## **Supporting information**

## **Determination methods**

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded at 297 K on a Bruker Avance 300 or 500 MHz NMR spectrometers using CDCl<sub>3</sub> as solvent and TMS as internal standard. Infrared spectra were obtained with a Bruker Tensor 27 FT-IR spectrometer. Differential scanning calorimetry (DSC) patterns and thermogravimetric analysis (TGA) patterns were recorded with a Mettler-Toledo TGA/DSC 1 Thermogravimetric Analyzer with the temperature scanned from 50 to 300 °C at 10 °C /min. Fluorescence microscopy images were obtained on Olympus BX51 imaging system excited at 365 nm. UV-Vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer. Fluorescence spectra were obtained on a Horiba FluoroMax 4 spectrofluorometer. Solid fluorescent quantum yields were performed using Quanta– $\phi$  accessory with excitation wavelength at 320 nm. Elemental analysis was carried out on Vario MICRO.



Figure 1S. <sup>1</sup>H NMR spectrum of AMPP.

Assignments of each H in the NMR spectrum of AMPP:  $\delta$  (ppm) 2.55 (CO-CH<sub>3</sub>), 3.17-3.20 (one H of CH<sub>2</sub>), 3.80-3.81 (-OCH<sub>3</sub>), 3.94-3.99 (another H of CH<sub>2</sub>), 6.54-6.56 (CH), 6.86-8.25 (13H, Ar-H from pyrene and benzene rings).



Figure 2S. <sup>13</sup>C NMR spectrum of AMPP.

Assignments of C in the NMR spectrum of AMPP:  $\delta$  (ppm) 21.97 (C\*-CO), 42.79 (CH<sub>2</sub>), 55.27 (-OCH<sub>3</sub>), 57.47 (CH-N), 114.00-134.75 (the rest Ar-C from pyrene and benzene rings), 153.98 (C=N), 161.26 (C\*-OCH<sub>3</sub>), 168.80 (C=O). (21.97 and 161.26 are assigned to the two C\* respectively).



**Figure 4S.** <sup>1</sup>H NMR spectrum of AMPP-(2-naphthol) cocrystal.



**Figure 5S.** The hydrogen bonding networks constructed by AMPP and phenol molecules in crystal II, hydrogen bonds are presented by dashed lines. (a) view along the bc plane (b) view along the ac plane. Partial hydrogen atoms not participating in the interactions have been omitted for clarity.



**Figure 6S.** The hydrogen bonding networks constructed by AMPP and 2-naphthol molecules in crystal III, hydrogen bonds are presented by dashed lines. (a) view along the *bc* plane (b) view along the *ac* plane. Partial hydrogen atoms not participating in the interactions have been omitted for clarity.



**Figure 7S.** The simulated PXRD patterns of crystals I (a), II (b) and III (c) and the partial magnified observed PXRD patterns of crystals I (d), II (e) and III (f).



Figure 8S. Excitation spectra for the three crystals.

 Table 1S. Hydrogen bonds parameters in crystals I-III

D-HA	D-H(Å)	HA(Å)	DA(Å)	∠D-H…A (°)
Ι				
C22-H22O4	0.930	2.655	3.520	155.00
C23-H23O4	0.980	2.668	3.581	155.22
С39-Н39О3	0.929	2.719	3.604	159.46
II				
O3-H3AO4	0.821	1.922	2.793	173.11
C30-H30AO4	0.930	2.576	3.275	132.29
C57-H57AO2	0.930	2.613	3.425	146.29
O6-H6AO1	0.821	1.856	2.677	179.44
C68-H68AO1	0.930	2.584	3.285	132.47
III				
O3-H3BO1	0.820	1.840	2.659	178.84
C38-H38AO1	0.930	2.627	3.291	128.88
<b>Table 2S.</b> C-H $\pi$ interactions in crystals I-III				
		$d_{H-c}(\text{\AA})$	∠C-H <i>c</i> (°)	
I				
C34-H34Pyrene(B)		2.825	148.06	
C52-H52CPyrene (B)		2.979	107.57	
C48-H48Pyrene (A)		2.842	147.15	
C13-H13Pyrene (B)		2.986	176.75	
II				
C30-H30APyrene (B)		2.975	141.71	
C31-H31APyrene (B)		2.808	150.93	
C17-H17APyrene (B)		2.810	140.00	
C67-H67APyrene (A)		2.774	156.64	
C51-H51APyrene (A)		2.820	140.04	