



## Supplementary Materials

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### 1. Synthesis and calculation

#### Materials and Methods

**General:** All operations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. The starting materials 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-pyrazole, 1,2,4,5-tetrabromobenzene, 1,3,6,8-tetrabromopyrene, 1,1,2,2-tetrakis(4-bromophenyl)ethane and other reagents were obtained as analytical grade from variety commercial providers and used without further purification.

**Measurements:** <sup>1</sup>H NMR and <sup>13</sup>C NMR experiments were performed on Bruker Avance DMX400. Elemental analyses (C, H, N) were carried out with a PECHN 2400 analyzer. Column chromatographic separations were carried out on silica gel (200-300 mesh).

#### Experimental Details

##### 1,2,4,5-tetra(1H-pyrazol-4-yl)benzene (1).

Compound 1 was synthesized via Suzuki coupling reaction. A mixture of n-Butanol/water (180 mL, 3:1 v/v) containing 1,2,4,5-tetrabromobenzene (1.5 g, 3.81 mmol), 1-(tetrahydro-pyran-2-yl)-4-pyrazoleboronic acid pinacol ester (8.0 g, 28.76 mmol), tetrakis(triphenylphosphine)palladium (0.66 g, 0.29 mmol) and potassium carbonate (3.90 g, 14.29 mmol) was heated at 75-80 °C under stirring for 72 h. The resulting white precipitate was filtered off, dried under vacuum and then purified by column chromatography using ethyl acetate/petroleum ether (15:1) as eluent. 1,2,4,5-tetra(1H-pyrazol-4-yl)benzene (1) was obtained by deprotecting 1,2,4,5-tetrakis(1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazol-4-yl)benzene in methanol (10 mL) and dichloromethane (20 mL) in the presence of 1 M HCl (5 mL) at room temperature. The product precipitated as a white solid which was filtered off and dried under vacuum (yield: 82%). <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO, 298 K) δ: 12.79 (s, 4H), 7.56 (s, 4H), 7.36 (s, 2H), 7.36 (s, 4H). <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-DMSO, 298 K) δ: 138.55, 131.778, 130.37, 127.58, 120.65. Elem. Anal. Calcd. for C<sub>18</sub>H<sub>14</sub>N<sub>8</sub>: C, 63.15; H, 4.12; N, 32.73%. Found: C, 63.64; H, 4.02; N, 32.65%.

##### 1,3,6,8-tetra(1H-pyrazol-4-yl)pyrene (2).

Compound 2 was synthesized by performing a Suzuki coupling reaction. A mixture of n-Butanol/water (300 mL, 3:1 v/v) containing 1,3,6,8-tetrabromopyrene (3.94 g, 7.62 mmol), 1-(tetrahydro-pyran-2-yl)-4-pyrazoleboronic acid pinacol ester (8.0 g, 28.76 mmol), tetrakis(triphenylphosphine)palladium (0.66 g, 0.29 mmol) and potassium carbonate (3.90 g, 14.29 mmol) was heated at 75-80 °C under stirring for 72 h. The resulting blackish green precipitate was filtered off, dried under vacuum and then purified by column chromatography using ethyl acetate/petroleum ether (15:1) as eluent. 1,3,6,8-tetra(1H-pyrazol-4-yl)pyrene (2), was obtained by deprotecting 1-(tetrahydro-pyran-2-yl)-4-pyrazoleboronic acid pinacol ester in methanol (5 mL) and dichloromethane (10 mL) in the presence of 1 M HCl (4 mL) at room temperature. The product precipitated as a green solid which was filtered off and dried under vacuum (yield: 72%). <sup>1</sup>H NMR (400 MHz, d<sub>6</sub>-DMSO, 298 K) δ: 13.16 (s, 1H), 8.42 (s, 4H), 8.16 (s, 8H), 8.11 (s, 2H). <sup>13</sup>C NMR (100 MHz, d<sub>6</sub>-DMSO, 298 K)

$\delta$ : 130.57, 129.18, 128.80, 127.20, 126.31, 125.02, 120.13. Elem. Anal. Calcd. For  $C_{28}H_{18}N_8$ : C, 72.09; H, 3.89; N, 24.02%. Found: C, 72.04; H, 3.90; N, 24.05%.

Synthesis of 1,1,2,2-tetrakis(4-(1H-pyrazol-4-yl)phenyl)ethene (3).

Compound 3 was synthesized by performing a Suzuki coupling reaction. A mixture of n-Butanol/water (300 mL, 3:1 v/v) containing 1,1,2,2-tetrakis(4-bromophenyl)ethene (4.94 g, 7.62 mmol), 1-(tetrahydro-pyran-2-yl)-4-pyrazoleboronic acid pinacol ester (8.0 g, 28.76 mmol), tetrakis(triphenylphosphine)palladium (0.66 g, 0.28 mmol) and potassium carbonate (3.90 g, 14.29 mmol) was heated at 75–80 °C under stirring for 72 h. The resulting baby blue precipitate was filtered off, dried under vacuum and then purified by column chromatography using ethyl acetate/petroleum ether (15:1). 1,1,2,2-tetrakis(4-(1H-pyrazol-4-yl)phenyl)ethene (3), was obtained by deprotecting 1,1,2,2-tetrakis(4-(1-(tetrahydro-2H-pyran-2-yl)-1H-pyrazol-4-yl)phenyl)ethane in methanol (10 mL) and dichloromethane (20 mL) in the presence of 1 M HCl (6 mL) at room temperature. The product precipitated as a yellowish solid which was filtered off and dried under vacuum (yield: 83%).  $^1H$  NMR (400 MHz,  $d_6$ -DMSO, 298 K)  $\delta$ : 12.90 (s, 1H), 8.14 (s, 1H), 7.86 (s, 1H), 7.40 (s, 1H), 6.99 (s, 1H).  $^{13}C$  NMR (100 MHz,  $d_6$ -DMSO, 298 K)  $\delta$ : 141.58, 140.04, 131.86, 131.49, 124.97, 121.27. Elem. Anal. Calcd. For  $C_{38}H_{28}N_8$ : C, 76.49; H, 4.73; N, 18.78 %. Found: C, 76.44; H, 4.72; N, 18.95%.

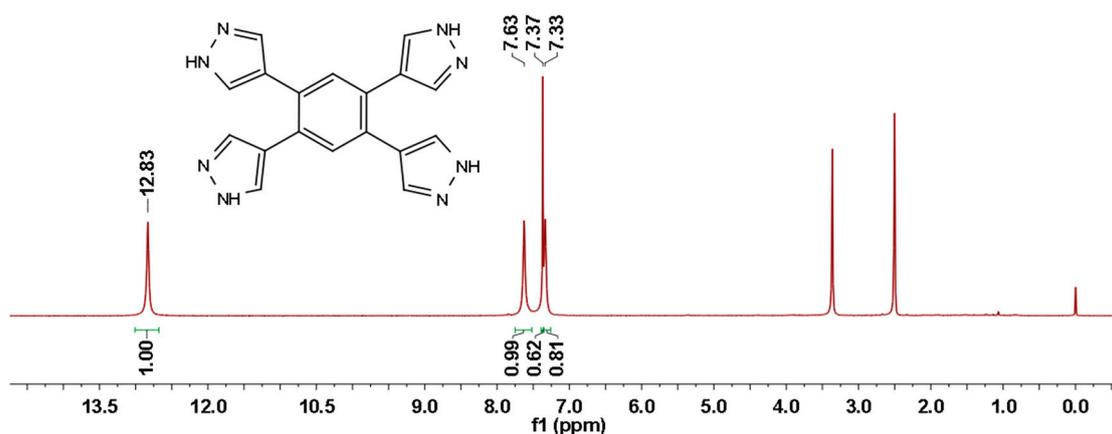


Figure S1.  $^1H$  NMR (400 MHz, 298 K) spectrum of compound 1 in  $d_6$ -DMSO.

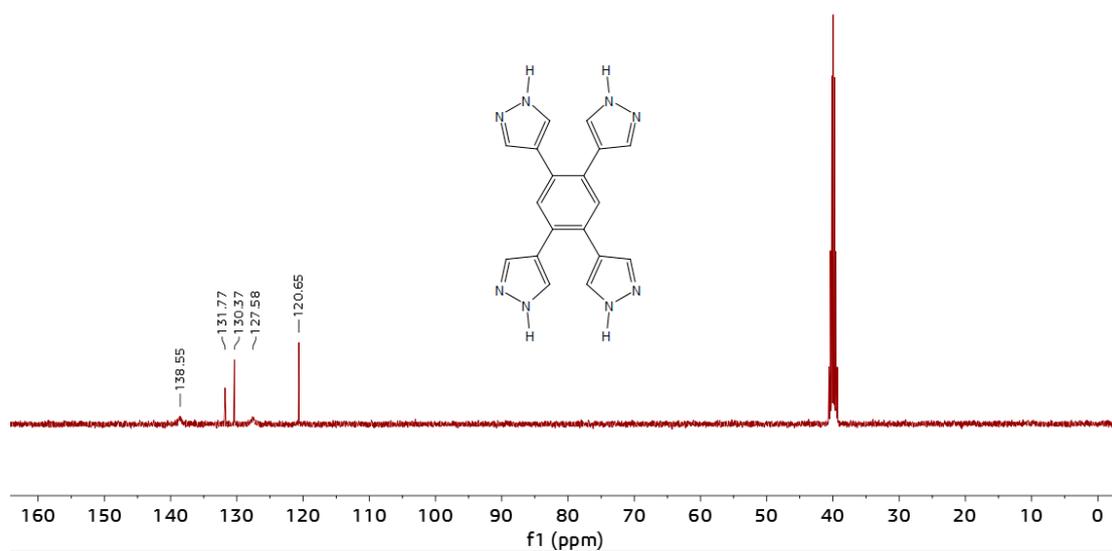


Figure S2. <sup>13</sup>C NMR (100 MHz, 298 K) spectrum of compound 1 in d<sub>6</sub>-DMSO.

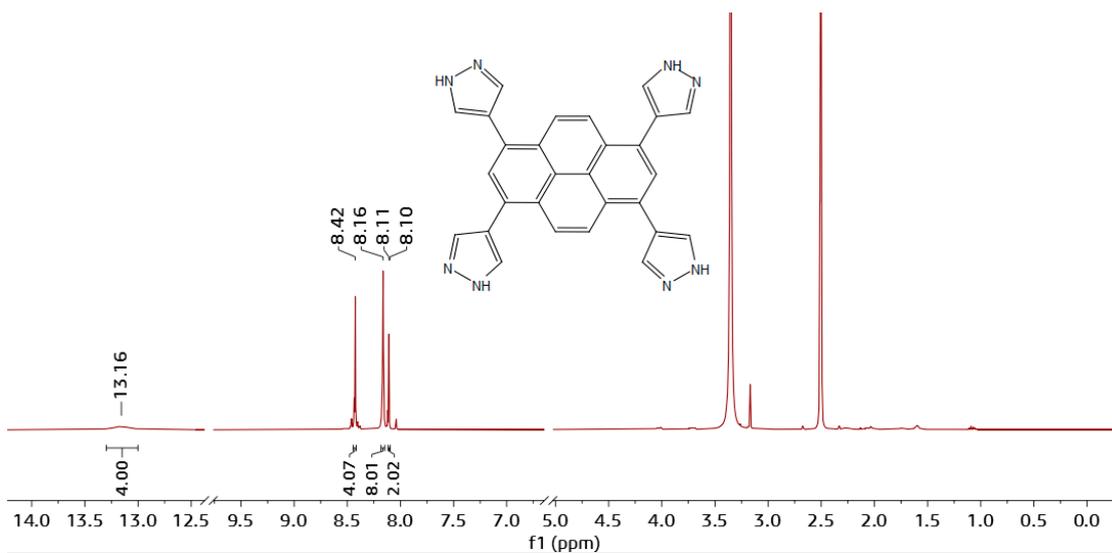


Figure S3. <sup>1</sup>H NMR (400 MHz, 298 K) spectrum of compound 2 in d<sub>6</sub>-DMSO.

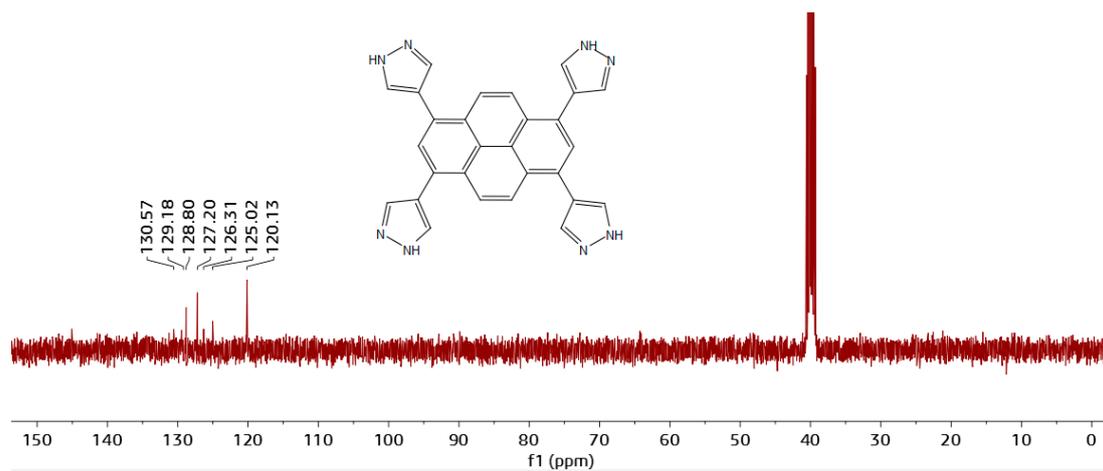


Figure S4. <sup>13</sup>C NMR (100 MHz, 298 K) spectrum of compound 2 in d<sub>6</sub>-DMSO.

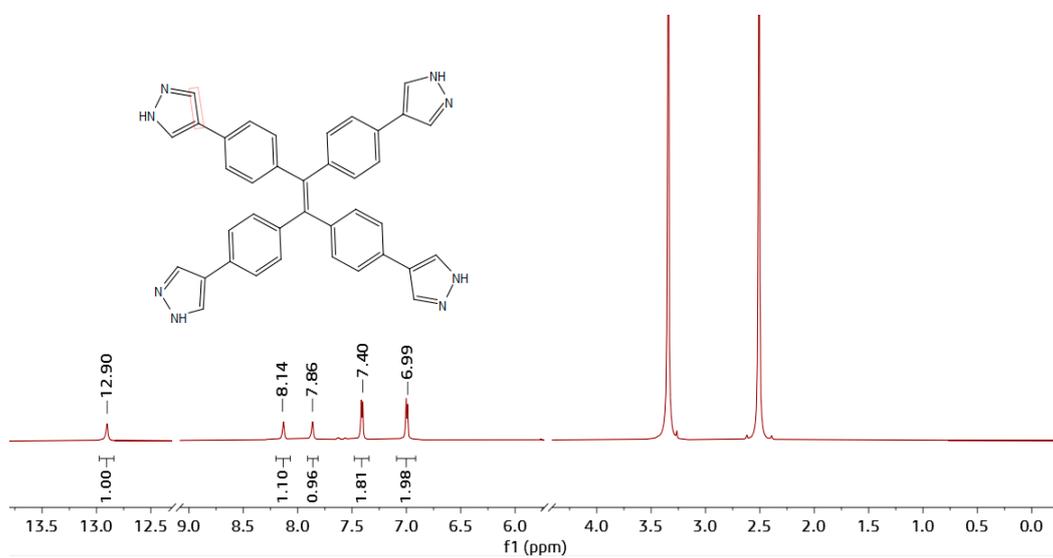


Figure S5. <sup>1</sup>H NMR (400 MHz, 298 K) spectrum of compound 3 in d<sub>6</sub>-DMSO.

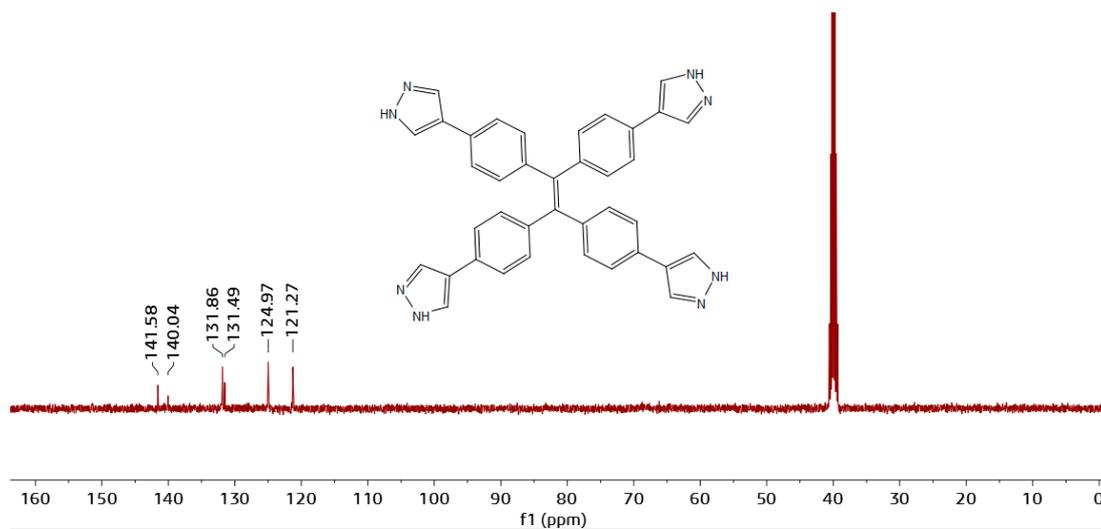


Figure S6.  $^{13}\text{C}$  NMR (100 MHz, 298 K) spectrum of **3** in  $d_6$ -DMSO.

## 2. X-ray diffraction measurement

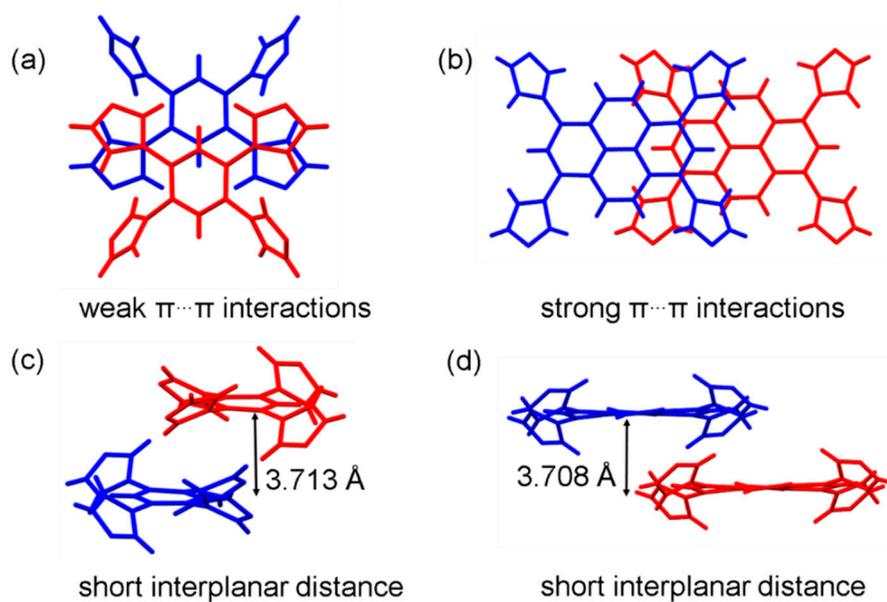
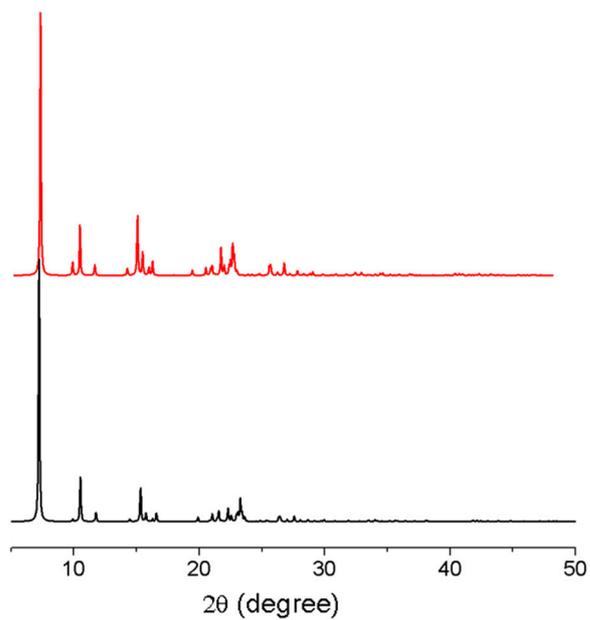


Figure S7.  $\pi \cdots \pi$  stacking between adjacent layers observed in structures of **HOF-1** and **HOF-2**.

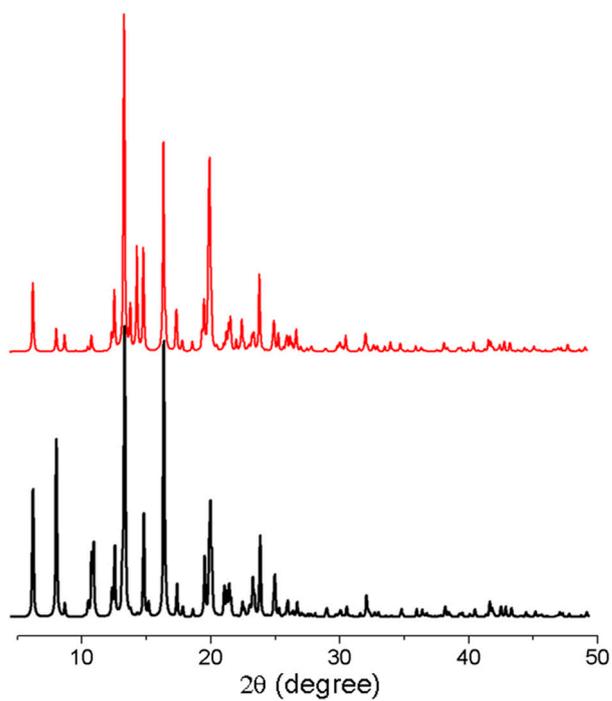
**Table S1.** Crystal data and structure refinement for **HOF-1**, **HOF-2**, and **HOF-3**.

	<b>HOF-1</b>	<b>HOF-2</b>	<b>HOF-3</b>
Formula	C <sub>9</sub> H <sub>7</sub> N <sub>4</sub>	C <sub>14</sub> H <sub>9</sub> N <sub>4</sub>	C <sub>38</sub> H <sub>28</sub> N <sub>8</sub>
Formula weight	171.19	233.25	596.68
Temperature/K	293(2)	293(2)	293(2)
Crystal system	monoclinic	orthorhombic	tetragonal
Space group	<i>C12/c1</i>	<i>Pnma</i>	<i>P-421c</i>
a/Å	18.2734(17)	20.7995(16)	15.2584(4)
b/Å	17.8342(19)	22.4471(18)	15.2584(4)
c/Å	8.3083(9)	7.0754(5)	19.5201(12)
α/°	90	90	90
β/°	113.162(3)	90	90
γ/°	90	90	90
Volume/Å <sup>3</sup>	2489.4(4)	3303.4(4)	4544.6(4)
Z	8	8	4
ρ <sub>calc</sub> /cm <sup>3</sup>	0.914	0.938	0.872
μ/mm <sup>-1</sup>	0.060	0.059	0.054
F(000)	712	968	1248
Crystal size/mm <sup>3</sup>	0.34 × 0.34 × 0.32	0.23 × 0.23 × 0.22	0.34 × 0.32 × 0.30
2θ range for data collection/°	1.665 – 25.136	1.814 – 23.308	1.694 – 25.100
Index ranges	-21 ≤ h ≤ 21, -21 ≤ k ≤ 18, -9 ≤ l ≤ 9	-23 ≤ h ≤ 22, -24 ≤ l ≤ 24, -7 ≤ k ≤ 7	-15 ≤ h ≤ 14, -17 ≤ k ≤ 13, -21 ≤ l ≤ 23
Reflections collected	14233	25790	22134
Independent reflections [R <sub>int</sub> ]	2217[0.0687]	2449 [0.1069]	4000 [0.0445]
Data/restraints/parameters	22217/0/120	2449/0/163	4000 / 0 / 208
Goodness-of-fit on F <sup>2</sup>	1.076	1.171	1.032
R1, wR2 (I > 2(I))	0.0674, 0.2067	0.1129, 0.3652	0.0685, 0.2042
R1, wR2 (all data)	0.0925, 0.2306	0.1445, 0.3912	0.0965, 0.2268
resid. el. dens. [ e/Å <sup>3</sup> ]	-0.474/1.059	-0.473 / 0.571	-0.228 / 0.174
CCDC number	2056570	2056571	2056572

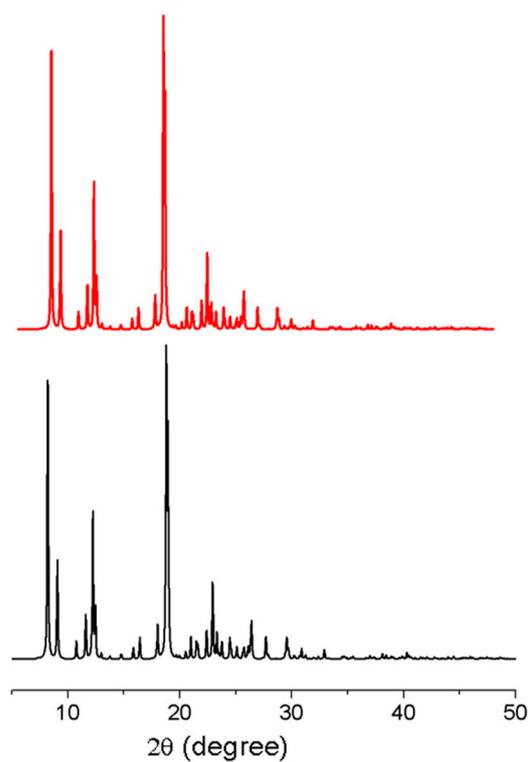
### 3. Powder X-ray diffraction



**Figure S8.** Powder X-ray diffraction (XRD) patterns of as-synthesized and simulated HOF-1.

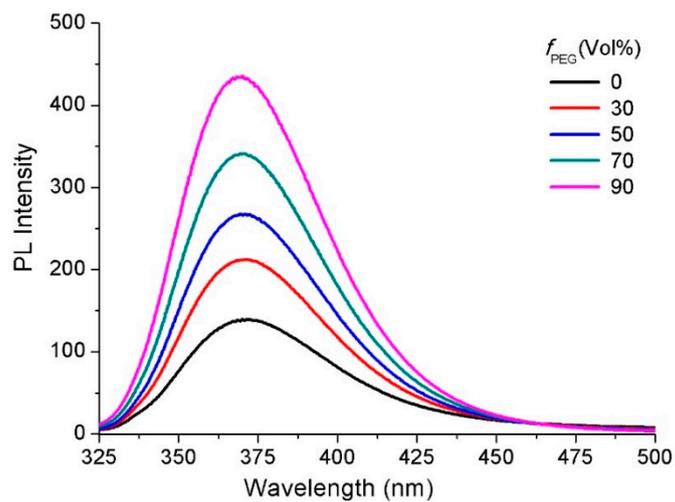


**Figure S9.** Powder X-ray diffraction (XRD) patterns of as-synthesized and simulated HOF-2.

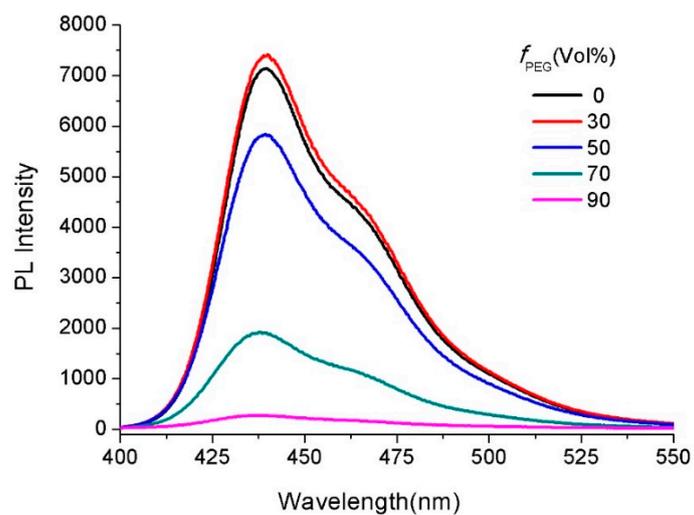


**Figure S10.** Powder X-ray diffraction (XRD) patterns of as-synthesized and simulated HOF-3.

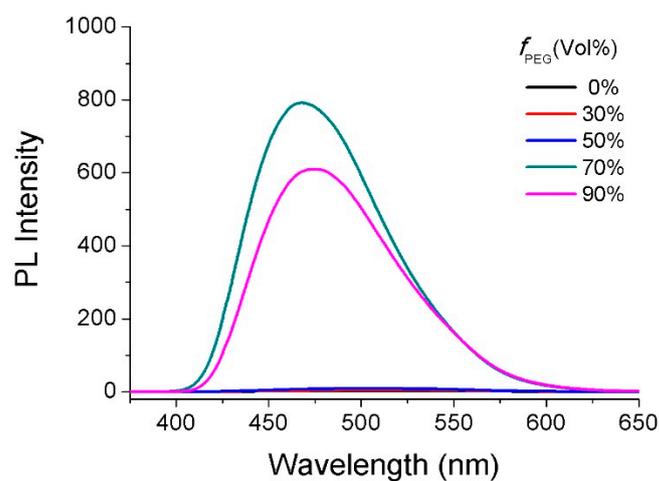
#### 4. Photoluminescence properties



**Figure S11.** PL spectra of the dilute solutions of **1** ( $1.0 \cdot 10^{-5}$  mol L<sup>-1</sup>) in DMA – PEG1000 mixtures with different volume fractions of PEG1000. Excitation wavelength = 306 nm.



**Figure S12.** PL spectra of the dilute solutions of **2** ( $1.0 \cdot 10^{-5}$  mol L<sup>-1</sup>) in DMA – PEG1000 mixtures with different volume fractions of PEG1000. Excitation wavelength = 385 nm.



**Figure S13.** PL spectra of the dilute solutions of **3** ( $1.0 \cdot 10^{-5}$  mol L<sup>-1</sup>) in DMA – PEG1000 mixtures with different volume fractions of PEG1000. Excitation wavelength = 376 nm.