Supporting Information

A reversible photochromic coordination polymer by phototriggered subtle molecular conformation variations

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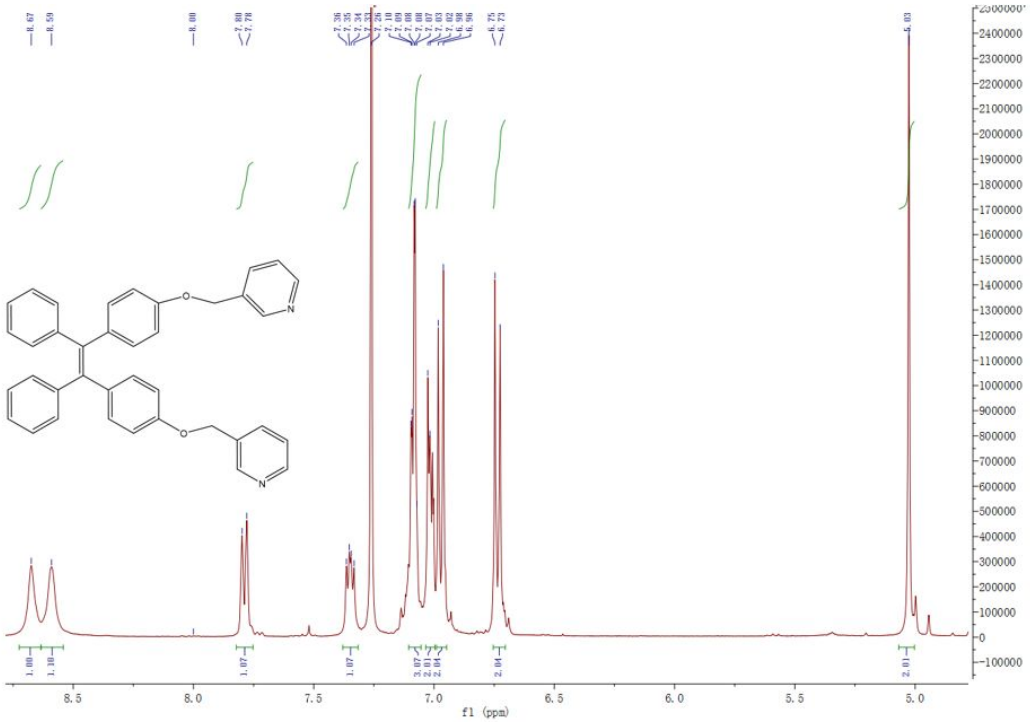
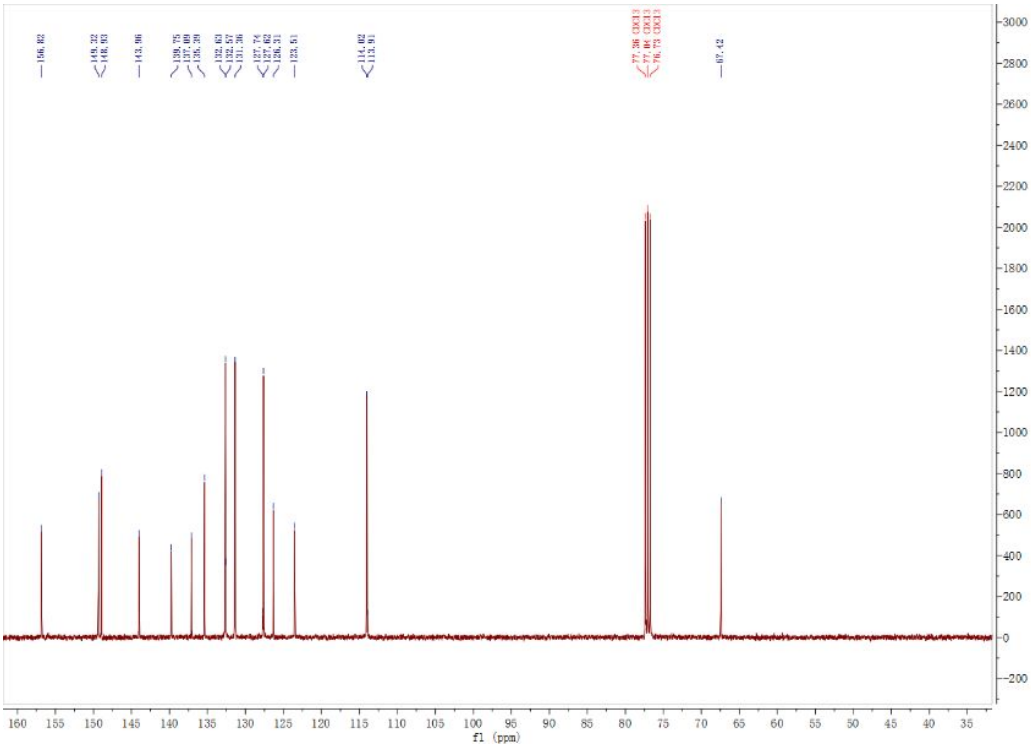
TPE-2by-2-Z: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ (TMS, ppm) 8.67 (1H, s) 8.59 (1H, s) 7.79 (1H, d, *J* = 8 Hz) 7.33-7.36 (1H, m) 7.07-7.10 (3H, m) 7.02 (2H, d, *J* = 4 Hz) 6.97 (2H, d, J = 8 Hz) 6.74 (2H, d, *J* = 8 Hz) 5.03 (2H, s). ^{13}C NMR ($CDCl_3$) δ (TMS, ppm) 156.82, 149.32, 148.93, 143.96, 139.75, 137.09, 135.39, 132.63, 132.57, 131.36, 127.74, 127.62, 126.31, 123.51, 114.62, 113.91, 67.42. HRMS: m/z calculated for $C_{38}H_{31}N_2O_2$ $[M+H]^+$ 547.238, found 547.238 (high resolution).

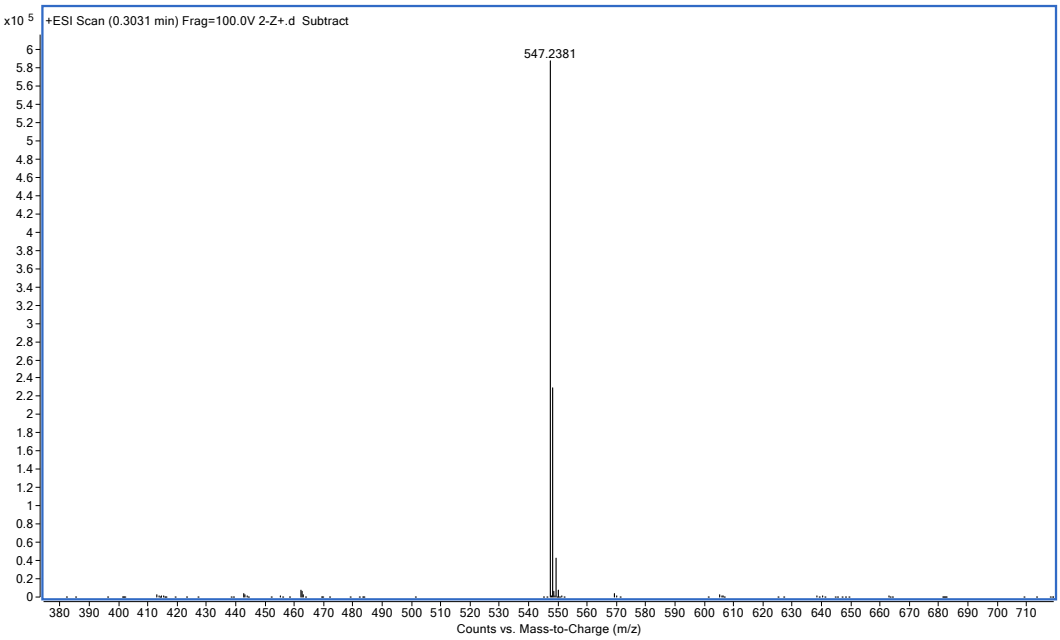
TPE-2by-2-E: ^{1}H NMR (400 MHz, $CDCl_3$, 25 ℃) δ (TMS, ppm) 8.64 (1H, s) 8.57 (1H, s) 7.73 (1H, d, J = 8 Hz) 7.29-7.32 (1H, m) 7.10-7.13 (3H, m) 7.06 (2H, d, *J* = 4 Hz) 6.94 (2H, d, *J* = 12 Hz) 6.70 (2H, d, *J* = 8 Hz) 4.98 (2H, s). ^{13}C NMR ($CDCl_3$) δ (TMS, ppm) 156.81, 149.35, 148.98, 144.04, 139.73, 136.99, 135.33, 135.30, 132.62, 132.52, 131.34, 127.72, 126.30, 123.45, 113.91, 67.39. HRMS: m/z calculated for $C_{38}H_{31}N_2O_2$ $[M+H]^+$ 547.238, found 547.238 (high resolution).



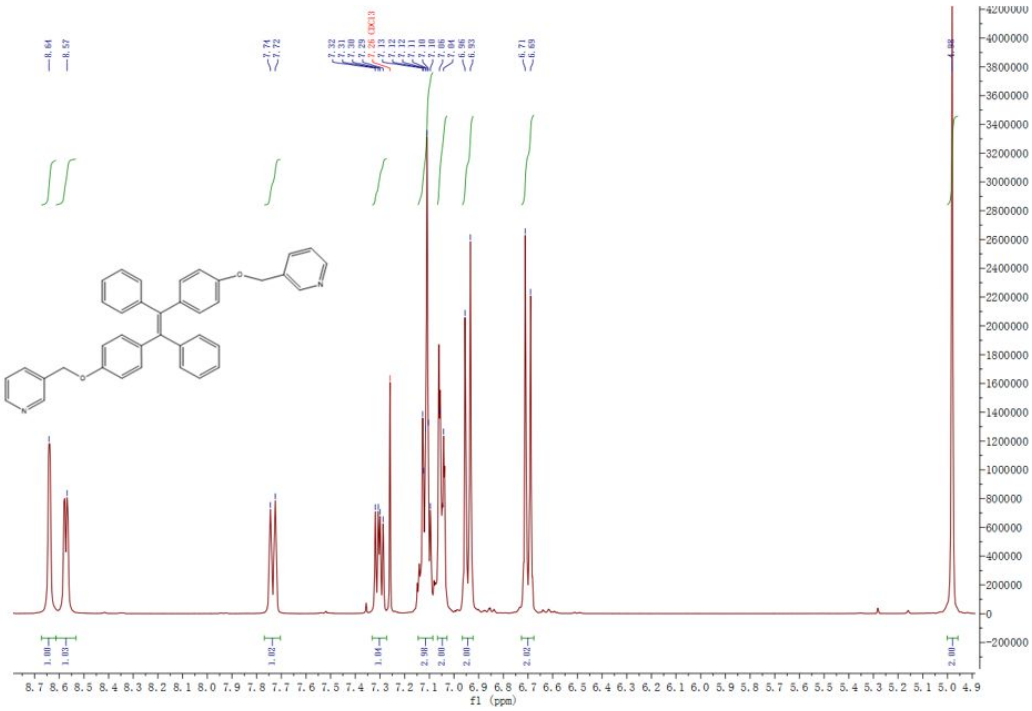
S1.^{1}H NMR spectrum of TPE-2by-2-Z in $CDCl_3$.



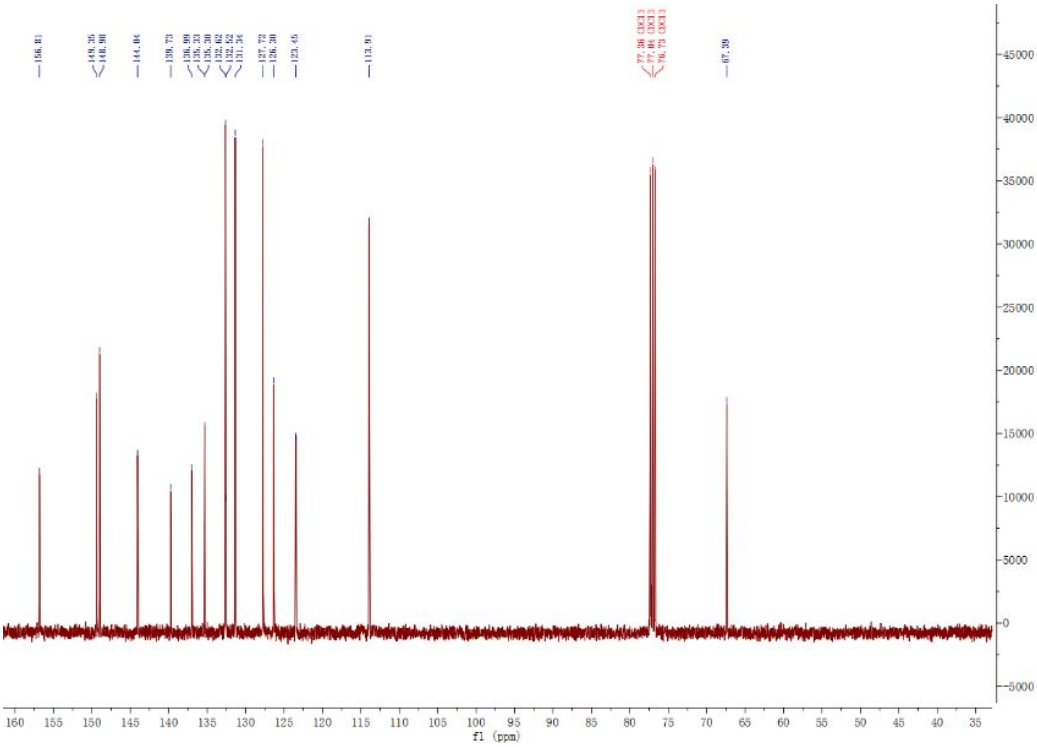
S2.^{13}C NMR spectrum of TPE-2by-2-Z in $CDCl_3$.



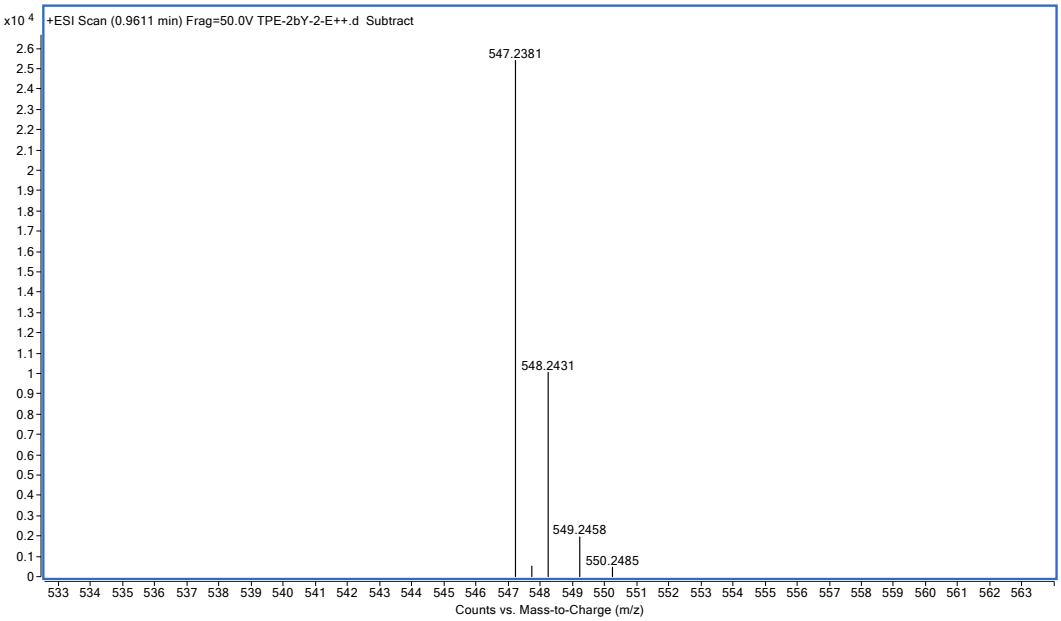
S3. High-resolution mass spectrum of TPE-2by-2-Z.



S4. ^{1}H NMR spectrum of TPE-2by-2-E in $CDCl_3$.



S5.^{13}C NMR spectrum of TPE-2by-2-E in $CDCl_3$.

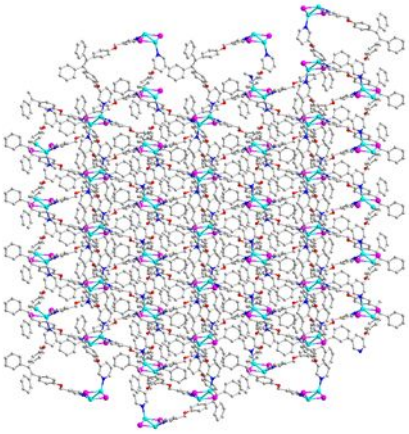


S6. High-resolution mass spectrum of TPE-2by-2-E.

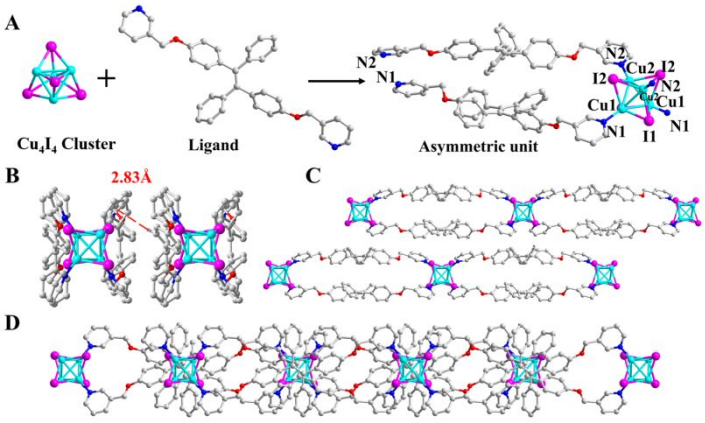
Table S1. Crystal Dataand Structure Refinement Summary for CIT-Z and CIT-E.

	CIT-Z	CIT-Z-UV light irradiation	CIT-E
formula	$C_{38}H_{30}CuIN_2O_2$	$C_{38}H_{30}CuIN_2O_2$	$C_{76}H_{60}Cu_4I_4N_4O_4$
formula weight	737.08	737.08	1855.04
temperature/K	293(2)	293(2)	300.93(10)
crystal system	Monoclinic	Monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	C2/c
a/Å	19.0059(2)	19.0180(3)	23.6651(7)

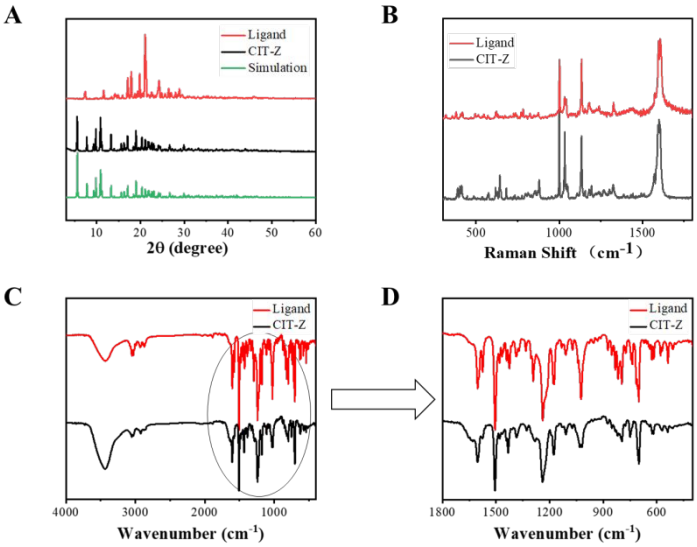
b/Å	9.07299(9)	9.07440(9)	18.1534(6)
c/Å	20.0473(3)	20.0448(3)	20.1054(7)
α/°	90	90	90
β/°	108.7137(13)	108.7509(15)	97.928(3)
γ/°	90	90	90
V/Å^3	3274.21(7)	3275.67(8)	8554.8(5)
Z	4	4	4
ρ_{calc}g/cm^3	1.495	1.495	1.440
μ/mm^{-1}	8.620	8.616	2.467
F (000)	1480.0	1480.0	3616.0
θ_{min}–θ_{max}[deg]	5.578-152.05	5.574-152.59	3.354-59.08
R/Wr [I > $2_{\sigma (I)}$]	0.0265/0.0678	0.0284/0.0723	0.0730/0.2258



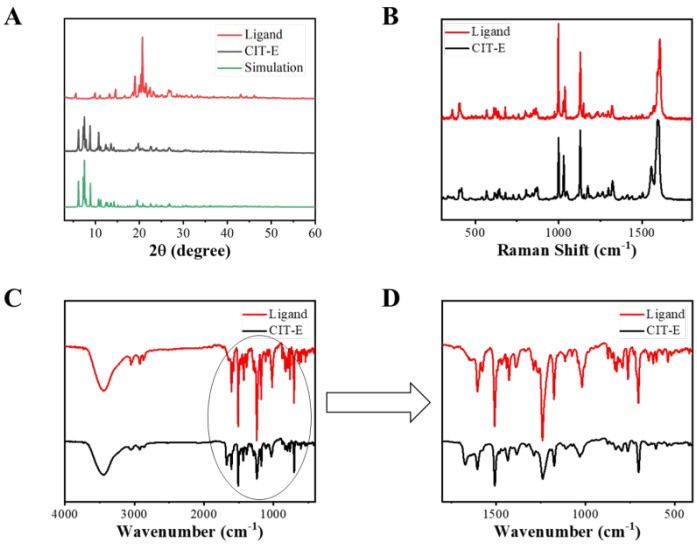
S7. Two layers of CIT-Z nets crystal view from the c direction.



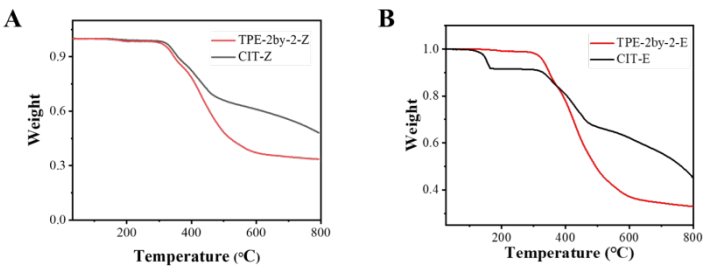
S8. (A) Structures of Cu_4I_4 cluster and ligand TPE-2by-2-E and asymmetric unit of CIT-E. 1D beaded chain structure of CIT-E view along (B) a, (C) b or (D) c direction and (B) C-H…π interaction in CIT-E. (Part of the H atoms are omitted for clarity. Color legend: Cu, blue; N, deep blue; I, purple; O, red; C, gray; H, deep gray.)



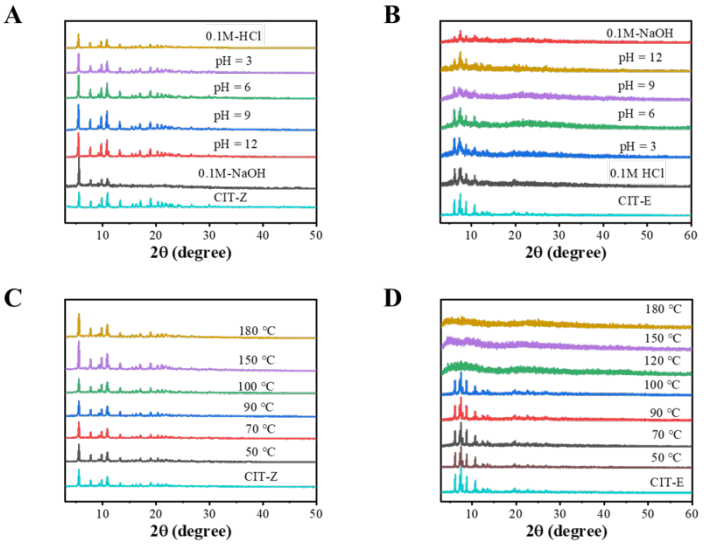
S9. (A)PXRD spectra, (B) Raman spectra, (C) and (D) FT-IR spectra of CIT-Z and ligand (TPE-2by-2-Z).



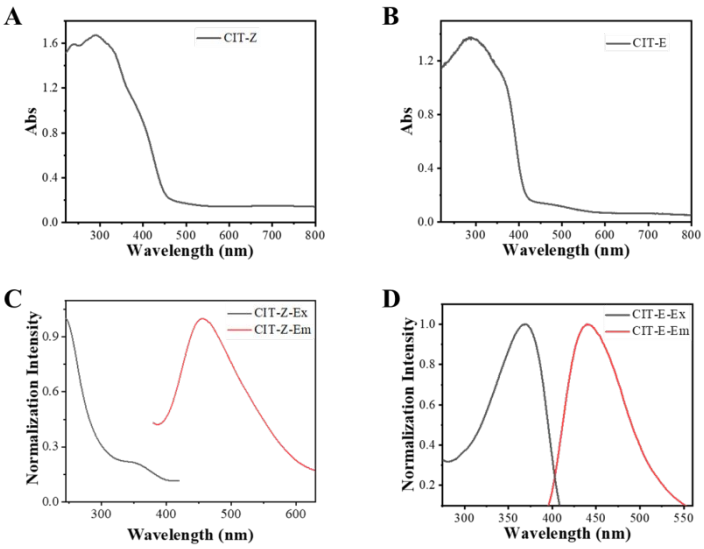
S10. (A)PXRD spectra, (B) Raman spectra and (C) & (D) FT-IR spectra of CIT-E and ligand (TPE-2by-2-E).



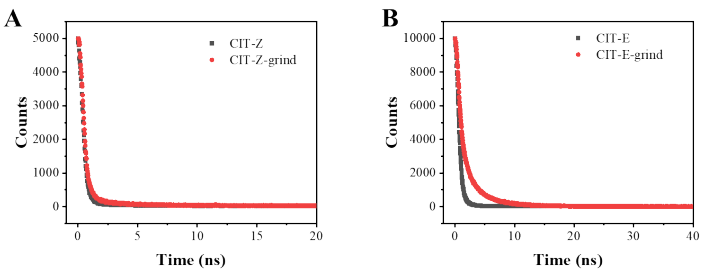
S11. TG curves of (A) CIT-Z and TPE-2by-2-Z, (B) CIT-E and TPE-2by-2-E.



S12. XRD spectra at different pH of (A) CIT-Z and (B) CIT-E, XRD spectra at different temperature of (C) CIT-Z and (D) CIT-E.



S13. Solid UV-vis Absorption Spectra of (A) CIT-Z and (B) CIT-E. Fluorescence excitation emission spectra of (C) CIT-Z (λ_{ex} = 325 nm, λ_{em} = 457 nm) and (D) CIT-E (λ_{ex} = 325 nm, λ_{em} = 440 nm).

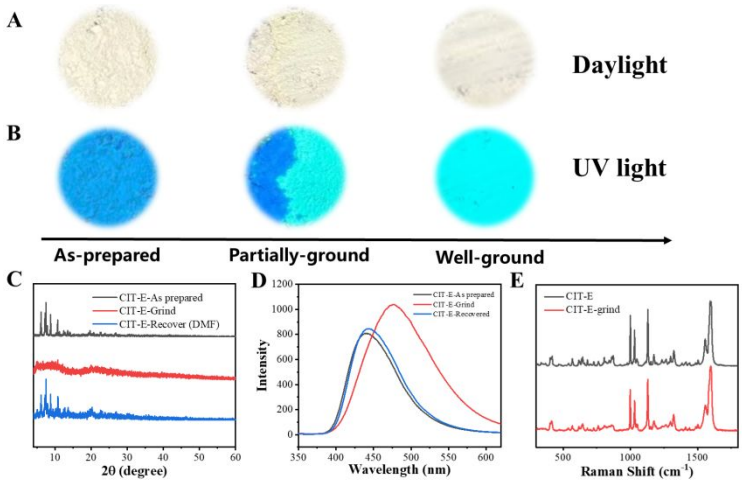


S14. Fluorescence lifetime of (A) CIT-Z and (B) CIT-E before and after grinding.

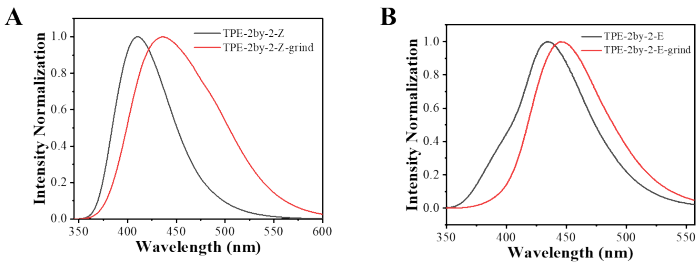
Table S2. Spectral data of CIT-Z and CIT-E

Name	Treatment	E_m (nm)	φ_f (%)	τ (ns)	k_r /10^7 (s^{-1})	k_{nr} /10^8 (s^{-1})
CIT-Z	Pristine	457	2.65	0.44	6.02272727	22.125
	Grind	471	9.5	0.74	12.8378378	12.22973
CIT-E	Pristine	440	1.1	2.09	0.52631579	4.7320574
	Grind	477	2.23	4.11	0.54257908	2.3788321

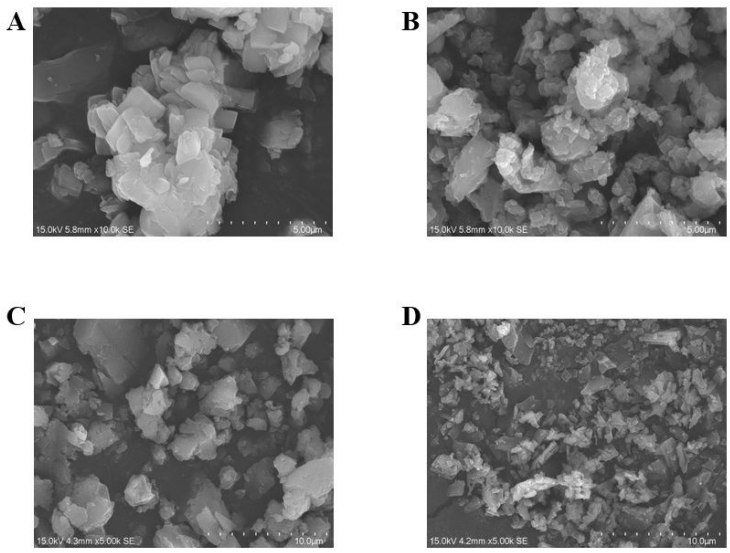
(Em-maxim um emission wavelength, φ_f-quantum yield, τ-fluorescence lifetime, k_r-radiation constant, k_{nr}-non-radiation rate constant, $\varphi_f = k_r/(k_r+k_{nr})$, $\tau = (k_r+k_{nr})^{-1}$)



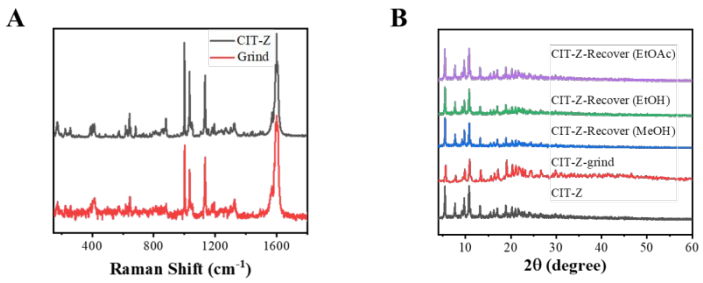
S15. The as-prepared, partially-ground and well-ground CIT-E (A) in daylight and (B) under UV light irradiation. (C) XRD spectra, D) fluorescence emission spectra (Ex=325 nm) and E) raman spectra before and after grinding of CIT-E.



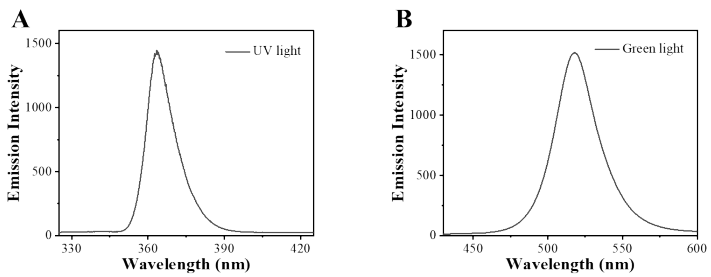
S16. Emission spectra of (A) TPE-2by-2-Z (Ex=325 nm) and (B) TPE-2by-2-E (Ex=290 nm) before and after grinding.



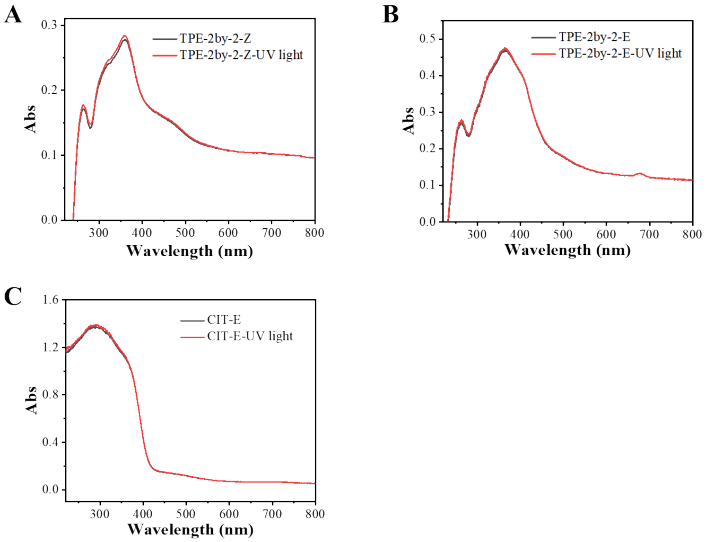
S17. SEM images of CIT-Z (A) before and (B) after grinding; SEM images of CIT-E (C) before and (D) after grinding.



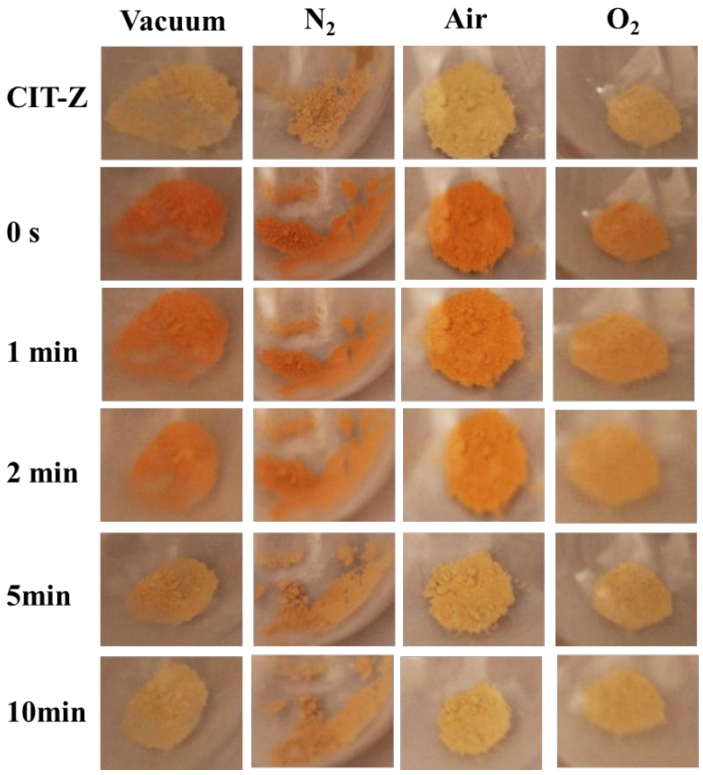
S18. (A) Raman spectra; (B) XRD spectra of CIT-Z before and after grinding.



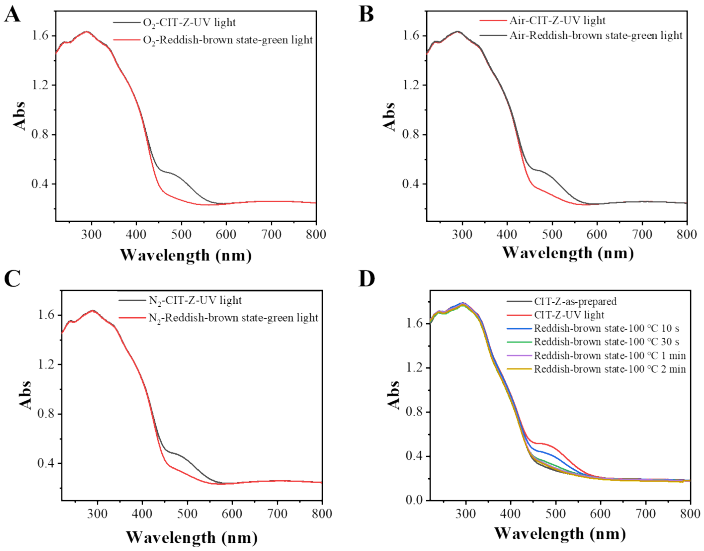
S19. Emission spectra of (A) UV light and (B) green light.



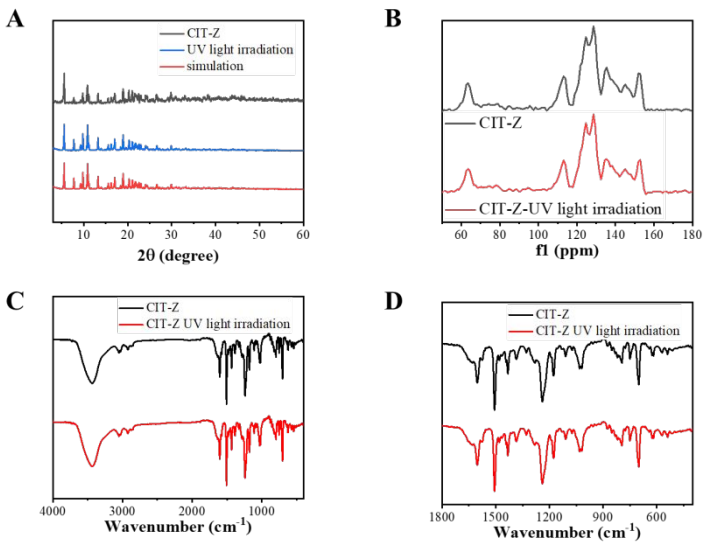
S20. UV-vis absorption spectra of (A) TPE-2by-2-Z, (A) TPE-2by-2-E and (D) CIT-E before and after irradiation.



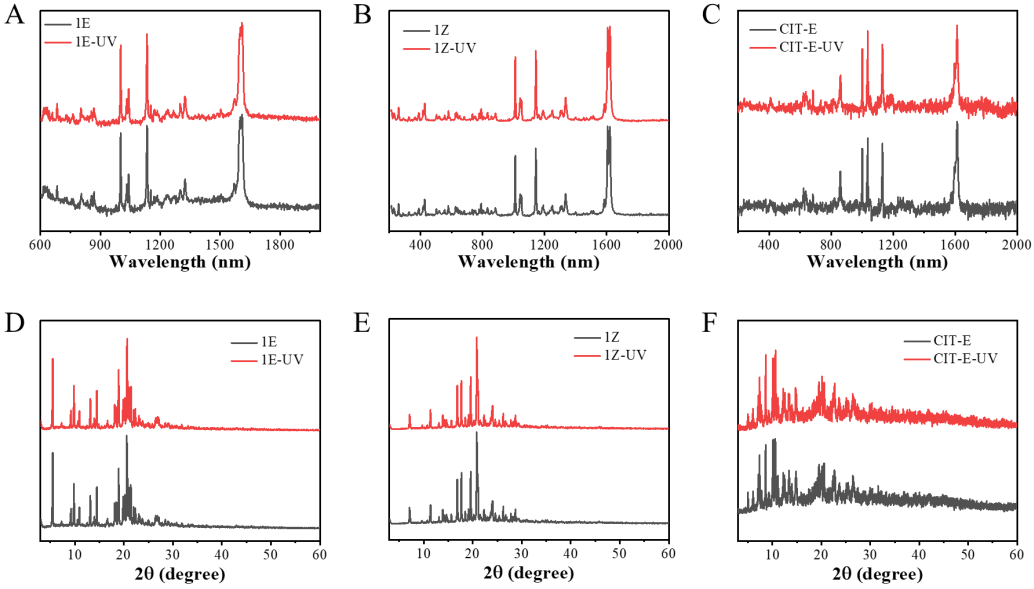
S21. The recovery of CIT-Z in different atmospheres without green light irradiated.



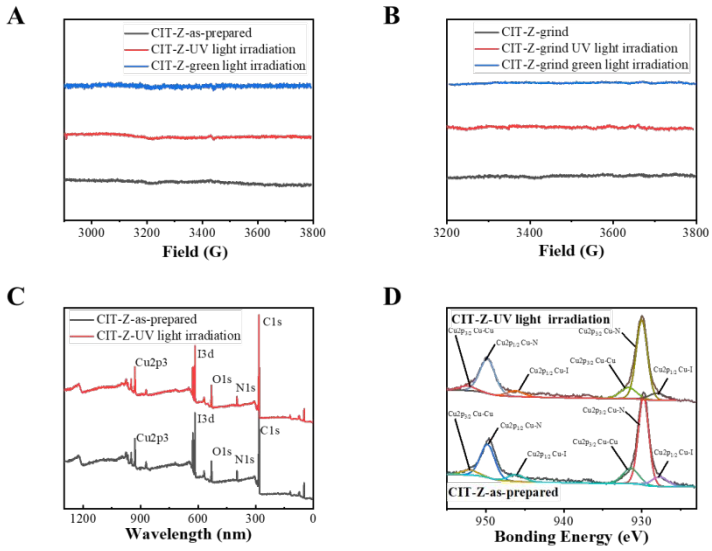
S22. The recovery of CIT-Z in (A) O_2、(B) Air、(C) N_2 atmospheres. (D) The influence of temperature on the recovery of CIT-Z.



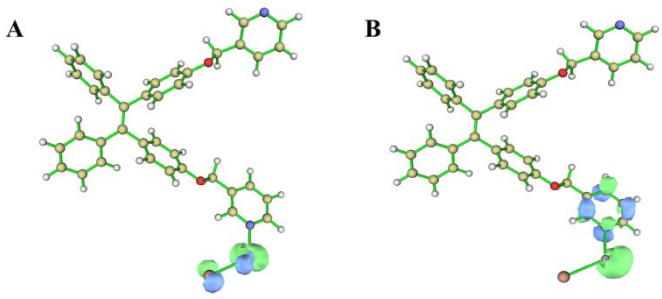
S23. (A)XRD spectra, (B)Solid-state ^{13}C NMR spectra and (C) FT-IR spectra of CIT-Z before and after UV light irradiation.



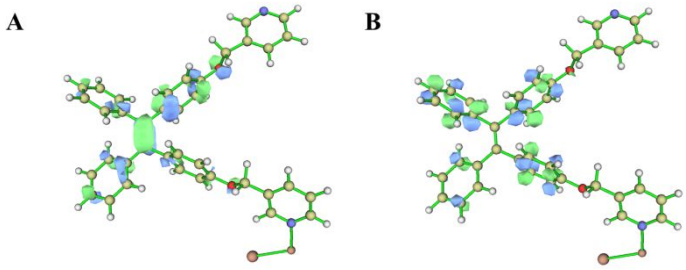
S24. Raman spectra of (A) 1E, (B) 1Z and (C) CIT-E before and after irradiation. XRD spectra of (D) 1E, (E) 1Z and (F) CIT-E before and after irradiation.



S25. CIT-Z (A) as made and (B) grind EPR spectra before and after irradiation, (C) XPS spectra of CIT-Z and D) Cu 2p XPS peak fitting spectra.



S26. (A) NTO analysis [4] and the corresponding (A) HOMO and (B) LUMO orbitals electron densities of CIT-Z band 1.



S27. NTO analysis and the corresponding (A) HOMO and (B) LUMO orbitals electron densities of CIT-Z band 2.

Table S3. Simulated electronic transitions of CIT-Z obtained from TD-DFT.

Compound	Absorption Band 1	Absorption Band 2
CIT-Z	260.68 nm (f=0.0808) HOMO-14→LUMO+3 3.05% HOMO-11→LLUMO+4 5.40% HOMO-10→LUMO+3 29.46% HOMO-2→LUMO+7 3.39% HOMO-2→LUMO+9 41.13% HOMO-2→LUMO+11 11.83%	322.08 nm (f=0.0261) HOMO-9→LUMO 18.10% HOMO-6→LUMO+1 15.76% HOMO-8→LUMO 4.26% HOMO-8→LUMO+1 32.32% HOMO-5→LUMO 8.69% HOMO-5→LUMO+1 2.60% HOMO-4→LUMO+1 10.65% HOMO-4→LUMO+3 1.14%

Table S4. Simulated electronic transitions of CIT-Z before and after irradiation obtained from TD-DFT.

Compound	CIT-Z	CIT-Z-UV light irradiation
Absorption band 3	439.67 nm (f=0.0041) HOMO-3→LUMO 96.21%	439.24 nm (f=0.0156) HOMO-3→LUMO 66.79% HOMO-1→LUMO 4.10% HOMO-1→LUMO+1 17.27%

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