyren-2-yl)phenyl)-3-(4-(1,2,2-triphenylvinyl)phenyl)acrylonitrile (**Py-2-TPE**).



## High Resolution Mass Spectrometry (HRMS)

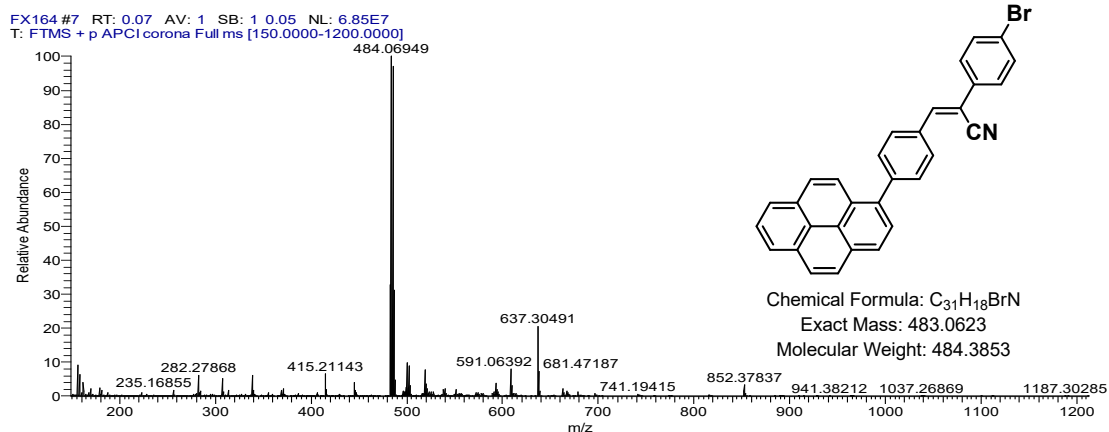


Figure S17 HRMS spectra of (Z)-2-(4-bromophenyl)-3-(4-(pyren-1-yl)phenyl)acrylonitrile (**3a**)

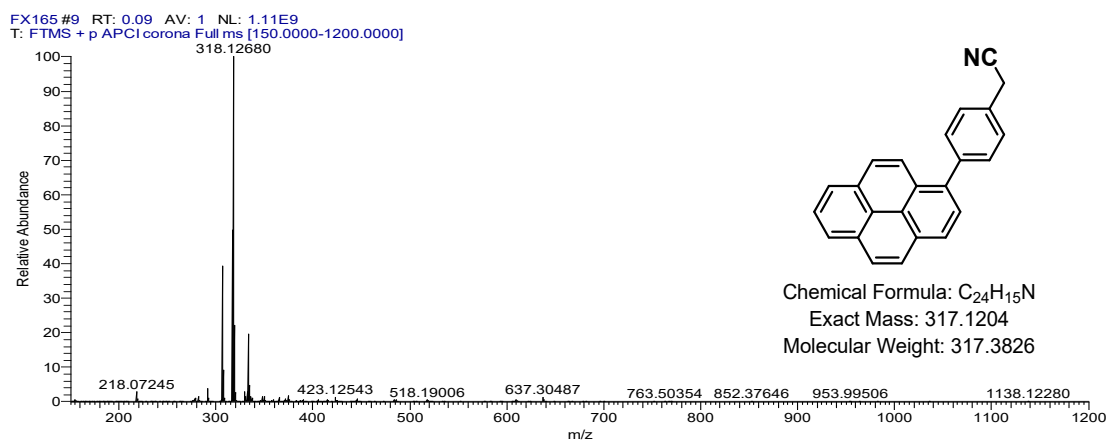


Figure S18 HRMS spectra of 1-(4-(pyren-1-yl)phenyl)acetonitrile (**2c**).

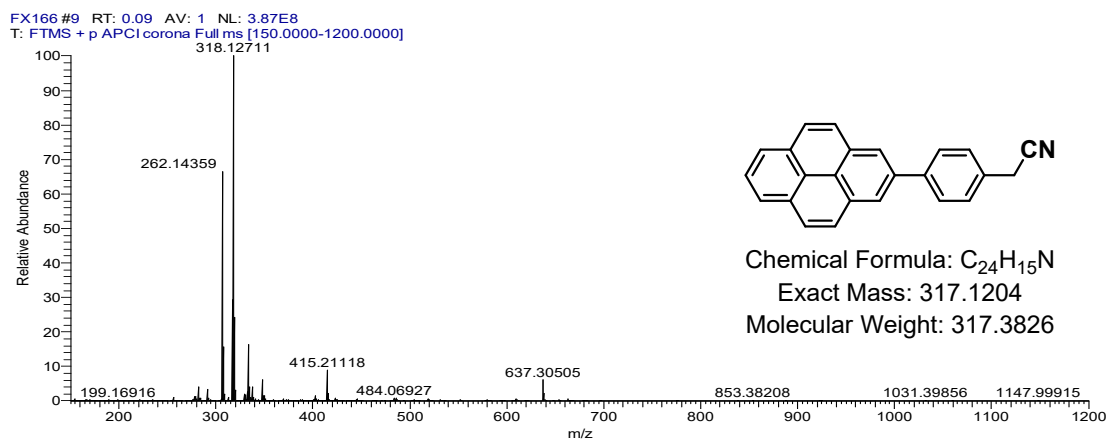
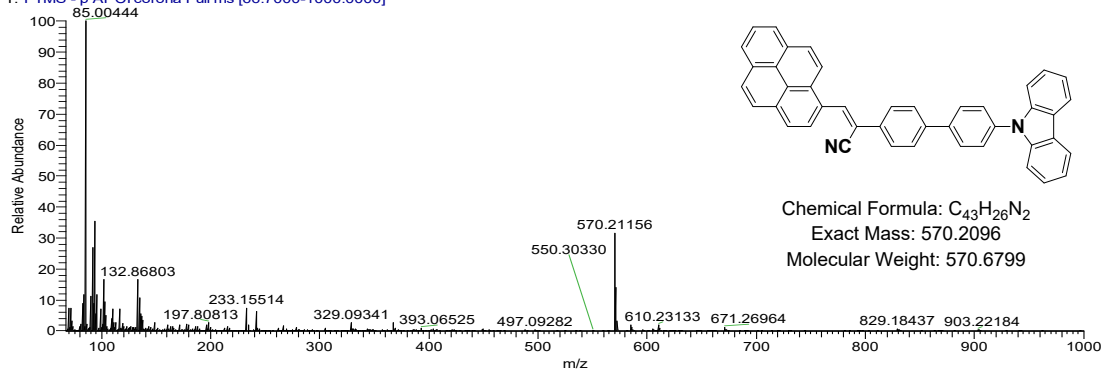


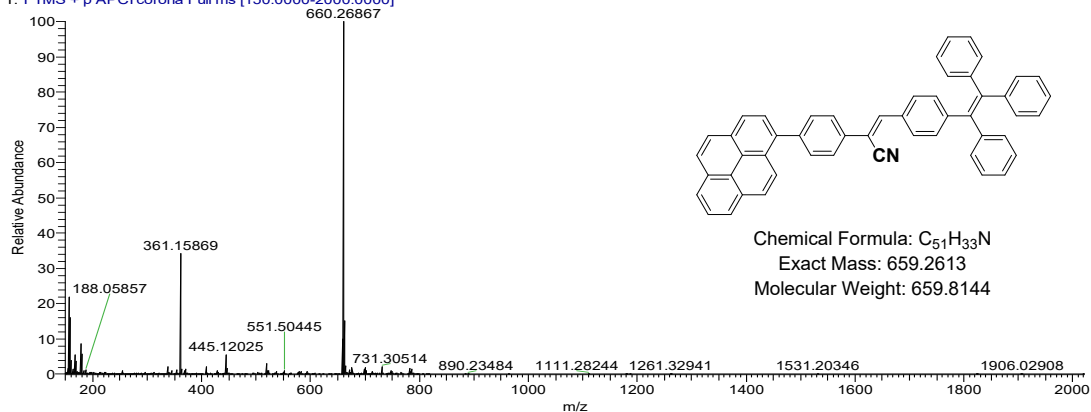
Figure S19 HRMS spectra of 2-(4-(pyren-1-yl)phenyl)acetonitrile (**2d**).

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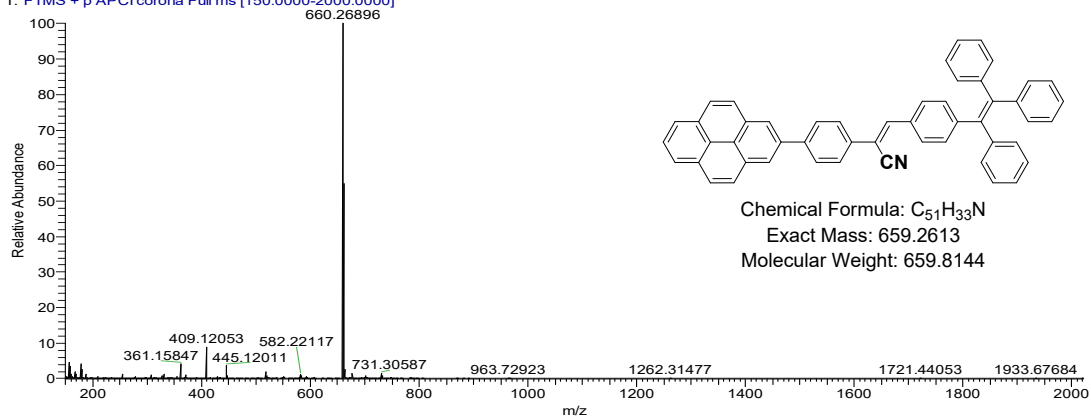
**Figure S20** HRMS spectra of (Z)-2-(4'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)-3-(pyren-1-yl) acrylonitrile (**Py-2Ph-Cz**).

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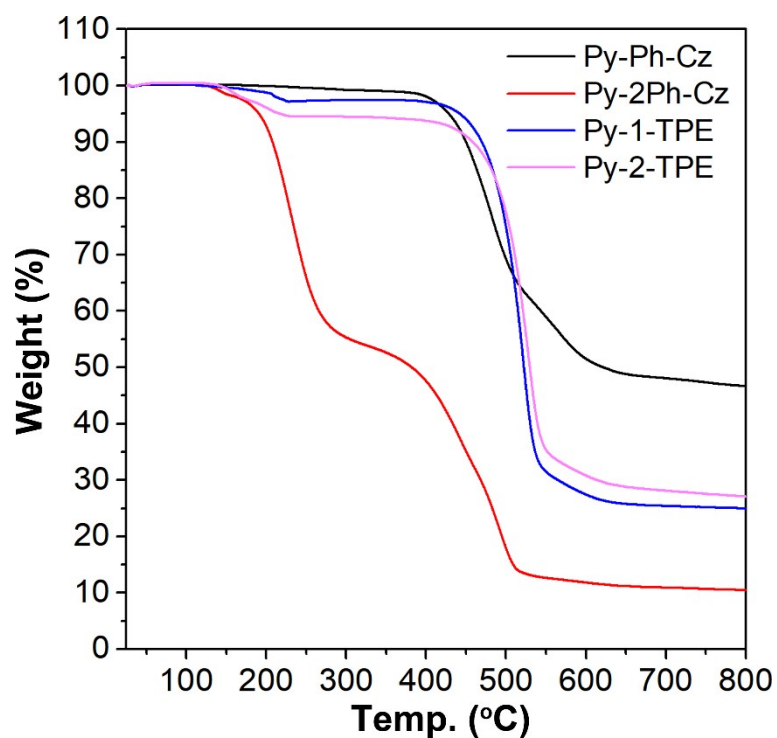
**Figure S21** HRMS spectra of (Z)-2-(4-(pyren-1-yl)phenyl)-3-(4-(1,2,2-triphenylvinyl)phenyl)acrylonitrile (**Py-1-TPE**).

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T: FTMS + p APCI corona Full ms [150.0000-2000.0000]

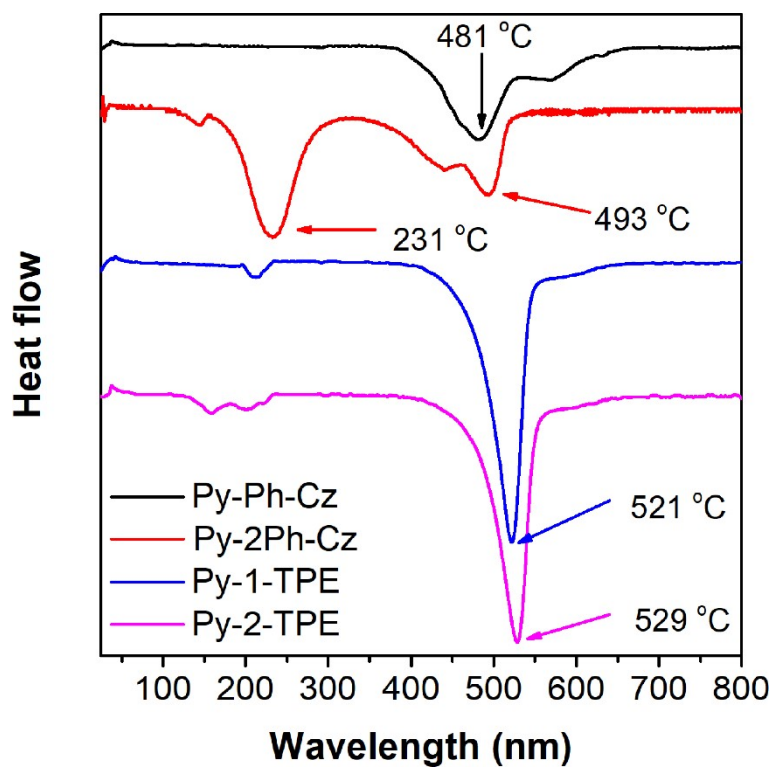


**Figure S22** HRMS spectra of (Z)-2-(4-(pyren-2-yl)phenyl)-3-(4-(1,2,2-triphenylvinyl)phenyl)acrylonitrile (**Py-2-TPE**).

### Thermal Properties



**Figure S23** TGA curve of the four pyrene-based compounds under N<sub>2</sub> atmosphere.



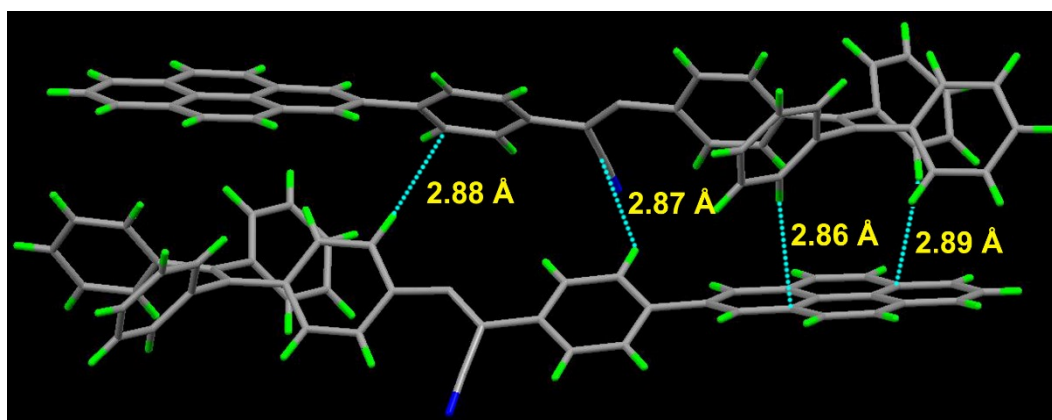
**Figure S24** TG curve of four pyrene-based compounds under N<sub>2</sub> atmosphere.

## Single Crystal X-ray diffraction analysis

**Table S1.** Crystal data for pyrene-based AIEgens **Py-1-TPE** and **Py-2-TPE**.

Parameter	Py-1-TPE	Py-2-TPE
Empirical formula	C <sub>51</sub> H <sub>33</sub> N, 1.38(H <sub>2</sub> O)	4(C <sub>51</sub> H <sub>33</sub> N), 3(H <sub>2</sub> O)
Formula weight [g mol <sup>-1</sup> ]	684.15	2689.14
Crystal system	monoclinic	monoclinic
Space group	C 1 2/c 1	C 1 2/c 1
<i>a</i> [Å]	49.1462(19)	51.028(4)
<i>b</i> [Å]	9.3232(3)	9.1493(5)
<i>c</i> [Å]	16.8479(7)	16.5315(12)
$\beta$ [°]	101.840(2)	99.496(3)
Volume [Å <sup>3</sup> ]	7555.5(5)	7612.3(9)
<i>Z</i>	8	2
Density, calcd [Mg m <sup>-3</sup> ]	1.203	1.173
Temperature [K]	300(2)	300(2)
Unique reflns	4041	4185
Obsd reflns [ <i>I</i> >2 $\sigma$ ( <i>I</i> )]	0.1044	0.0797
Parameters	496	500
<i>R</i> <sub>int</sub>	0.1617	0.1267
<i>R</i> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.2497	0.2297
<i>wR</i> [ <i>I</i> >2 $\sigma$ ( <i>I</i> )] <sup>b</sup>	0.2785	0.2554
GOF on <i>F</i> <sup>2</sup>	1.064	0.998

<sup>a</sup> Conventional *R* on  $F_{\text{hkl}}$ :  $\Sigma||F_o| - |F_c||/\Sigma|F_o|$ . <sup>b</sup> Weighted *R* on  $|F_{\text{hkl}}|^2$ :  $\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$



**Figure S25** The packing structure of **Py-2-TPE** by C-H $\cdots$  $\pi$  interaction.

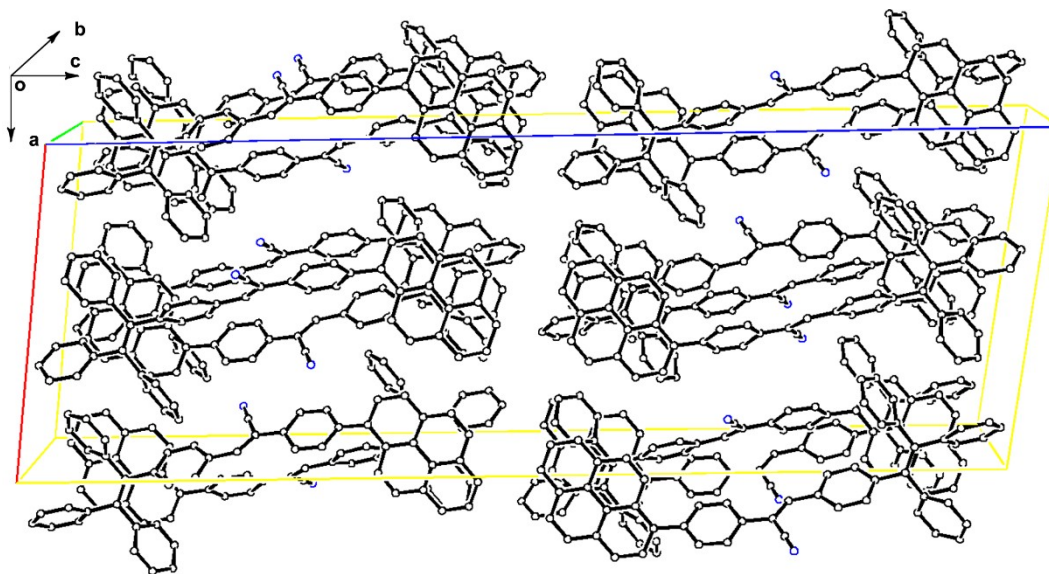


Figure S26 The packing structure of **Py-1-TPE** in unit cell.

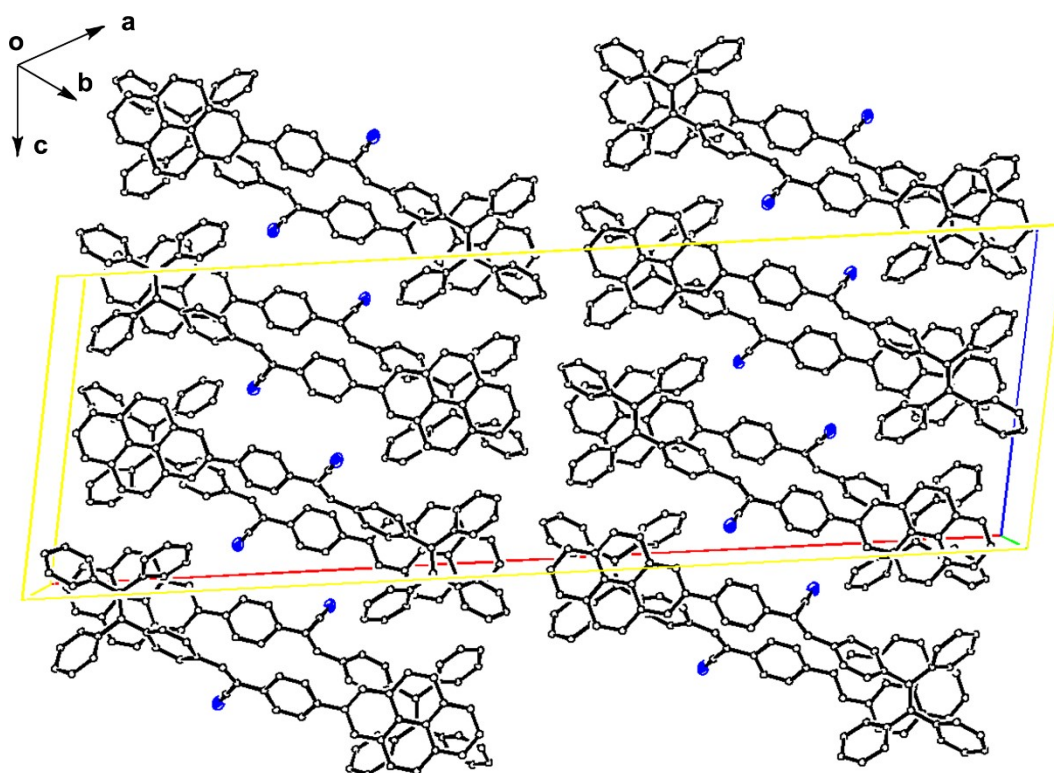
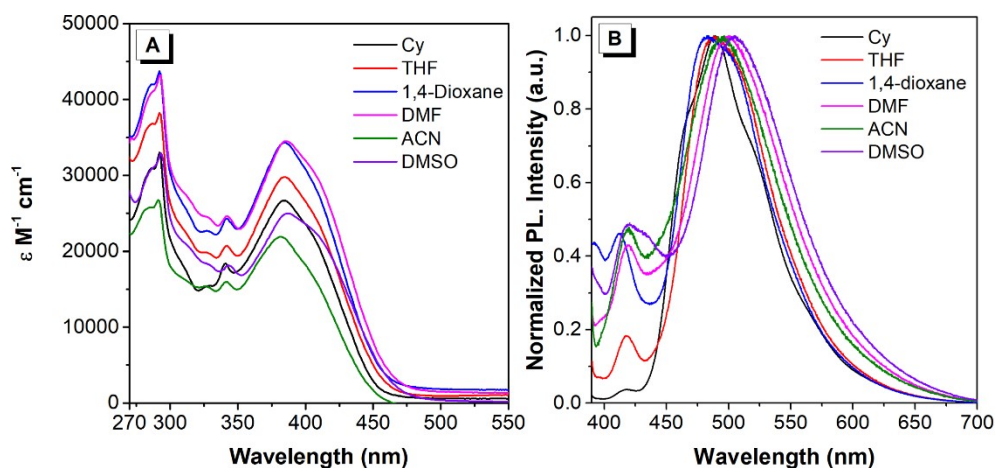
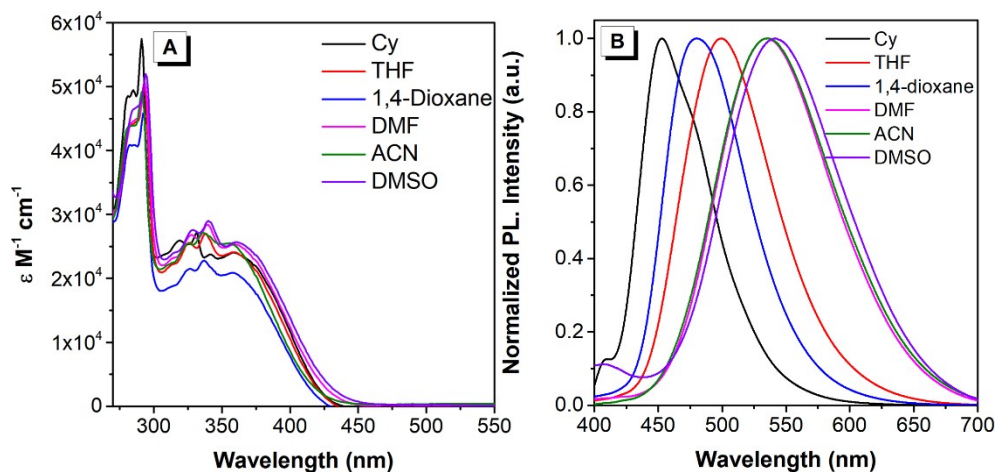


Figure S27 The packing structure of **Py-2-TPE** in unit cell.

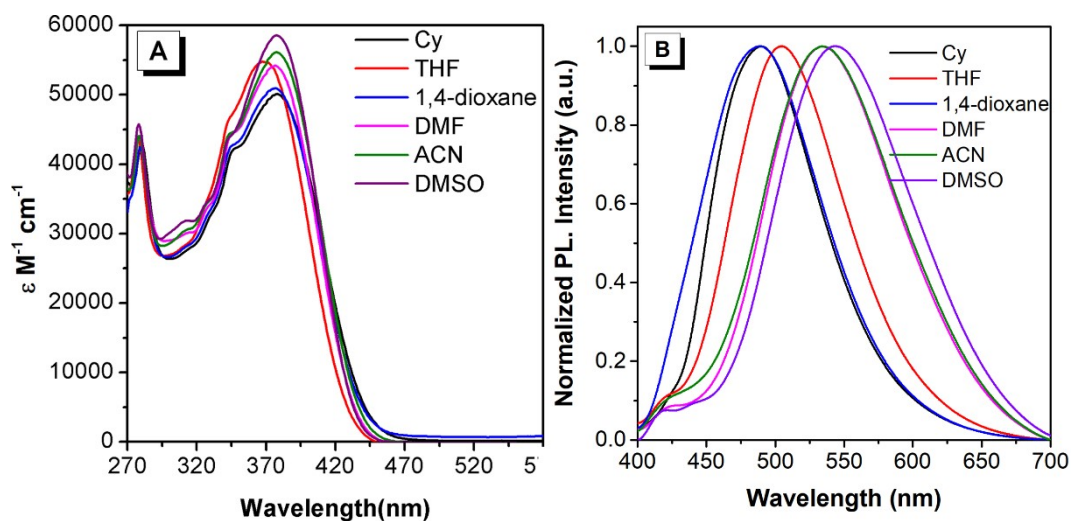
## Photophysical properties



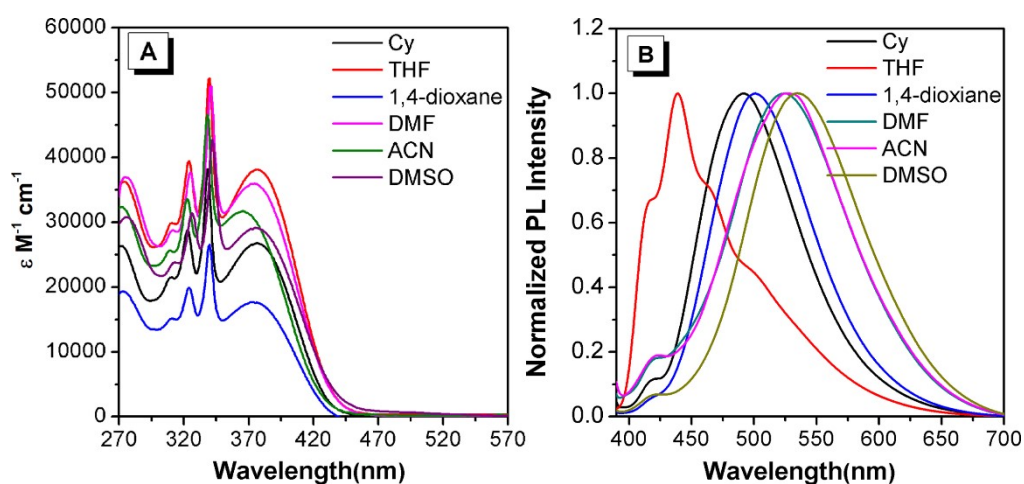
**Figure S28** (A) UV-vis and (B) fluorescence spectra of the compound **Py-2Ph-Cz** recorded in different solvents at  $10^{-5} \text{ M}$  and  $25 \text{ }^\circ\text{C}$  ( $\lambda_{\text{ex}} = 371 \text{ nm}$ ).



**Figure S29** (A) UV-vis and (B) fluorescence spectra of the compound **Py-Ph-Cz** recorded in different solvents at  $10^{-5} \text{ M}$  and  $25 \text{ }^\circ\text{C}$ .



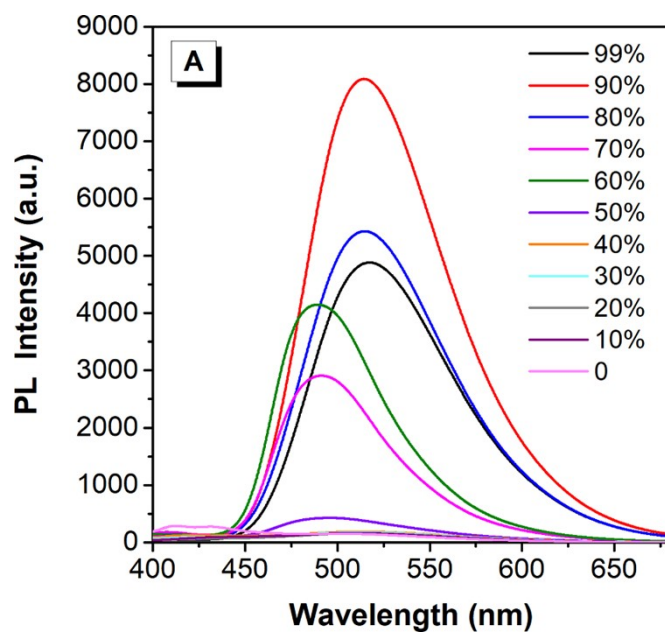
**Figure S30** (A) UV-vis and (B) fluorescence spectra of the compound **Py-1-TPE** recorded in different solvents at  $10^{-5} \text{ M}$  and  $25 \text{ }^\circ\text{C}$



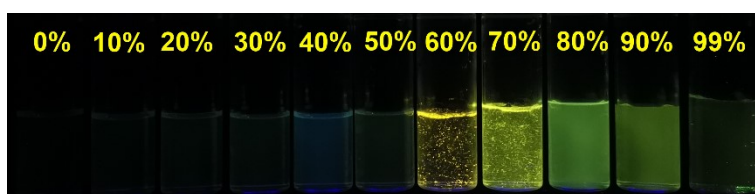
**Figure S31** (A) UV-vis and (B) fluorescence spectra of the compound **Py-2-TPE** recorded in different solvents at  $10^{-5}$  M and  $25\text{ }^{\circ}\text{C}$

**Table S2** Emission spectroscopic data for **3a-d** in different solvents at  $25\text{ }^{\circ}\text{C}$ .

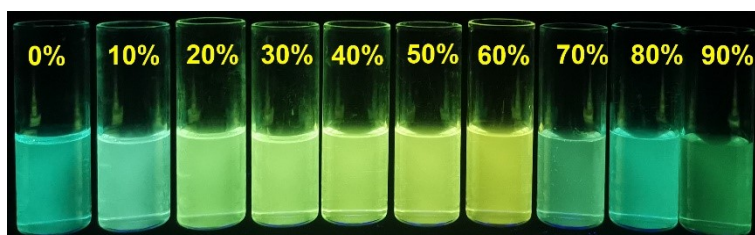
Comp.	Cy	THF	1,4-dioxane	DMF	ACN	DMSO
	$\lambda_{\text{abs}} / \lambda_{\text{em}}$ (nm)	$\lambda_{\text{abs}} / \lambda_{\text{em}}$ (nm)	$\lambda_{\text{abs}} / \lambda_{\text{em}}$ (nm)	$\lambda_{\text{abs}} / \lambda_{\text{em}}$ (nm)	$\lambda_{\text{abs}} / \lambda_{\text{em}}$ (nm)	$\lambda_{\text{abs}} / \lambda_{\text{em}}$ (nm)
<b>Py-2Ph-Cz</b>	385/488	385/488	385/483	386/500	384/496	387/505
<b>Py-Ph-Cz</b>	359/453	359/499	359/479	360/535	357/534	361/541
<b>Py-1-TPE</b>	379/489	379/498	379/488	379/534	368/534	379/542
<b>Py-2-TPE</b>	378/492	378/438, 496	374/501	374/523	365/527	376/533



**Figure S32** PL spectra of **Py-2-TPE** in THF/water mixtures with different water fractions ( $f_w$ ).



**Figure S33** Fluorescent photograph of **Py-2Ph-Cz** in THF/water mixtures ( $f_w$  from 0% to 99%) taken under UV irradiation ( $\lambda_{ex} = 365$  nm).

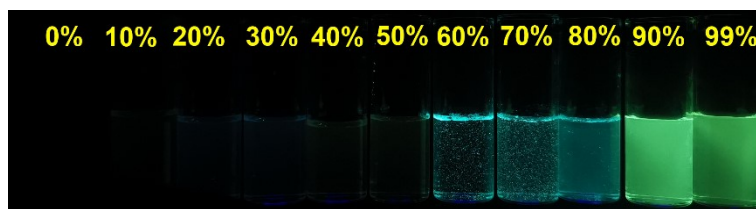


**Figure S34** Fluorescent photograph of **Py-Ph-Cz** in THF/water mixtures ( $f_w$  from 0% to 90%) taken under UV irradiation ( $\lambda_{ex} = 365$  nm).

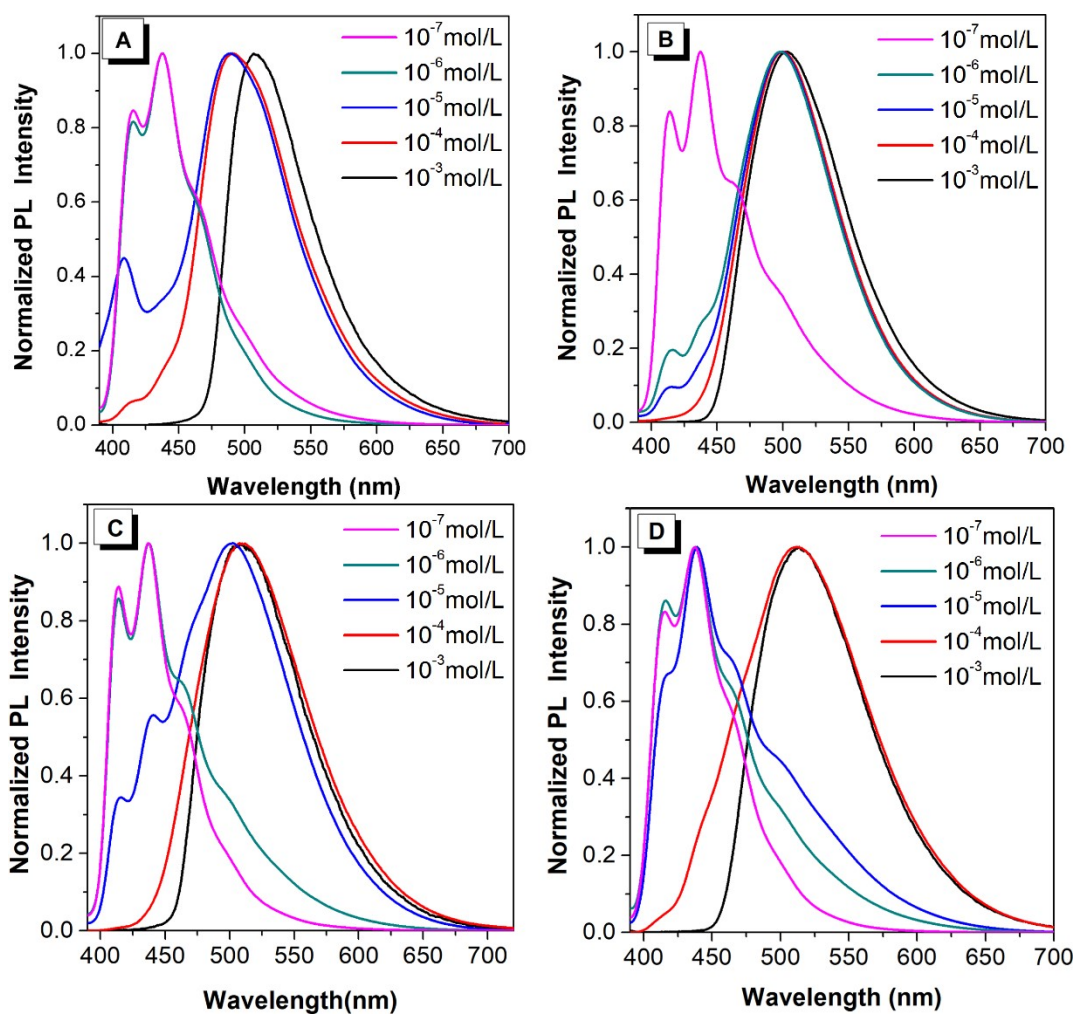


**Figure S35** Fluorescent photograph of **Py-1-TPE** in THF/water mixtures ( $f_w$  from 0% to 99%) taken under UV irradiation ( $\lambda_{ex} = 365$  nm)





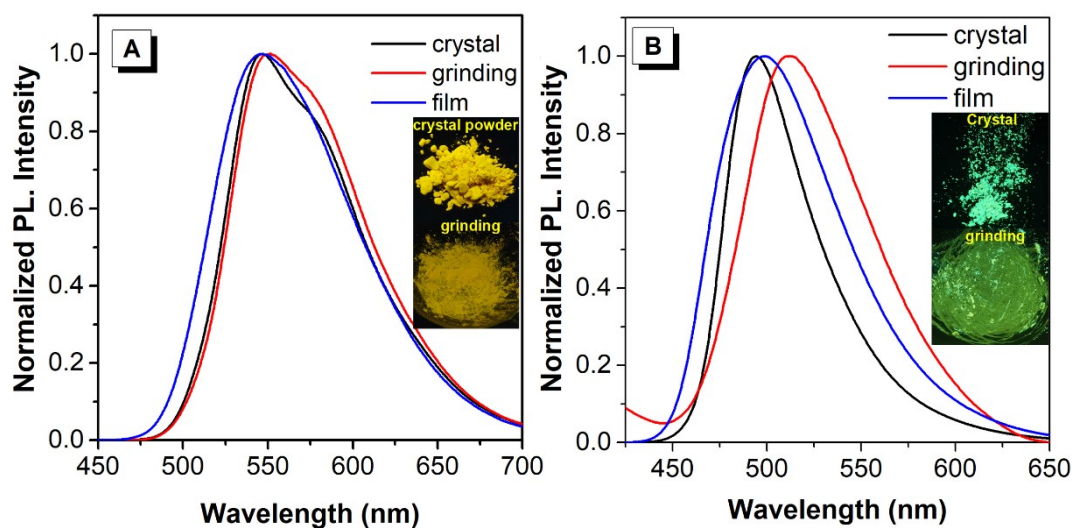
**Figure S36** Fluorescent photograph of **Py-2-TPE** in THF/water mixtures ( $f_w$  from 0% to 99%) taken under UV irradiation ( $\lambda_{ex} = 365$  nm)



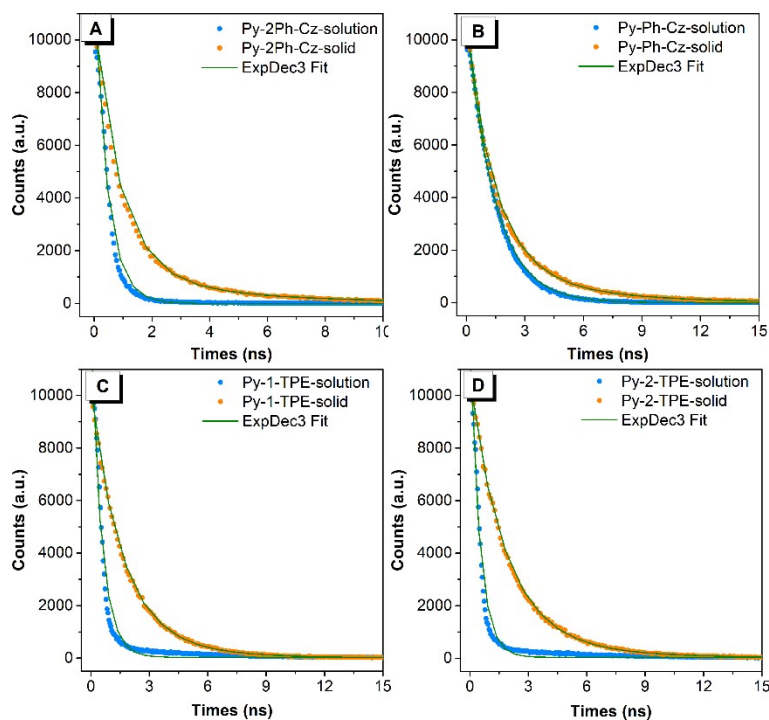
**Figure S37** PL spectra of (A) **Py-2Ph-Cz**, (B) **Py-Ph-Cz**, (C) **Py-1-TPE** and (D) **Py-2-TPE** in different concentration in THF solvents at 25 °C.

**Table S3** Emission spectroscopic data for Pyrene-based AIEgens in different concentration in THF solvents at 25 °C.

Concentration (mol/L)	Py-2Ph-Cz $\lambda_{\text{max em}}$ (nm)	Py-Ph-Cz $\lambda_{\text{max em}}$ (nm)	Py-1-TPE $\lambda_{\text{max em}}$ (nm)	Py-2-TPE $\lambda_{\text{max em}}$ (nm)
$10^{-7}$	438	438	438	438
$10^{-6}$	438	499	438	438
$10^{-5}$	488	497	498	438
$10^{-4}$	491	501	508	512
$10^{-3}$	508	502	508	513



**Figure S38** The PL spectrum of (A) Py-2Ph-Cz and (B) Py-2-TPE before and after grinding, Inset: the images of compounds in the crystalline state and after grinding taken under 365 nm UV light.



**Figure S39** decay plots of A) **Py-2Ph-Cz**, (B) **Py-2Ph-Cz** C) **Py-1-TPE** and **Py-2-TPE** in solution and in solid state.

**Table S4** Emission spectroscopic data for Py-2Ph-Cz , Py-Ph-Cz, Py-1-TPE and Py-2-TPE in different states at 25 °C.

	<b>Py-Ph-Cz</b>	<b>Py-2Ph-Cz</b>	<b>Py-1-TPE</b>	<b>Py-2-TPE</b>
	$\lambda_{\max \text{ em}}$ (nm)	$\lambda_{\max \text{ em}}$ (nm)	$\lambda_{\max \text{ em}}$ (nm)	$\lambda_{\max \text{ em}}$ (nm)
In THF ( $10^{-5}$ )	438	499	502	439
crystal	546	518	494	494
grinding	550	512	512	512
film	547	514	514	498

## The Powder X-ray Diffraction (PXRD) Analysis

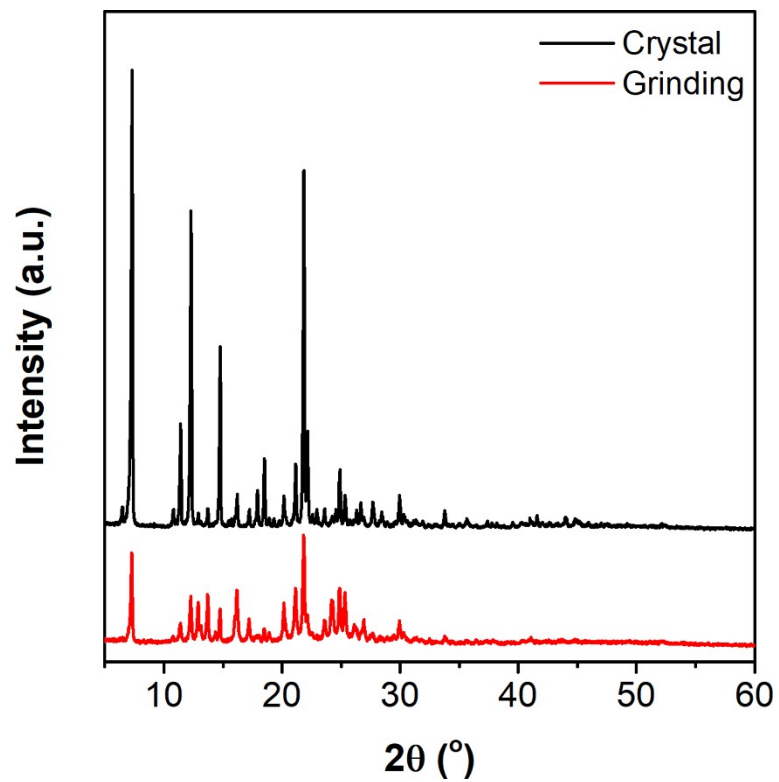
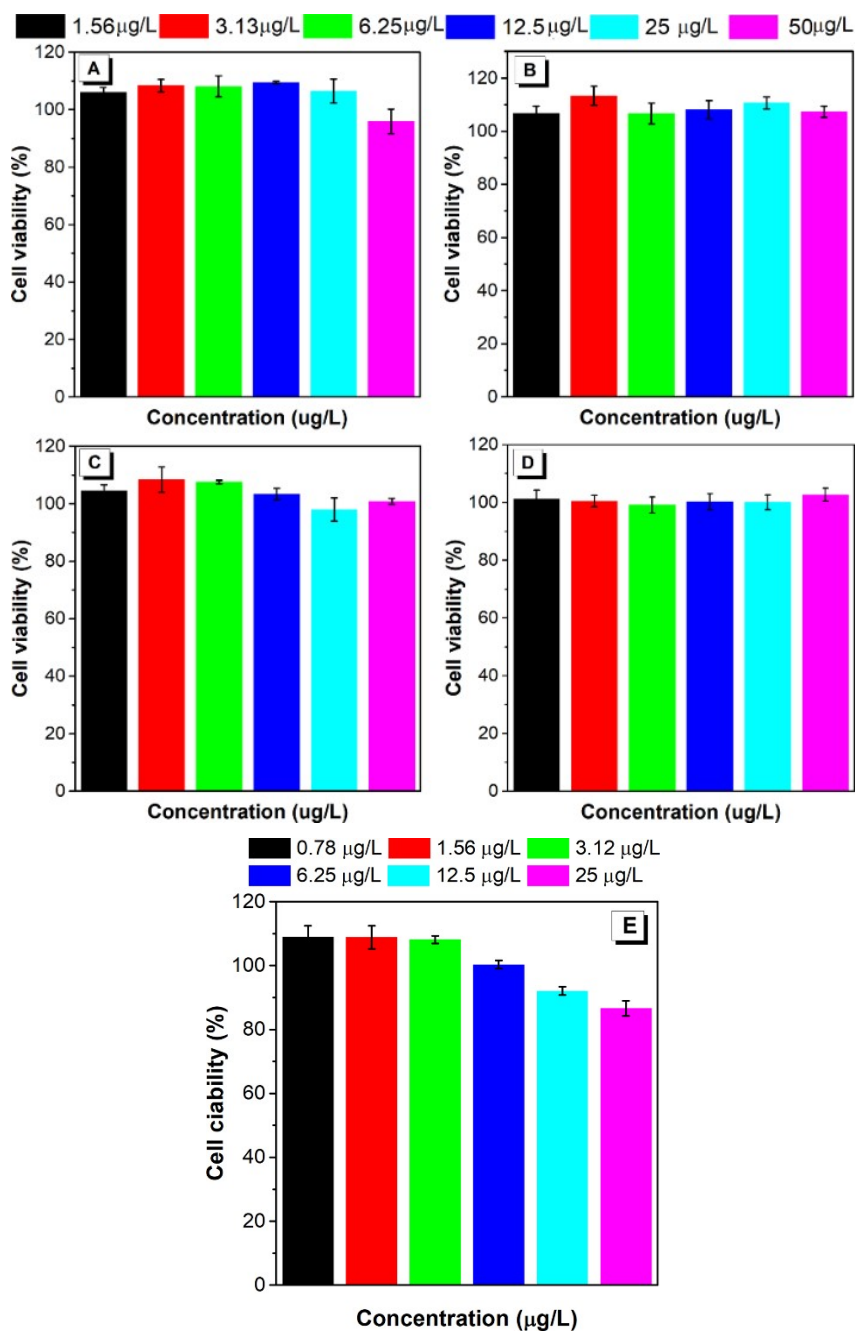


Figure S40 Powder XRD diffractograms of Py-2Ph-Cz in different states.

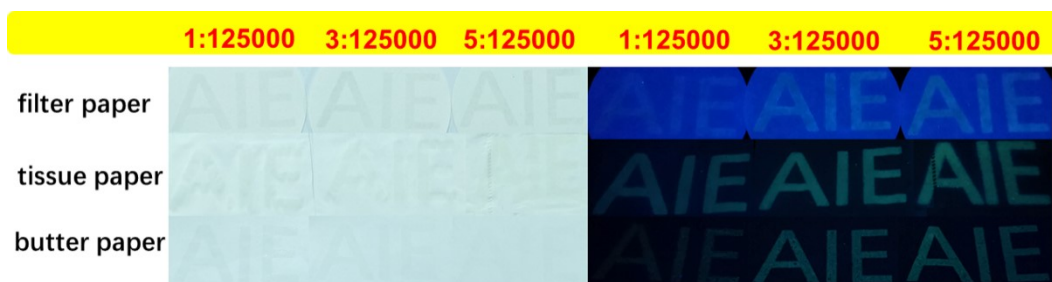
## Cell Cytotoxicity



**Figure S41** CCK8 assay of L cell, L-929 treated with different concentrations of (A) Py-2Ph-Cz, (B) Py-Ph-Cz, (C) Py-1-TPE, (D) Py-2-TPE and pyrene.

The L-929 cell viability decreased to 86% when treated with an unsubstituted pyrene compound of 25 $\mu$ M after 24h incubation, which suggested that the pyrene exhibits greater toxicity *versus* pyrene-based AIEgens (Figure S41E)

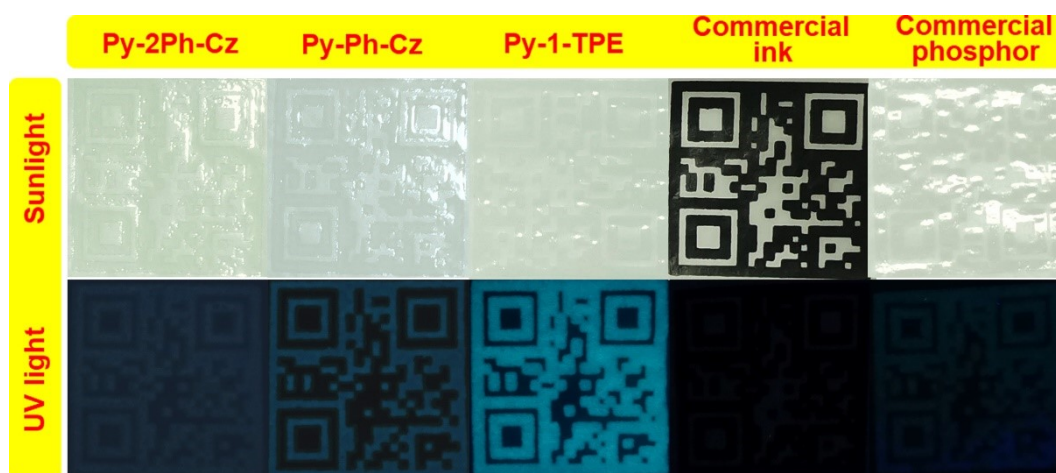
## Printing Pattern



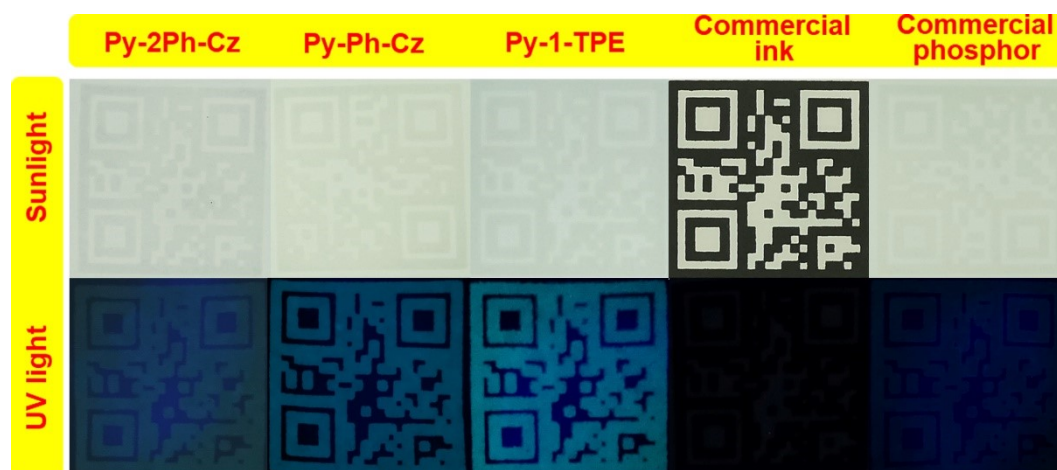
**Figure S42.** Digital photographs of letter “AIE” pattern printing on filter paper, butter paper and tissue paper using pyrene-based AIEgens **Py-2Ph-Cz** as fluorescence ink with different concentration under sunlight (Left) and UV irradiation of 365 nm (Right). (under UV irradiation: Aperture: f/1.8, Exposure time: 1/40s, ISO speed: ISO-400)



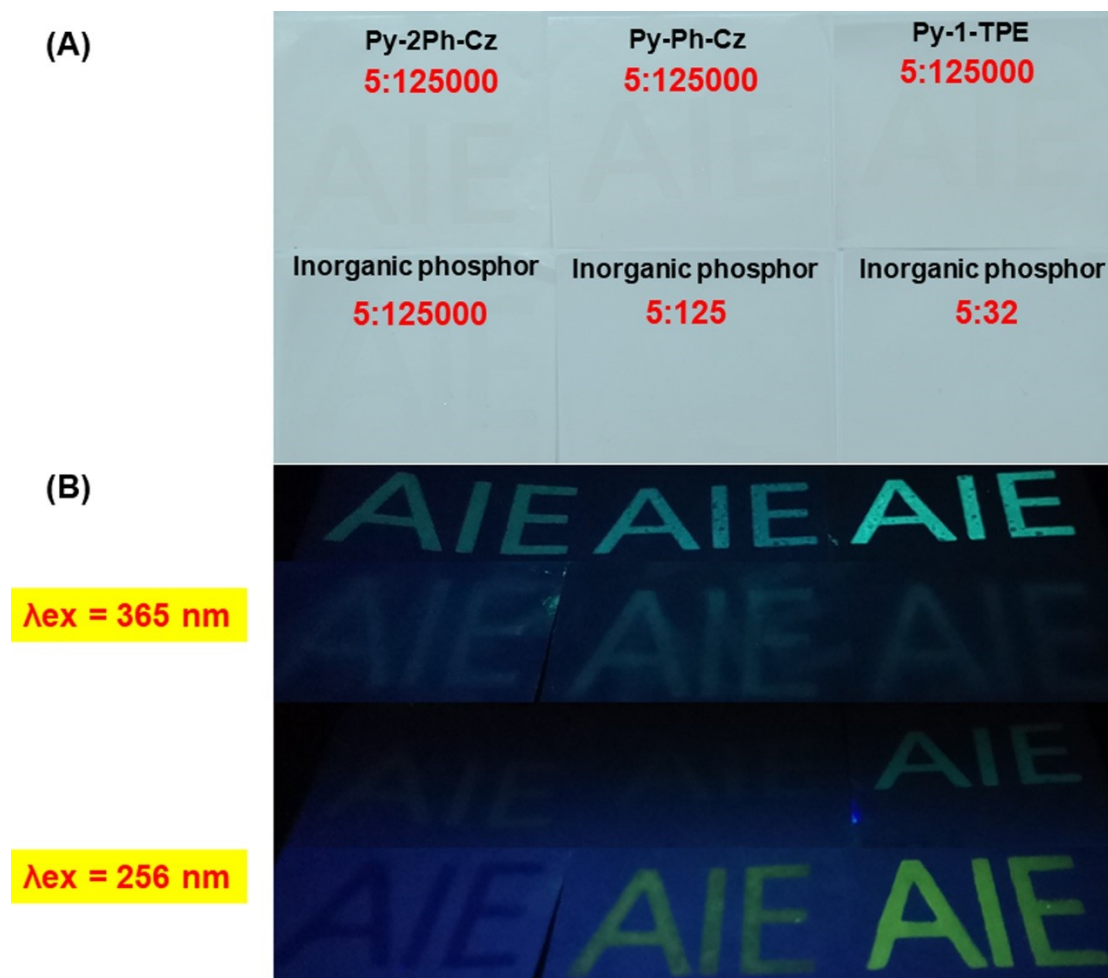
**Figure S43.** Digital photographs of letter “AIE” pattern printing on filter paper, butter paper and tissue paper using pyrene-based AIEgens **Py-Ph-Cz** as fluorescence ink with different concentration under sunlight (Left) and UV irradiation of 365 nm (Right). (under UV irradiation: Aperture: f/1.8, Exposure time: 1/40s, ISO speed: ISO-400)



**Figure S44.** Digital photographs of QR code pattern printing on butter paper using pyrene-based AIEgens fluorescence ink or commercial ink ( $\text{Weight}_{\text{AIEgens or inorganic phosphor}}:\text{Weight}_{\text{EpoxyLite+curing agent}} = 5:125000$ ) under sunlight, (right) under UV irradiation ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ). (under UV irradiation: Aperture: f/1.8, Exposure time: 1/40s, ISO speed: ISO-400).



**Figure S45.** Digital photographs of QR code pattern printing on filter paper using pyrene-based AIEgens fluorescence ink or commercial ink ( $\text{Weight}_{\text{AIEgens or inorganic phosphor}}:\text{Weight}_{\text{EpoxyLite+curing agent}} = 5:125000$ ) under sunlight, (right) under UV irradiation ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ). (under UV irradiation: Aperture: f/1.8, Exposure time: 1/40s, ISO speed: ISO-400).

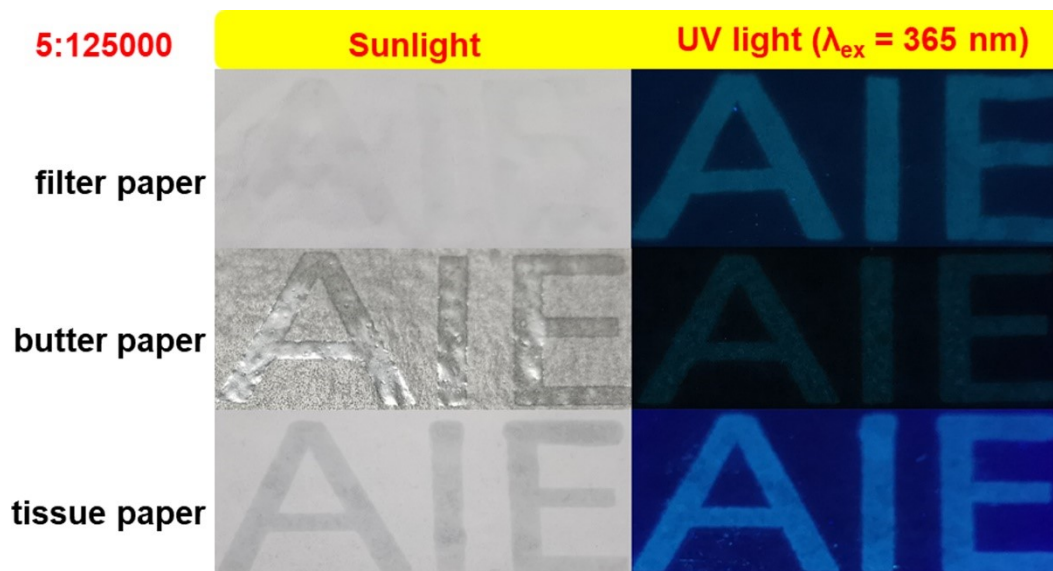


**Figure S46.** Digital photographs of letter “AIE” pattern printing on butter paper using pyrene-based AIEgens fluorescence ink at 0.004 wt% ( $\text{Weight}_{\text{AIEgens}}:\text{Weight}_{\text{EpoxyLite+curing agent}} = 5:125000$ ), or commercial phosphor with different concentration at  $\text{Weight}_{\text{inorganic phosphor}}:\text{Weight}_{\text{EpoxyLite+curing agent}} = 5:125000$ , 5:125 and 5:32, respectively. (A) under sunlight under and (B) under UV irradiation of 365 nm and 256 nm. (under UV irradiation: Aperture: f/1.8, Exposure time: 1/40s, ISO speed: ISO-400)

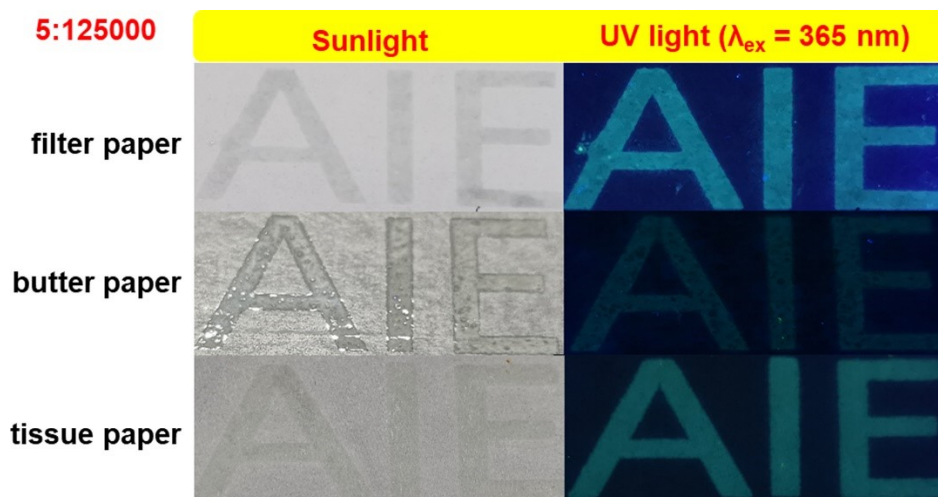




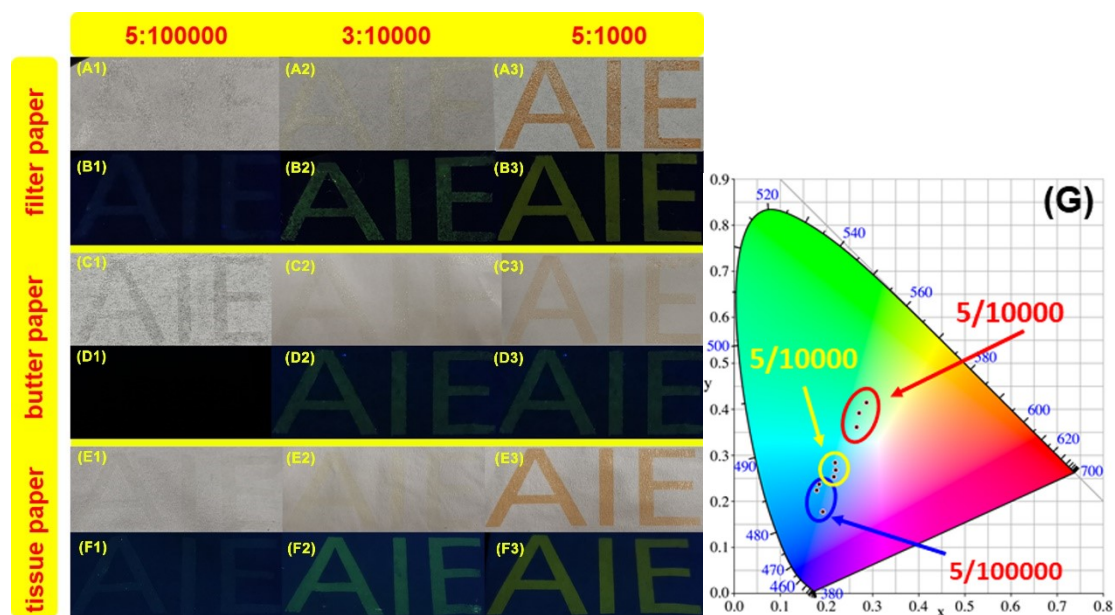
**Figure S47.** Digital photographs of letter “AIE” pattern printing on the white wall using three pyrene-based AIEgens as fluorescence ink with different concentration under a UV irradiation of 365 nm. (under UV irradiation: Aperture: f/1.8, Exposure time: 1/40s, ISO speed: ISO-400)



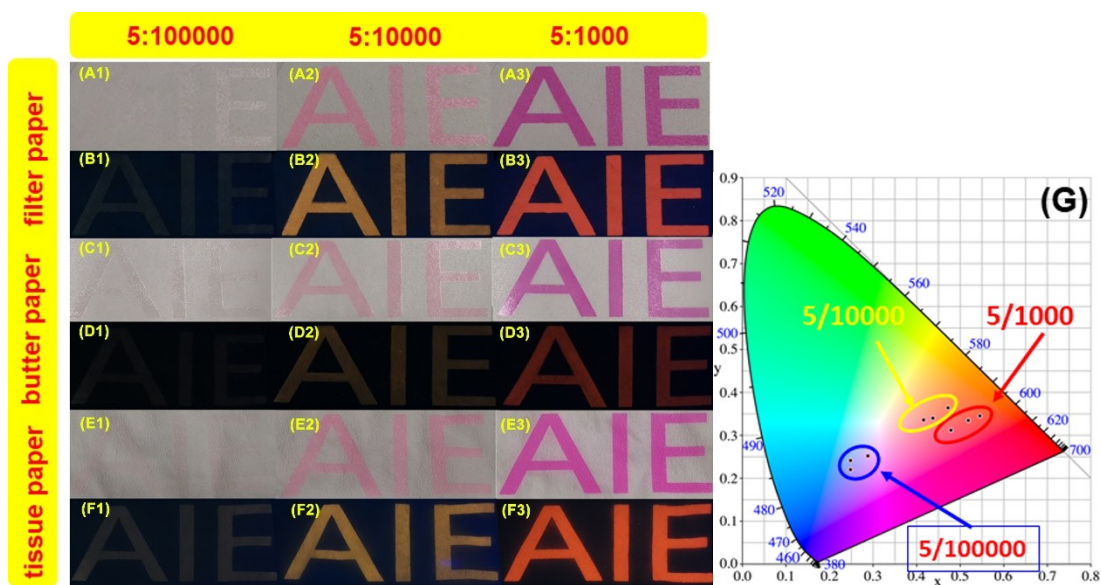
**Figure S48.** Digital photographs of letter “AIE” pattern printing on the butter paper using fluorescein as fluorescence ink at 0.004 wt% ( $\text{Weight}_{\text{fluorescein}}:\text{Weight}_{\text{Epoxyite+curing agent}} = 5:125000$ ), (left) under sunlight under and (right) under UV irradiation of 365 nm. (under UV irradiation: Aperture: f/1.8, Exposure time: 1/40s, ISO speed: ISO-400)



**Figure S49.** Digital photographs of letter “AIE” pattern printing on the butter paper using RhB as fluorescence ink at 0.004 wt% ( $\text{Weight}_{\text{fluorescein}}:\text{Weight}_{\text{Epoxyite+curing agent}} = 5:125000$ ), (left) under sunlight under and (right) under UV irradiation of 365 nm. (under UV irradiation: Aperture: f/1.8, Exposure time: 1/40s, ISO speed: ISO-400)

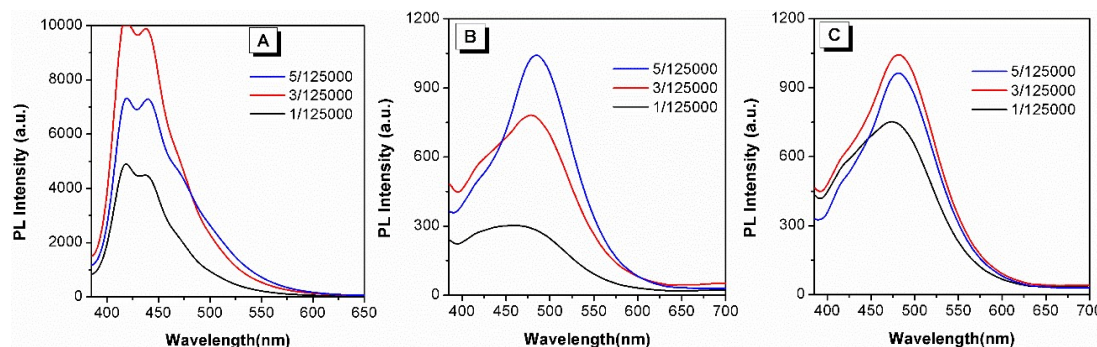


**Figure S50.** Digital photographs of letter “AIE” pattern printing on filter paper, butter paper and tissue paper using fluorescein as fluorescence ink with different concentration ( $\text{Weight}_{\text{AIEgens}}:\text{Weight}_{\text{pp}} = 5:100000, 5:10000$  and  $5:1000$ , respectively) under sunlight (A, C and E) and UV irradiation of 365 nm (B, D, and F). (under UV irradiation: Aperture: f/1.8, Exposure time: 1/40s, ISO speed: ISO-400) (G) CIE 1931 chromaticity diagram. the color coordinates for the corresponding concentration.

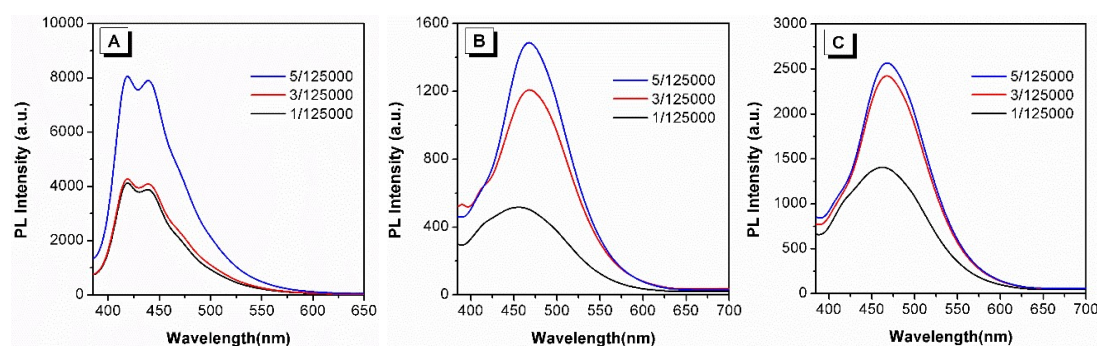


**Figure S51.** Digital photographs of letter “AIE” pattern printing on filter paper, butter paper and tissue paper using **RhB** as fluorescence ink with different concentration ( $\text{Weight}_{\text{AIEgens}}:\text{Weight}_{\text{pp}} = 5:100000, 5:10000$  and  $5:1000$ , respectively) under sunlight (A, C and E) and UV irradiation of 365 nm (B, D, and F). (under UV irradiation: Aperture: f/1.8, Exposure time: 1/40s, ISO speed: ISO-400) (G) CIE 1931 chromaticity diagram. the color coordinates for the corresponding concentration.

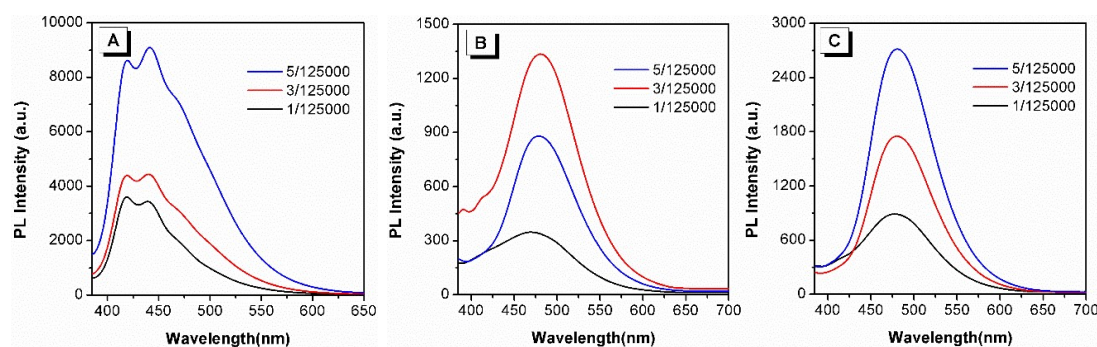
## Emission spectra of the printing pattern



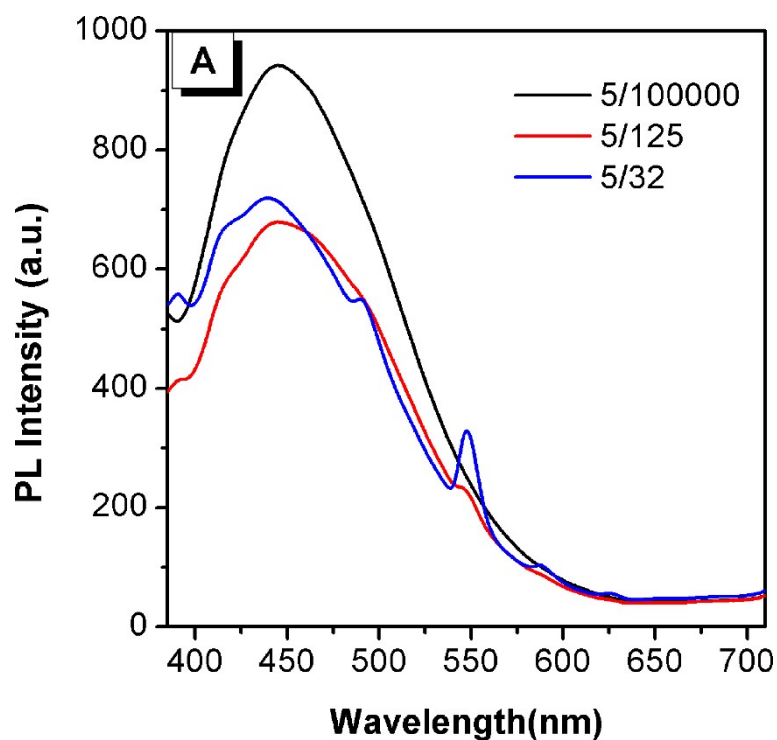
**Figure S52** PL spectra of letter “AIE” pattern printing on (A) filter paper, (B) butter paper and (C) tissue paper using **Py-2Ph-Cz** as fluorescence ink ( $\lambda_{\text{ex}} = 365$  nm).



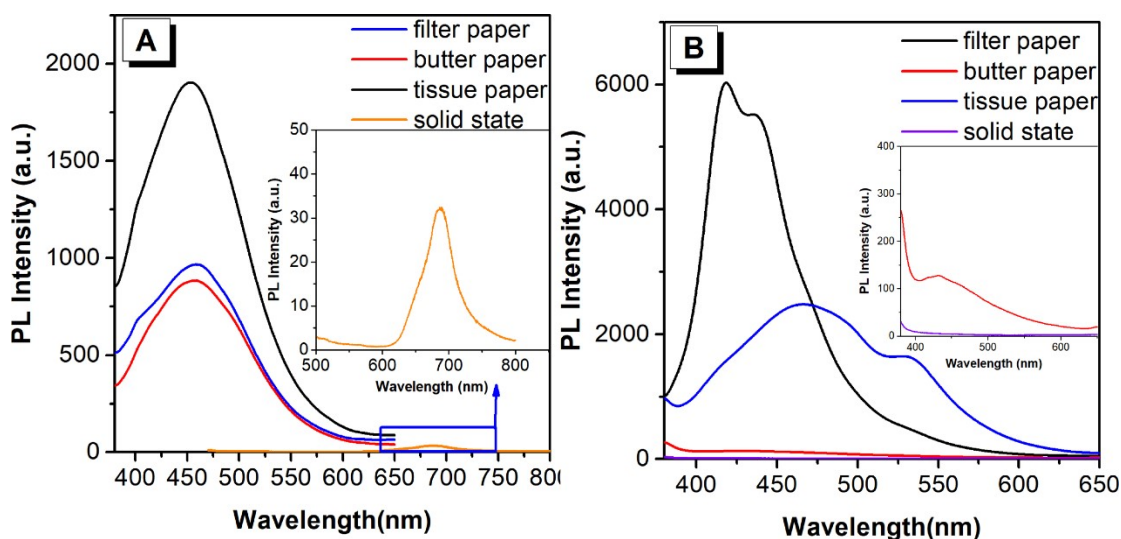
**Figure S53** PL spectra of letter “AIE” pattern printing on (A) filter paper, (B) butter paper and (C) tissue paper using **Py-Ph-Cz** as fluorescence ink ( $\lambda_{\text{ex}} = 365$  nm).



**Figure S54** PL spectra of letter “AIE” pattern printing on (A) filter paper, (B) butter paper and (C) tissue paper using **Py-1-TPE** as fluorescence ink ( $\lambda_{\text{ex}} = 365$  nm).



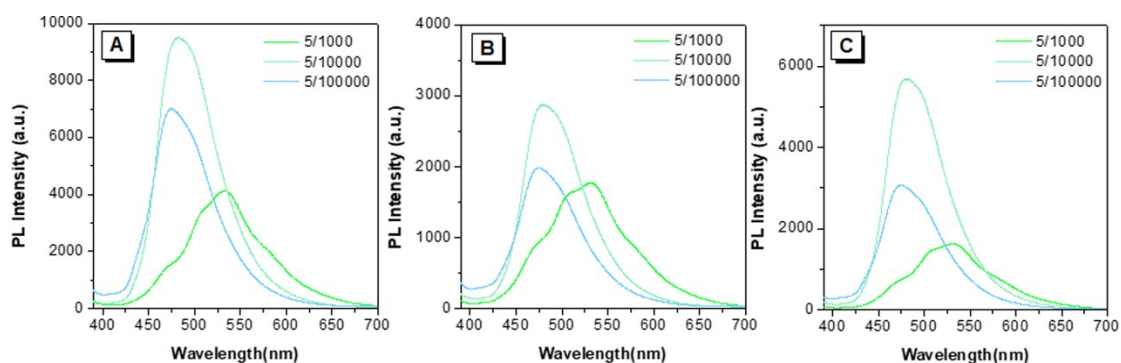
**Figure S55** PL spectra of letter “AIE” pattern printing on butter paper using commercial phosphor as fluorescence ink with different concentration at  $\text{Weight}_{\text{inorganic phosphor}}:\text{Weight}_{\text{Epoxy\textit{lite}+curing agent}} = 5:125000, 5:125$  and  $5:32$  ( $\lambda_{\text{ex}} = 365$  nm).



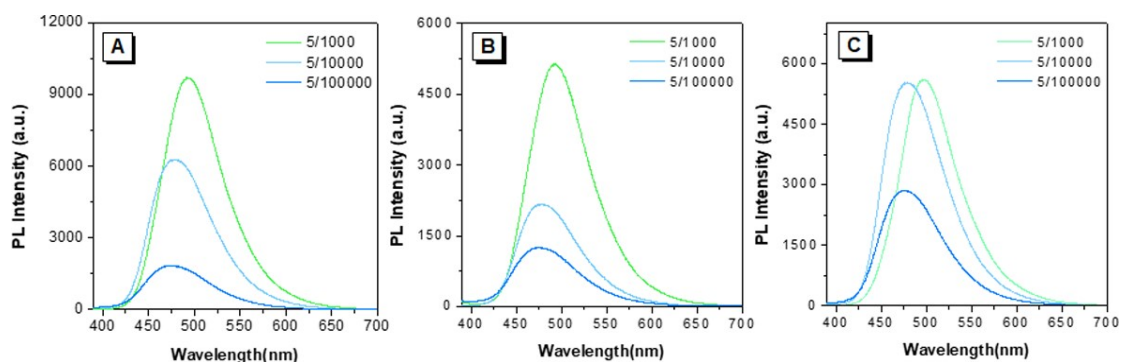
**Figure S56** PL spectra of letter “AIE” pattern printing on butter paper using (A) RhB (B) fluorescein as fluorescence ink with different concentration at  $\text{Weight}_{\text{inorganic phosphor}}:\text{Weight}_{\text{Epoxy\textit{lite}+curing agent}} = 5:125000$  ( $\lambda_{\text{ex}} = 365$  nm), due to the ACQ effect, the fluorescein didn’t show any emission in solid state.

**Table S5** Emission spectroscopic data using **Py-2Ph-Cz** , **Py-Ph-Cz**, **Py-1-TPE**, **RhB** and fluorescein as fluorescence ink in epoxy resin on three printing substrates.

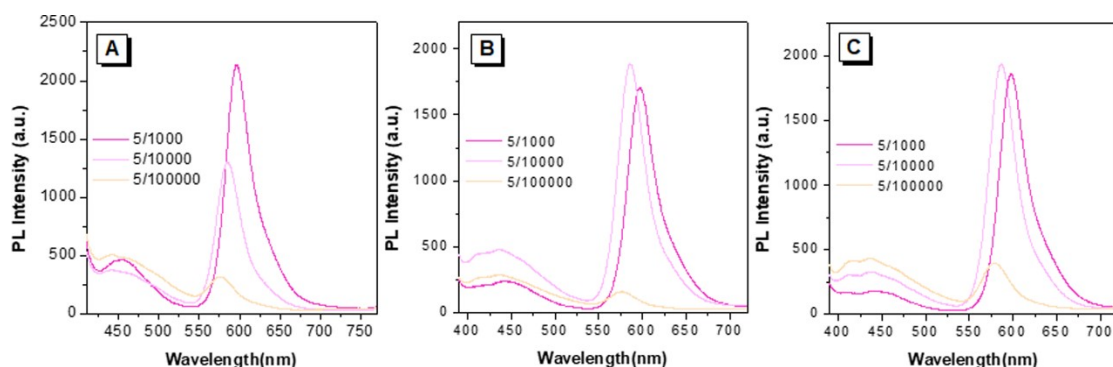
Concentration Wt <sub>AIEgens</sub> /Wt <sub>Epoxy+ curing agent</sub>	substrates	Py-2Ph-Cz	Py-Ph-Cz	Py-1-TPE	RhB	fluorescein
		$\lambda_{\max \text{ em}} \text{ (nm)}$	$\lambda_{\max \text{ em}} \text{ (nm)}$	$\lambda_{\max \text{ em}} \text{ (nm)}$	$\lambda_{\max \text{ em}} \text{ (nm)}$	
5/125000	filter paper	418/440	418/438	418/443	459	417
	butter paper	486	483	479	456	430
	tissue paper	482	467	481	452	466
3/125000	filter paper	418/438	418/438	418/441		
	butter paper	480	480	483		
	tissue paper	482	467	481		
1/125000	filter paper	418/437	418/438	418/437		
	butter paper	467	461	470		
	tissue paper	474	462	478		
Solid state		547	514	514	688	Non emission



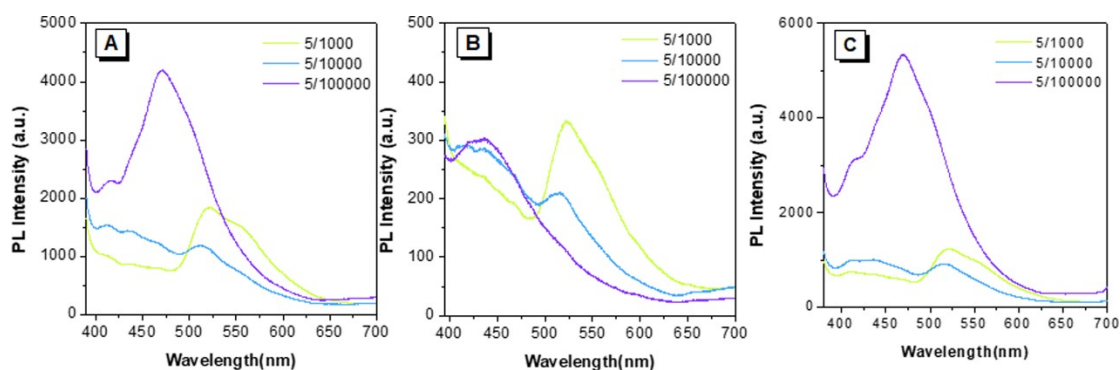
**Figure S57** PL spectra of letter “AIE” pattern printing printing on (A) filter paper, (B) butter paper and (C) tissue paper using **Py-2Ph-Cz** as fluorescence ink ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ) in PP resin



**Figure S58** PL spectra of letter “AIE” pattern printing printing on (A) filter paper, (B) butter paper and (C) tissue paper using **Py-1-TPE** as fluorescence ink ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ) in PP resin.



**Figure S59.** PL spectra of letter “AIE” pattern printing printing on (A) filter paper, (B) butter paper and (C) tissue paper using **RhB** as fluorescence ink ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ) in PP resin.



**Figure S60.** PL spectra of letter “AIE” pattern printing printing on (A) filter paper, (B) butter paper and (C) tissue paper using fluorescein as fluorescence ink ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ) in PP resin.

**Table S6** Emission spectroscopic data using **Py-2Ph-Cz**, **Py-1-TPE**, fluorescein and RhB as fluorescence ink in PP resin on three printing substrates.

Concentration $W_{\text{t fluorescence}}/W_{\text{t PP}}$	substrates	Py-2Ph-Cz	Py-1-TPE	RhB	fluorescein
		$\lambda_{\text{max em}}$ (nm)	$\lambda_{\text{max em}}$ (nm)	$\lambda_{\text{max em}}$ (nm)	$\lambda_{\text{max em}}$ (nm)
5/1000	filter paper	532	492	454, 597	521
	butter paper	531	491	440, 597	522
	tissue paper	530	497	441, 597	523
5/10000	filter paper	483	479	442, 584	411, 510
	butter paper	479	471	437, 586	420, 515
	tissue paper	482	477	438, 586	436, 516
5/100000	filter paper	474	475	441, 575	471
	butter paper	474	473	435, 576	434
	tissue paper	474	474	438, 580	470