Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Confinement of electron-capturing unit within electron-donating framework for X-ray detection

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Photoluminescent kinetic rate calculation

After X-ray irradiation, photoluminescence spectra were recorded and the calculations of kinetics of photoreaction kinetic rates were based on the intensity values of the wavelength at 430 nm. The The following equation (1) is used for data treatment:

$$kt = \ln\left(\frac{I_o - I_\infty}{I_t - I_\infty}\right) \quad (1)$$

Where I_0, I_t, I_∞ refer to the observed emission intensity data at the beginning, versus time, and at the steady state, respectively.

Table S1. Crystallographic data collection and refinement result for **ZnATZ-BTB.**

Temperature	293 K
Empirical formula	$C_{39}H_{58}N_{14}O_{26}Zn_4$
Formula weight	1400.55
Crystal system	Monoclinic
Space group	*C2/c*
a (Å)	38.393(17)
b (Å)	14.694(6)
c (Å)	18.872(8)
α (°)	90.00
β (°)	95.907(10)
γ (°)	90.00
V (Å^3)	10590(8)
Z	8
Dc (g/cm^3)	1.892
μ (mm^{-1})	0.91
F(000)	5743
θ range (°)	2.12 - 25.00
*R(*int*)*	0.1150
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0990, 0.2357
GOF on F^2	1.066

Table S2. Select bonds (Å) and angles (˚).

Zn(1)-O(18)	1.950(8)	O(5)#1-Zn(1)-O(6)#1	59.0(5)
Zn(1)-O(14)	1.974(7)	O(2)#4-Zn(2)-O(15)#2	127.3(3)
Zn(1)-O(17)	2.007(8)	O(2)#4-Zn(2)-O(8)#5	101.2(3)
Zn(1)-O(5)#1	2.100(12)	O(15)#2-Zn(2)-O(8)#3	103.6(3)
Zn(1)-O(6)#1	2.379(14)	O(2)#4-Zn(2)-O(7)	98.1(3)
Zn(2)-O(2)#4	1.963(7)	O(15)#2-Zn(2)-O(7)	113.2(3)
Zn(2)-O(15)#2	1.977(7)	O(8)#3-Zn(2)-O(7)	113.2(3)
Zn(2)-O(8)#3	1.990(7)	O(10)-Zn(3)-O(12)	151.8(3)
Zn(2)-O(7)	1.998(7)	O(10)-Zn(3)-O(19)	99.7(3)
Zn(3)-O(10)	1.981(7)	O(12)-Zn(3)-O(19)	97.3(3)
Zn(3)-O(12)	2.000(7)	O(10)-Zn(3)-N(13)#1	99.3(3)
Zn(3)-O(19)	2.036(7)	O(12)-Zn(3)-N(13)#1	100.0(3)
Zn(3)-N(13)#1	2.090(8)	O(19)-Zn(3)-N(13)#1	99.1(3)
Zn(3)-N(12)	2.412(8)	O(10)-Zn(3)-N(12)	77.9(3)
Zn(4)-O(11)	2.027(7)	O(12)-Zn(3)-N(12)	78.2(3)
Zn(4)-O(1)#2	2.034(7)	O(19)-Zn(3)-N(12)	159.4(3)
Zn(4)-O(4)#2	2.046(7)	N(13)#1-Zn(3)-N(12)	101.5(3)
Zn(4)-N(14)	2.116(8)	O(11)-Zn(4)-O(1)#2	102.1(3)
Zn(4)-O(20)	2.255(8)	O(11)-Zn(4)-O(4)#2	109.4(3)
O(18)-Zn(1)-O(14)	107.2(3)	O(1)#2-Zn(4)-O(4)#2	145.4(3)
O(18)-Zn(1)-O(17)	113.2(4)	O(11)-Zn(4)-N(14)	101.1(3)
O(14)-Zn(1)-O(17)	100.6(3)	O(1)#2-Zn(4)-N(14)	88.7(3)
O(18)-Zn(1)-O(5)#1	90.6(4)	O(4)#2-Zn(4)-N(14)	98.7(3)
O(14)-Zn(1)-O(5)#1	150.3(5)	O(11)-Zn(4)-O(20)	83.2(3)
O(17)-Zn(1)-O(5)#1	93.6(4)	O(1)#2-Zn(4)-O(20)	86.6(3)
O(18)-Zn(1)-O(6)#1	122.8(4)	O(4)#2-Zn(4)-O(20)	83.4(3)
O(14)-Zn(1)-O(6)#1	91.2(4)	N(14)-Zn(4)-O(20)	174.2(3)
O(17)-Zn(1)-O(6)#1	115.7(4)		

Symmetry codes: #1 -x+1/2,-y+1/2,-z+1; #2 -x+1/2,y-1/2,-z+1/2; #3 -x+1/2,-y+1/2,-z; #4 x,-y+1,z-1/2.

Table S3. Hydrogen-bond geometry (Å, º).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O17—H17*A*···O10	0.85	2.07	2.889(11)	162.8
O20—H20*C*···O4W	0.85	1.83	2.671(12)	169.3
O20—H20*D*···O1W#1	0.85	2.22	3.032(16)	158.8
O3W—H3WA···O4#2	0.85	1.88	2.722(11)	170.6
O3W—H3WB···O1W#3	0.85	1.86	2.700(18)	169.9
O5W—H5WB···O2W#3	0.85	2.12	2.971(15)	175.0
O1W—H1WA···O19	0.85	1.94	2.790(16)	178.1
O1W—H1WB···O3#4	0.85	2.09	2.935(17)	178.0
O4W—H4WA···O2W#1	0.85	2.03	2.742(16)	141.3
O6W—H6WA···O13#5	0.85	1.95	2.784(10)	166.5
O6W—H6WB···O20	0.85	2.03	2.862(11)	166.8
O2W—H2WA···O3W	0.85	2.04	2.890(17)	175.7
O2W—H2WB···O5#2	0.85	1.98	2.83(2)	175.8

Symmetry codes: #1 x, -y, z-1/2; #2 -x+1/2, y-1/2, -z+1/2; #3 -x+1, -y, -z+1; #4 -x+1/2, -y+1/2, -z+1; #5 -x+1/2, -y+1/2, -z+1.

Table S4. Photoluminescent data for cMOC-3 at room temperature.

Sample	Excited Wavelength (nm)	Maximum emission Wavelength (nm)	Lifetime (ns)			Quantum yield (%)
			τ_1	τ_2	τ_3	
PTIA ligand	288	413	1.94 (43.68%)	9.25 (49.89%)	23.9 (6.43%)	26.34%
cMOC-3	284	430	1.32 (74.86%)	7.57 (19.87%)	26.3 (5.27%)	6.32%

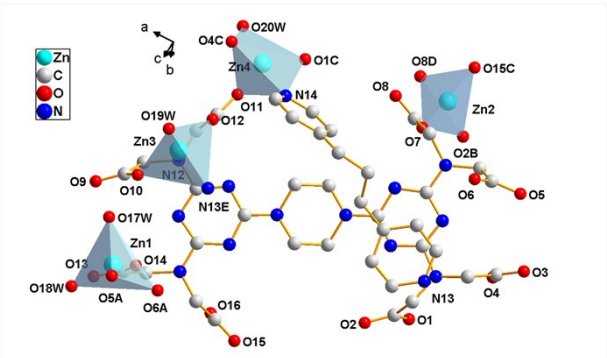

Figure S1. Coordination environment of the Zn centers in the asymmetric unit of cMOC-3. Symmetry codes: A) 0.5−y, 0.5−y, 1-z; B) x, 1–y, -0.5+z; C) 0.5–x, -0.5+y, 0.5-z; D) 0.5-x, 0.5-y, -z; C) 0.5–x, 0.5-y, 1-z.

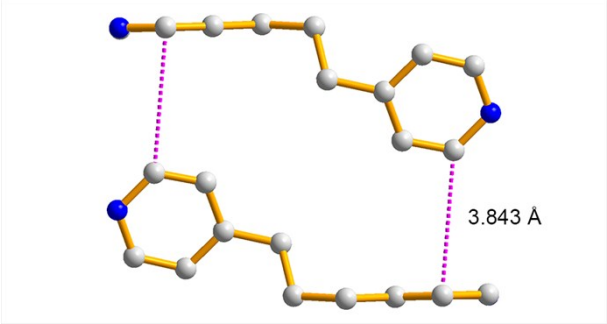

Figure S2. View of strong inter-molecular edge-to-face π…π stacking interactions between two captured BPP ligands in the cavity of the subunit.

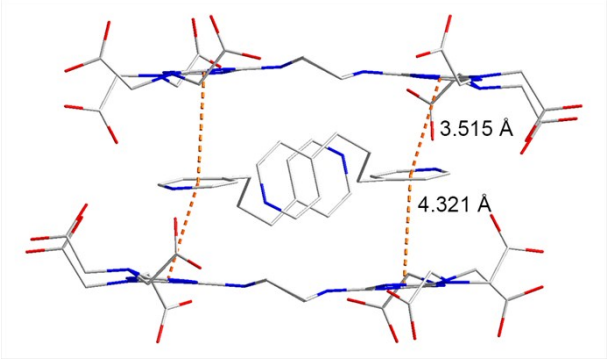

Figure S3. View of strong offset face-to-face π…π stacking interactions between BPP and PTIA ligands.

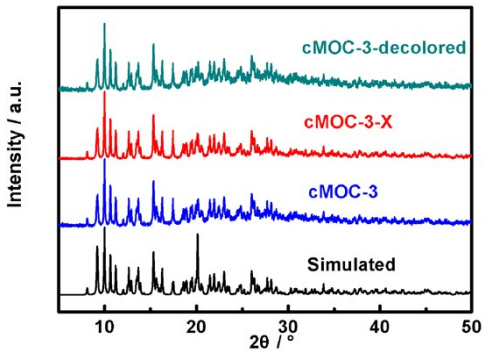

Figure S4. PXRD patterns for cMOC-3 before and after X-ray irradiation, and upon heat treatment.

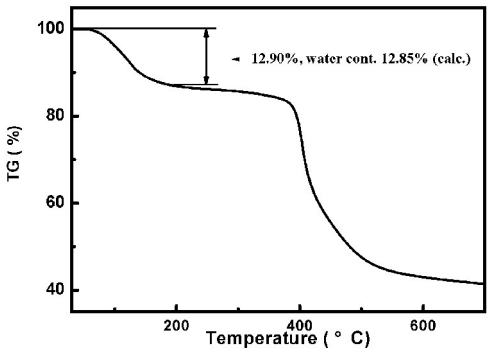

Figure S5. TGA curves of cMOC-3.

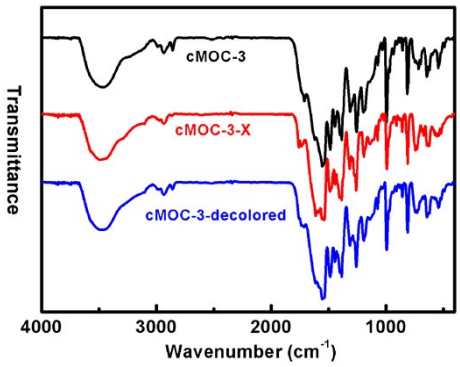

Figure S6. IR spectra of cMOC-3 before and after X-ray irradiation, and upon heat treatment.

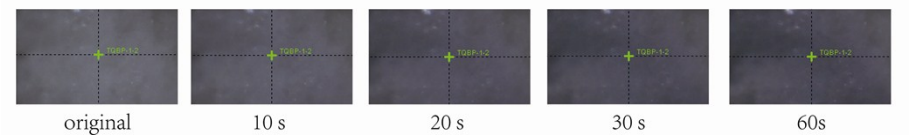

Figure S7. The X-ray-induced photochromic process of cMOC-3 irradiated by Al-Kα source. Note: TQBP-1-2 is sample name for testing.

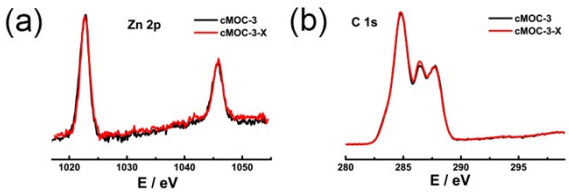

Figure S8. In situ (a) Zn 2p and (b) C 1s XPS core-level spectral of cMOC-3 and X-ray irradiated cMOC-3-X.

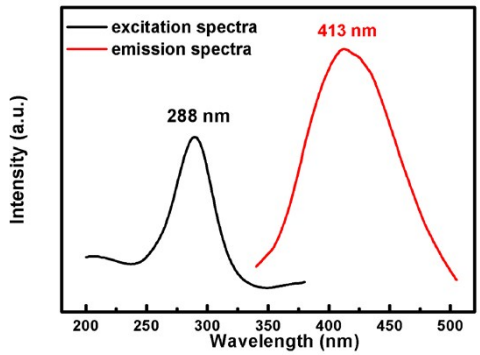

Figure S9. The excitation and emission spectra of the PTIA ligand.

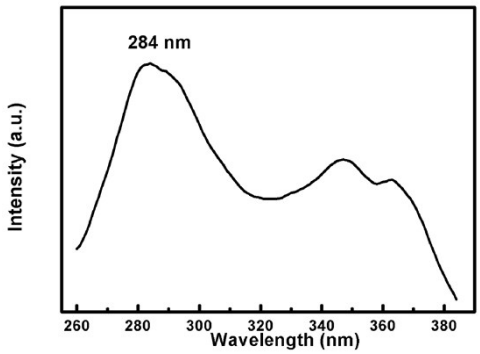

Figure S10. The excitation spectra of cMOC-3.

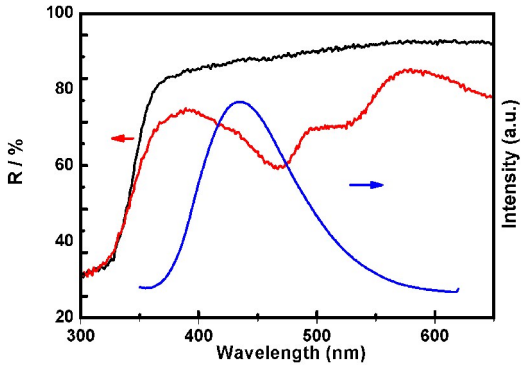

Figure S11. Solid-state diffuse reflectance spectra of cMOC-3 (black) and the colored photo-product cMOC-3-X (red); the emission spectra of cMOC-3 (blue).

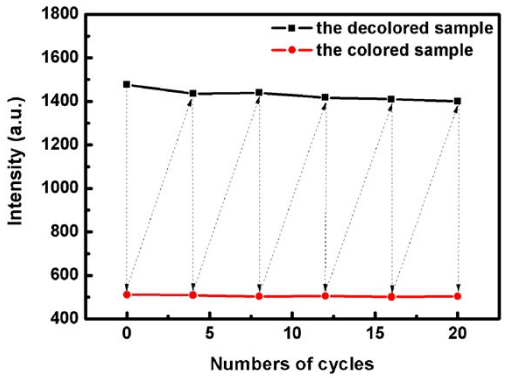

Figure S12. The emission intensity at 430 nm with different cycles upon alternating coloration states (red) and decoloration states (black) (excitation at 284 nm).