ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Luminescent Metal-Organic Frameworks Encapsulate Polycyclic Aromatic Hydrocarbons for Energy Transfer

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Synthesis of $[(ZnO)(TPTC)_{0.5}]$ ·4DMF·H_2O $Zn(NO_3)_2·6H_2O$ (30 mg, 0.8 mmol), H_4TPTC (10 mg, 0.2mmol) were dispersed in 10 mL acidic mixed solvent of N, N-dimethylformamide (DMF)/deionized water (v/ v=3/1) in a 15mL sealed vial and heated at 100°C for three days. Then we collected the colorless blocks at ambient temperature without purification. Yield: 53 % based on Zn. Anal. calc for $C_{23}H_{38}N_4O_9Zn$: C, 47.63; H, 6.60; O, 24.83; N, 9.66. Found: C, 47.56; H, 6.29; O, 24.91; N, 9.81.

Synthesis of PAHs@Zn-TPTC Composite Zn-TPTC was soaked in acetone for a week and renewal the solvent per 12h, and then the filtered crystals were evacuated. The mixture of degassed Zn-TPTC and PAHs (m/m=1:3) soaked in DMF for maximum 24 h. Then the filtered crystals were washed with DMF for several times.

Materials and Measurements Powder X-ray diffraction (PXRD), FT-IR spectra, thermogravimetric analysis (TGA), IR spectra, elemental analyses, UV-Vis absorption spectra and Single-crystal X-ray diffraction characterized the features of Zn-TPTC and composites.

X-ray Crystallographic Measurements Bruker SMART-CCD diffractometer with monochromatic Mo-Kα radiation (λ = 0.71069 Å) was used for collecting the crystallographic data of Zn-TPTC at 293 K. Absorption corrections were applied using multiscan technique and conducted by using the SADABS program. In order to solve and refine the structures of title compounds, we emploied the direct method and full matrix least-squares with the *SHELXTL*. We used the anisotropically operation to refine all the atoms except for hydrogen atoms.

Photoluminescence Experiments We use common solvents including DMF to investigated fluorescence of Zn-TPTC. 3 mg of the pre-ground sample of Zn-TPTC and PAHs was soaked in 3 mL solution and treated with ultrasonication for a couple of minutes. 3 mg PAHs@Zn-TPTC was soaked in 3 mL solvent of DMF containing 1% of TEOA. After then, the suspension was carried by quartz colorimetric utensil and placed in F-4600 FL Spectrophotometer with a xenon lamp to recorded Fluorescence spectra at room temperature.

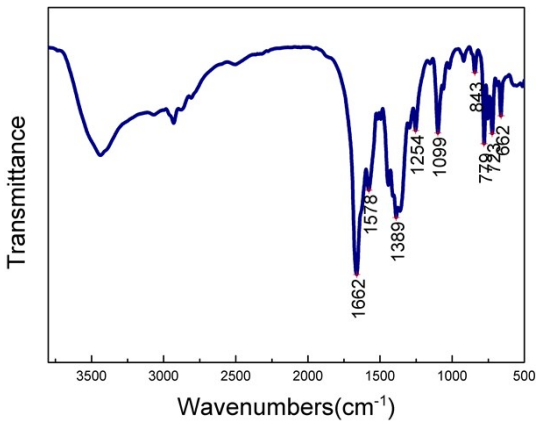

Fig. S1 FT-IR spectra of Zn-TPTC.

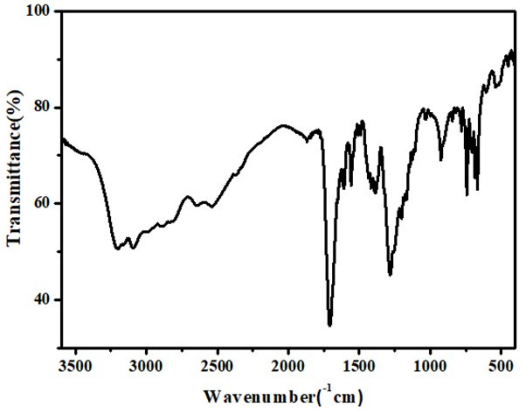

Fig. S2 FT-IR spectra of H_4TPTC.

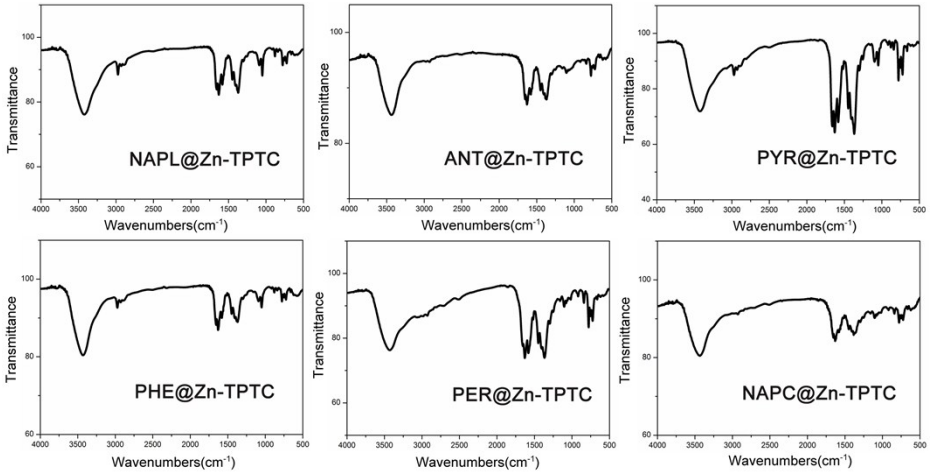

Fig. S3 FT-IR spectra of PAHs@Zn-TPTC.

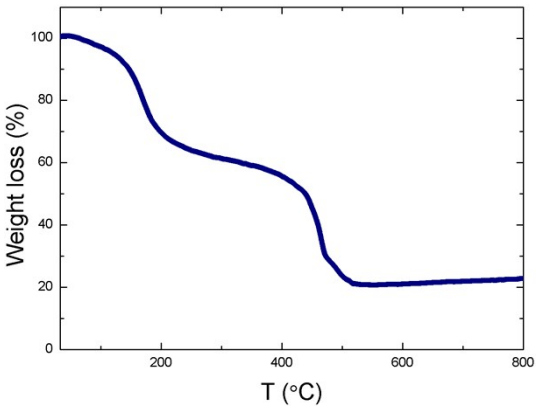

Fig. S4 The TGA curve of Zn-TPTC.

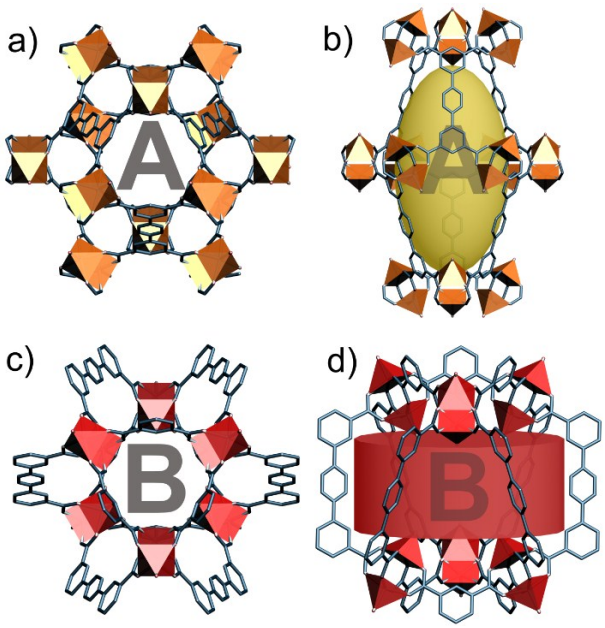

Fig. S5 CageA of Zn-TPTC along the (a) [0 0 1] direction and (b) [0 1 0] direction. CageB along the (c) [0 0 1] direction and (d) [0 1 0] direction.

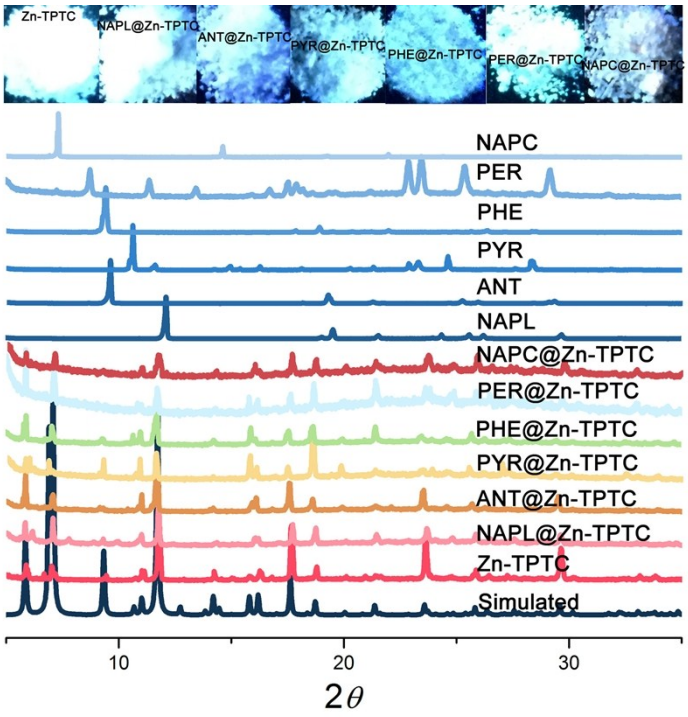

Fig. S6 The PXRD patterns and photos of Zn-TPTC, PAHs@Zn-TPTC and PAHs molecules.

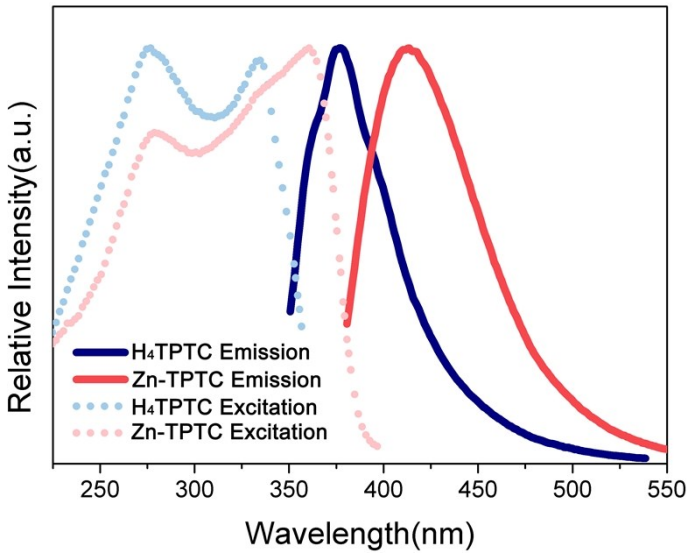

Fig. S7 Solid-state excitation (dashed lines) and emission (solid lines) spectra of the ligand (red) Zn-TPTC (blue) collected in the solid state at room temperature. The maximum emissions for them were 419 and 387 nm, respectively.

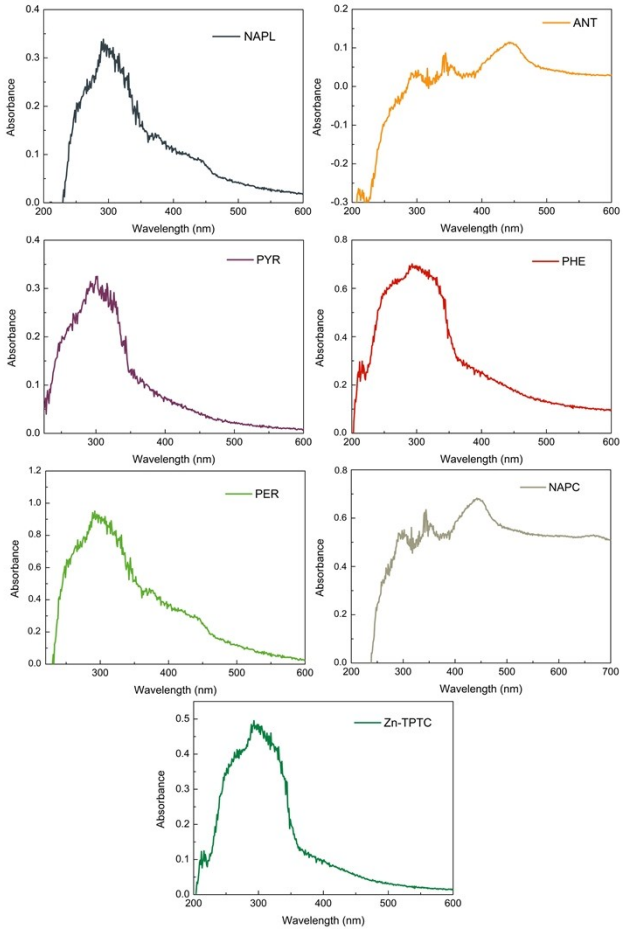

Fig. S8 The UV–vis spectrum of NAPL, ANT, PYR, PHE, PER and NAPC molecules and Zn-TPTC.

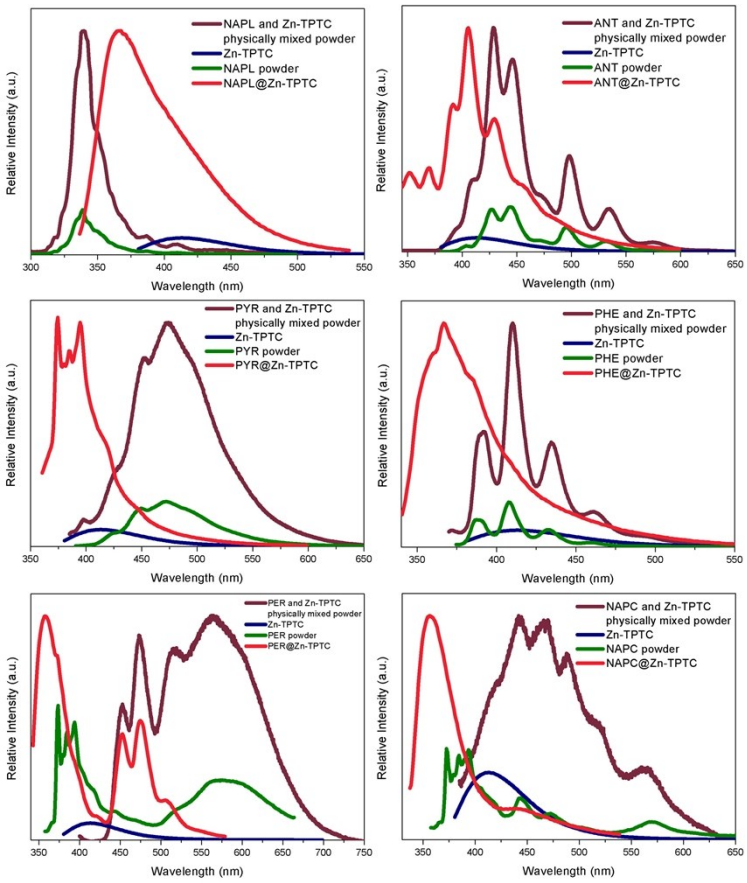

Fig. S9 Solid-state emission spectra of PAHs and Zn-TPTC physically mixed powders.

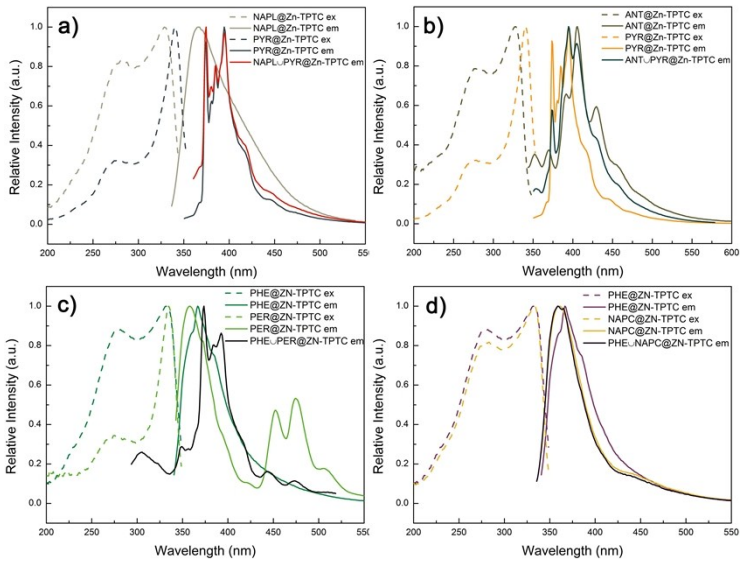

Fig. S10 Solid-state excitation (dashed lines) and emission (solid lines) spectra of a) NAPL@Zn-TPTC, PYR@Zn-TPTC and NAPLUPYR@ZN-TPTC upon excitation at λ=332 nm; b) ANT@Zn-TPTC, PYR@Zn-TPTC and ANTUPYR@ZN-TPTC upon excitation at λ=340 nm; c) PHE@Zn-TPTC, PER@Zn-TPTC and PHEUPER@ZN-TPTC upon excitation at λ=332 nm; d) PHE@Zn-TPTC, NAPC@Zn-TPTC and PHEUNAPC@ZN-TPTC upon excitation at λ=332 nm.

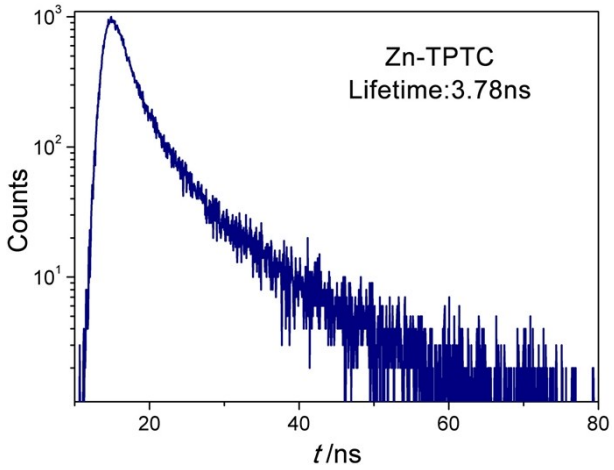

Fig. S11 Fluorescence lifetime decays of Zn-TPTC following excitation at λ=360 nm.

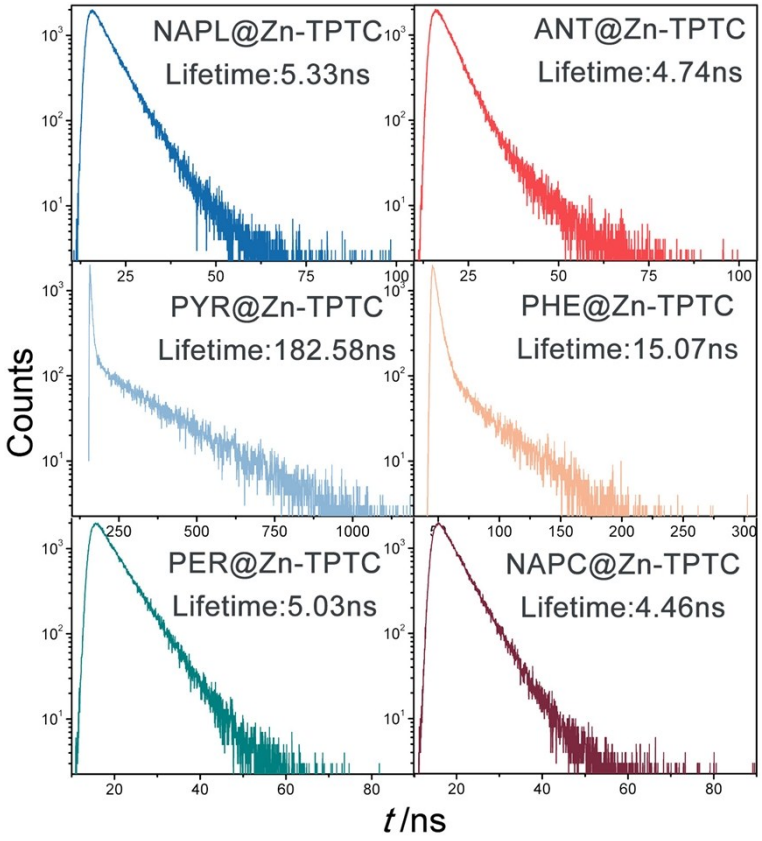

Fig. S12 Fluorescence lifetime decays of NAPL@Zn-TPTC (blue), ANT@Zn-TPTC (red), PYR@Zn-TPTC (light blue), PHE@Zn-TPTC (yellow), PER@Zn-TPTC (green) and NAPC@Zn-TPTC (purple).

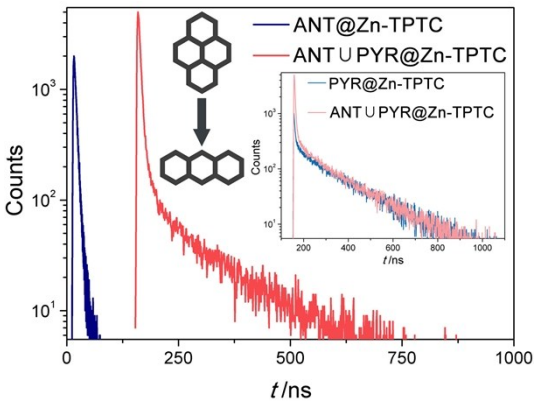

Fig. S13 Fluorescence lifetime decays of ANT@Zn-TPTC (blue) and ANT∪PYR@ZN-TPTC (red) with excitation at λ_{ANT}=334 nm. Insert: schematic representation of ANT and PYR, and fluorescence lifetime decays of PYR@Zn-TPTC (light blue) and ANT∪PYR@ZN-TPTC (light red) with excitation at λ_{PYR}=340 nm.

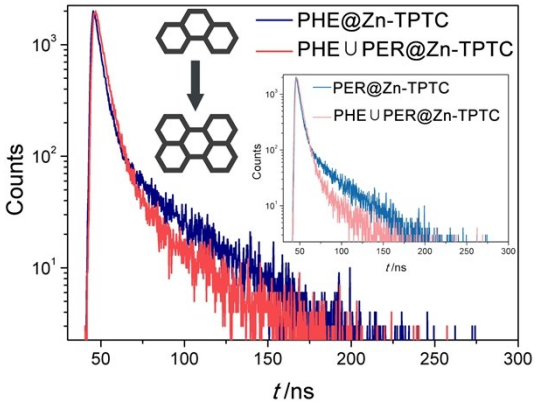

Fig. S14 Fluorescence lifetime decays of PHE@Zn-TPTC (blue) and PHEUPER@ZN-TPTC (red) with excitation at λ_{PHE}=332 nm. Insert: schematic representation of PHE and PER, and fluorescence lifetime decays of PER@Zn-TPTC (light blue) and PHEUPER@ZN-TPTC (light red) with excitation at λ_{PER}=334 nm.

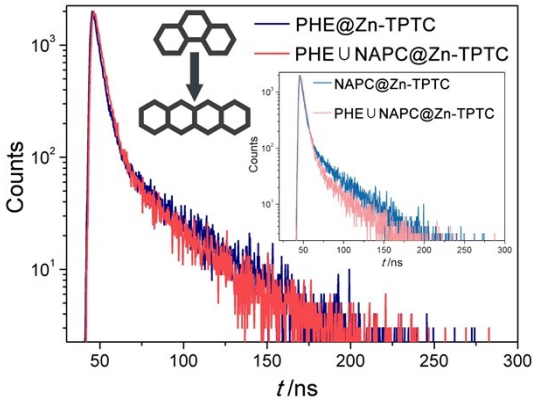

Fig. S15 Fluorescence lifetime decays of PHE@Zn-TPTC (blue) and PHEUNAPC@ZN-TPTC (red) with excitation at λ_{PHE}=332 nm. Insert: schematic representation of PHE and NAPC, and fluorescence lifetime decays of NAPC@Zn-TPTC (light blue) and PHEUNAPC@ZN-TPTC (light red) with excitation at λ_{NAPC}=333 nm.

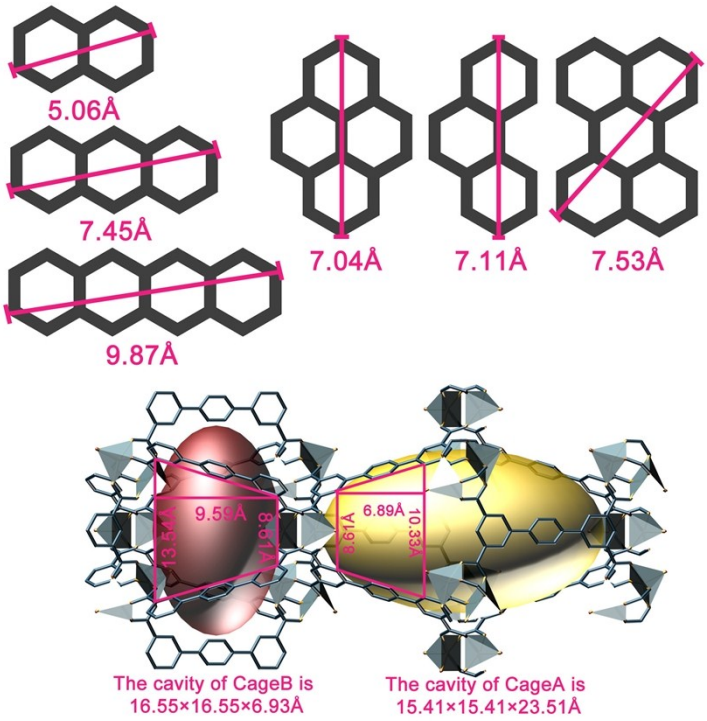

Fig. S16 The molecular size information of the optimized PAHs and Zn-TPTC cages.

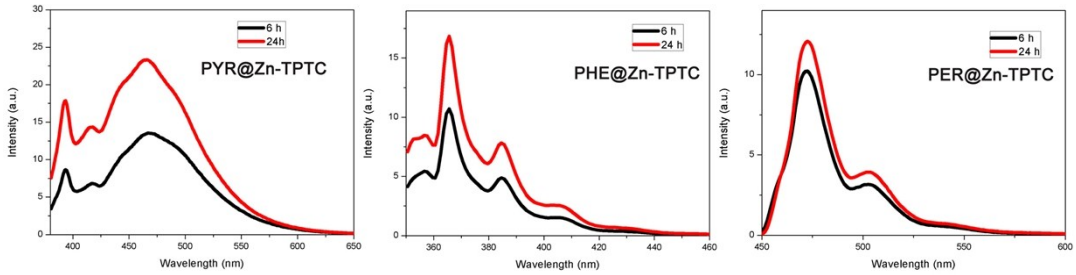

Fig. S17 The PL spectra and intensity of PYR@Zn-TPTC, PHE@Zn-TPTC and PER@Zn-TPTC after soaking in DMF solution for 6 and 24 hours.

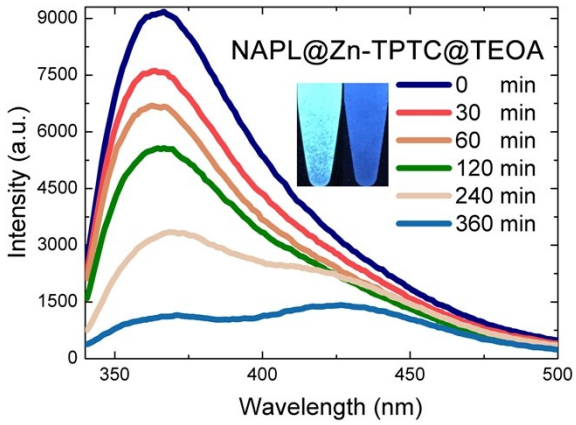

Fig. S18 The PL spectra and relative intensity of NAPL@Zn-TPTC@TEOA. Insert: photos of NAPL@Zn-TPTC@TEOA at 0 min and 360 min. The quenching percentage is 87.9%.

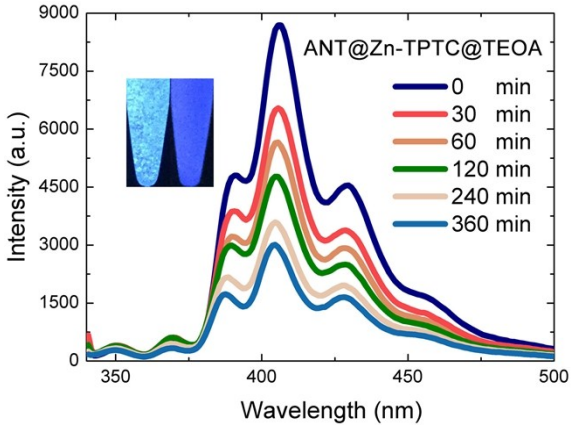

Fig. S19 The PL spectra and relative intensity of ANT@Zn-TPTC@TEOA. Insert: photos of ANT@Zn-TPTC@TEOA at 0 min and 360 min. The quenching percentage is 67.3%.

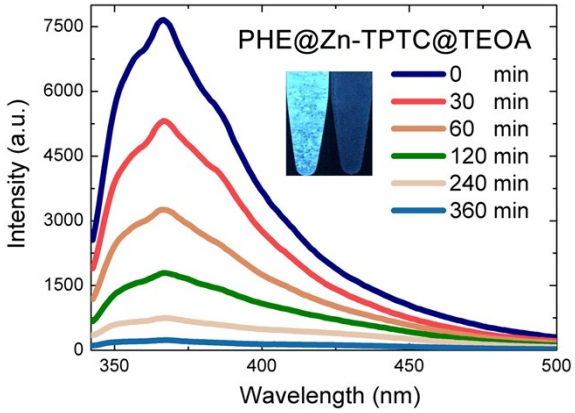

Fig. S20 The PL spectra and relative intensity of PHE@Zn-TPTC@TEOA. Insert: photos of PHE@Zn-TPTC@TEOA at 0 min and 360 min. The quenching percentage is 96.9%.

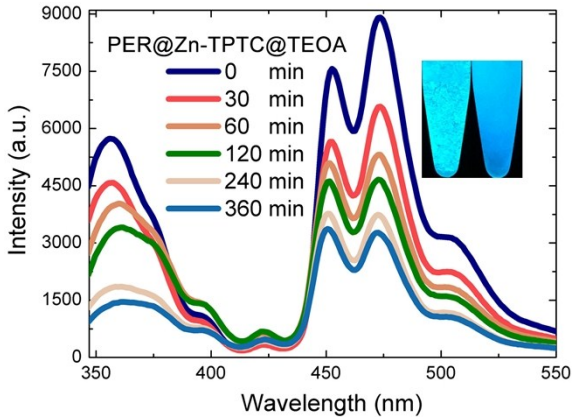

Fig. S21 The PL spectra and relative intensity of PER@Zn-TPTC@TEOA. Insert: photos of PER@Zn-TPTC@TEOA at 0 min and 360 min. The quenching percentage is 56.7%.

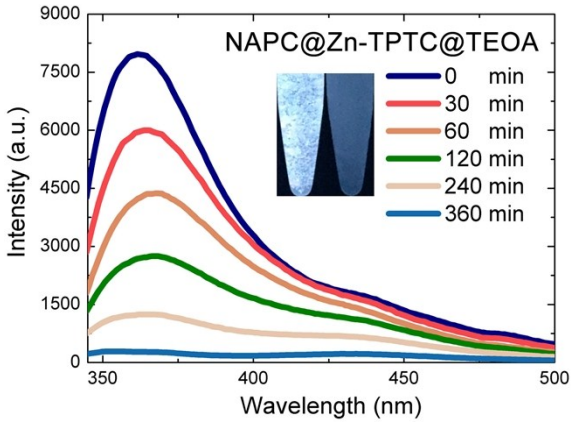

Fig. S22 The PL spectra and relative intensity of NAPC@Zn-TPTC@TEOA. Insert: photos of NAPC@Zn-TPTC@TEOA at 0 min and 360 min. The quenching percentage is 96.4%.

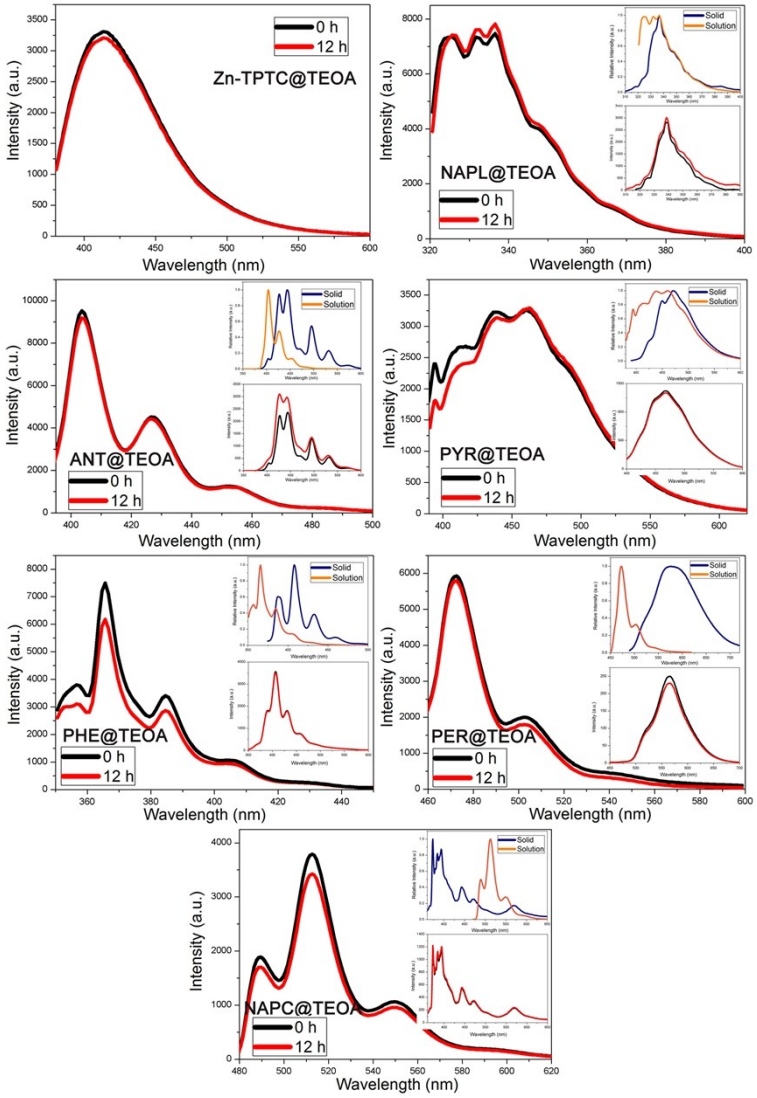

Fig. S23 The PL spectra and intensity of Zn-TPTC@TEOA and PAHs@TEOA. Insert: the corresponding PL spectra of PAHs at solid and solution state.

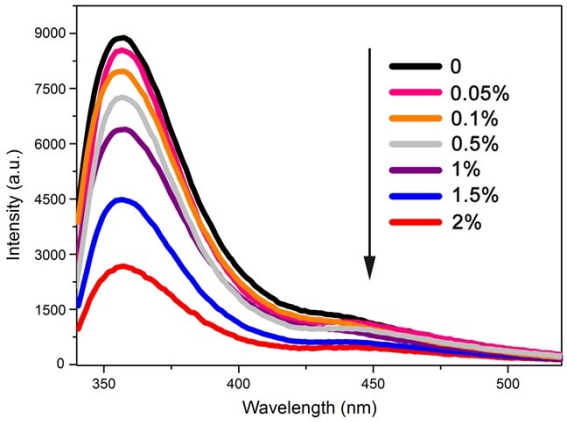

Fig. S24 The PL spectra of NAPC@Zn-TPTC in the DMF solvent with TEOA at different concentration.

Table S1. The fluorescence lifetimes (τ) of Zn-TPTC and its composites, and the photoluminescence quenching efficiency of TEOA in the presence of the PAHs@Zn-TPTC.

Compounds	Fluorescence lifetimes (τ)/ns	Quenching efficiency (%)
Zn-TPTC	3.78	---
NAPL@Zn-TPTC	5.33	87.9
ANT@Zn-TPTC	4.74	67.3
PYR@ZN-TPTC	182.58	97.2
PHE@Zn-TPTC	15.07	96.9
PER@Zn-TPTC	5.03	56.7
NAPC@Zn-TPTC	4.46	96.4
NAPL∪PYR@ZN-TPTC	4.7 (λ_{NAPL}=332 nm); 207.5 (λ_{PYR}=340 nm)	
ANT∪PYR@ZN-TPTC	118.7 (λ_{ANT}=334 nm); 167.7 (λ_{PYR}=340 nm)	
PHE∪PER@ZN-TPTC	6.1 (λ_{PHE}=332 nm); 5.3 (λ_{PER}=334 nm)	
PHE∪NAPC@ZN-TPTC	8 (λ_{PHE}=332 nm); 6.4 (λ_{NAPC}=333 nm)	

Table S2. Crystal data and structure refinement for Zn-TPTC.

Compound reference	**Zn-TPTC**
Chemical formula	$C_{23}H_{38}N_4O_9Zn$
Formula Mass	579.98
Crystal system	Trigonal
a/Å	18.9400
b/Å	18.9400
c/Å	38.3480
α/°	90
β/°	90
γ/°	120
Unit cell volume/Å3	282.54
Temperature/K	293(2)
Space group	*R-3m*
No. of formula units per unit cell, *Z*	18
No. of reflections measured	48223
Final R_1 values ($I > 2\sigma(I)$)	0.0745
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2652
Final R_1 values (all data)	0.0966
Final $wR(F^2)$ values (all data)	0.2870
Goodness of fit on F^2	1.141
CCDC no.	1527717

[a] $R_1 = \sum \| F_o | - | F_c \| / \sum | F_o |$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$

Table S3. Selected bonds lengths (Å) and angles (°) for Zn-TPTC.

O(1)-Zn(1)	2.042(4)	O(2)-Zn(1)#3	2.021(5)
O(5)-Zn(1)	1.961(7)	Zn(1)-O(1)#5	2.042(4)
Zn(1)-O(2)#3	2.021(5)	Zn(1)-O(2)#4	2.021(5)
Zn(1)-Zn(1)#3	2.9811(15)	O(5)-Zn(1)-O(2)#3	102.3(3)
O(5)-Zn(1)-O(2)#4	102.3(3)	O(2)#3-Zn(1)-O(2)#4	87.0(3)
O(5)-Zn(1)-O(1)#5	99.1(3)	O(2)#3-Zn(1)-O(1)#5	88.9(2)
O(2)#4-Zn(1)-O(1)#5	158.6(2)	O(5)-Zn(1)-O(1)	99.1(3)
O(2)#3-Zn(1)-O(1)	158.6(2)	O(2)#4-Zn(1)-O(1)	88.9(2)
O(1)#5-Zn(1)-O(1)	87.3(3)	O(5)-Zn(1)-Zn(1)#3	175.7(3)
O(2)#3-Zn(1)-Zn(1)#3	80.72(14)	O(2)#4-Zn(1)-Zn(1)#3	80.72(14)
O(1)#5-Zn(1)-Zn(1)#3	77.85(14)	O(1)-Zn(1)-Zn(1)#3	77.85(14)

Symmetry transformations used to generate equivalent atoms: #1 = x, x-y, z; #2 = -x+2/3, -x+y+1/3, -z+1/3; #3 = -x+1, -y+1, -z; #4 = y, x, -z; #5 = -y+1, -x+1, z.