Supplementary Information (SI) for Journal of Materials Chemistry C.

Supporting Information

Ultralong Room Temperature Phosphorescence in Cd-MOFs Regulated by the Multimode Coordination Configuration of Niacin Ligand

Zheng Wang,[a] Chen-Qi Li,[a] Jia-Yu Zhu,[a] Xin-Qi Chen[a], Meng-Yang Li[b] and Dan Wang*[a]

[a] Key Laboratory of Chemical Additives for China National Light Industry, College of Chemistry and Chemical Engineering, Shaanxi University of Science & Technology, Xi'an 710021, People's Republic of China.

[b] School of Physics, Xidian University, Xi'an 710071, China.

Corresponding author:

E-mail address:

wangdan0919@163.com (D. Wang)

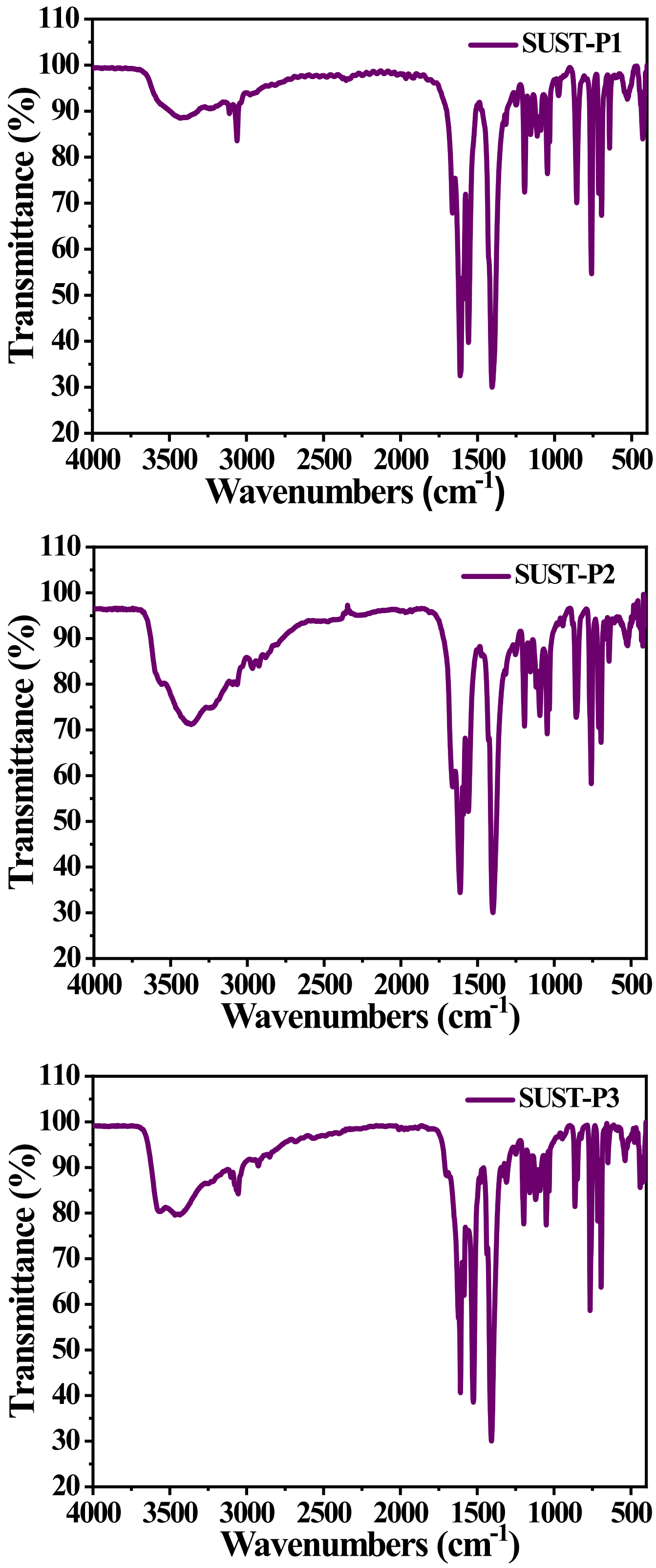

Figure S1. FT-IR spectra of SUST-P1, SUST-P2 and SUST-P3.

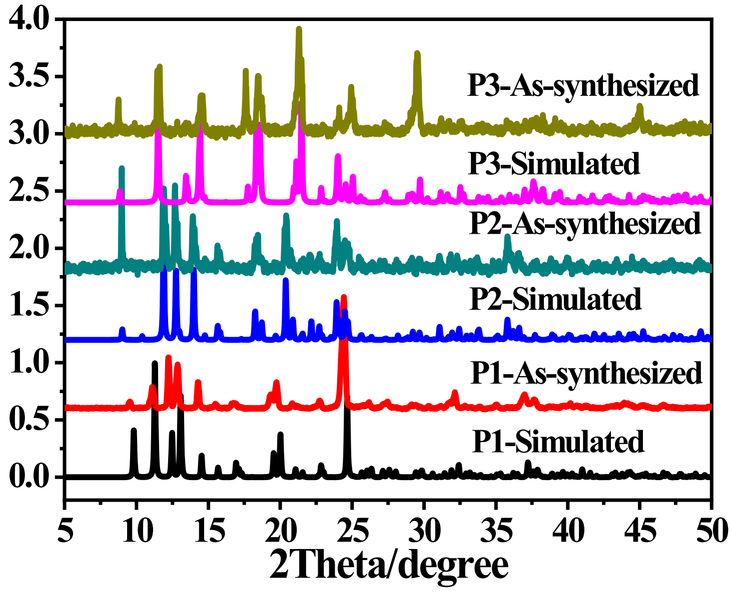

Figure S2. PXRD pattern of SUST-P1, SUST-P2 and SUST-P3: as-synthesized and simulated.

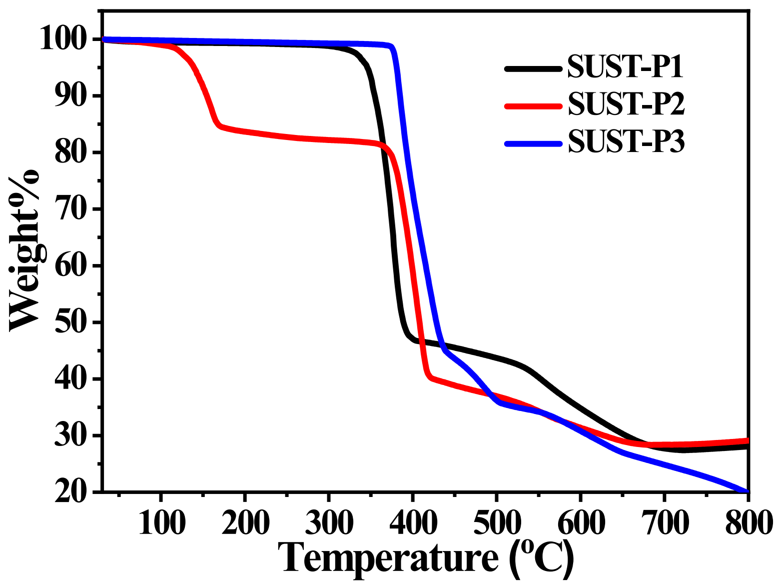

Figure S3. TGA curves of SUST-P1, SUST-P2 and SUST-P3.

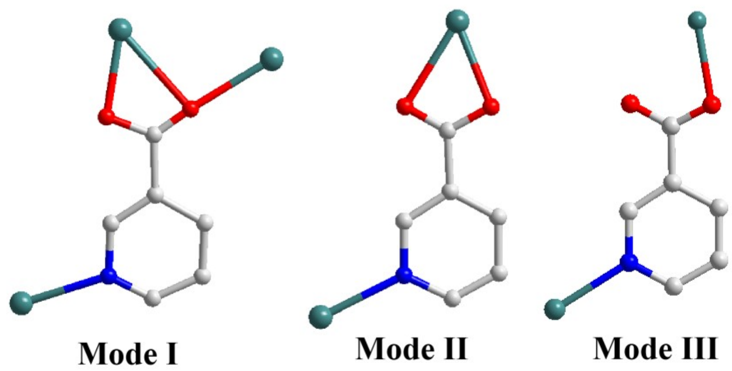

Figure S4. The coordination modes of SUST-P1~3.

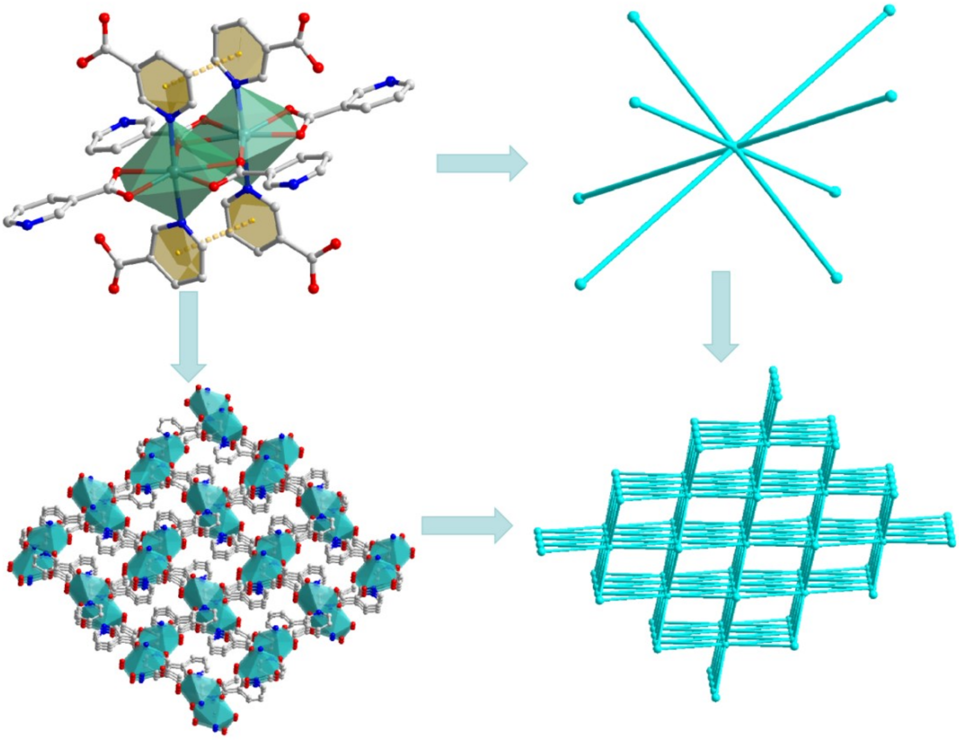

Figure S5. The 3D framework and simplified network of SUST-P1.

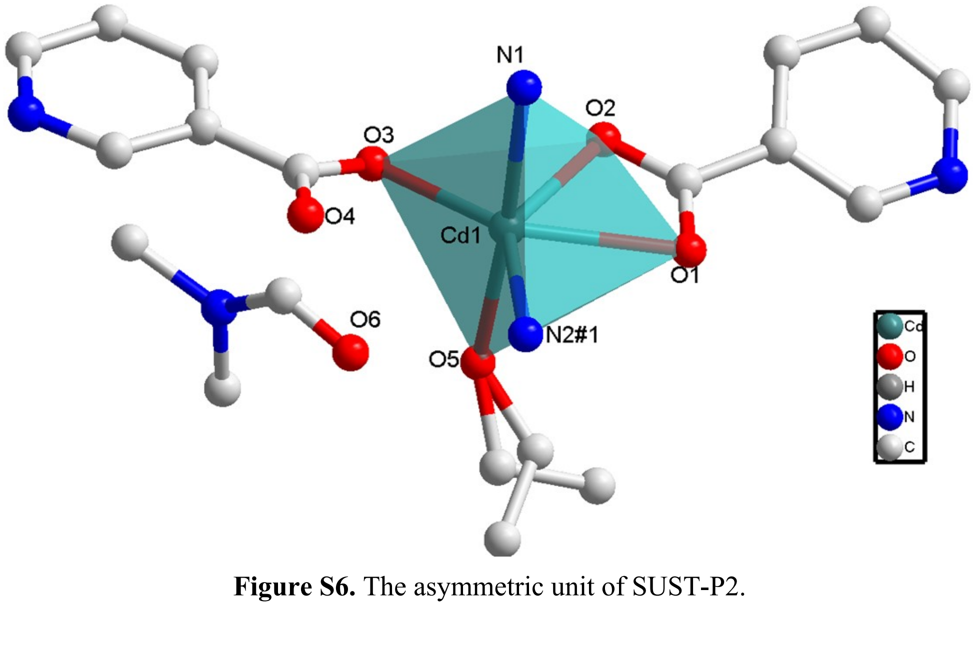

Figure S6. The asymmetric unit of SUST-P2.

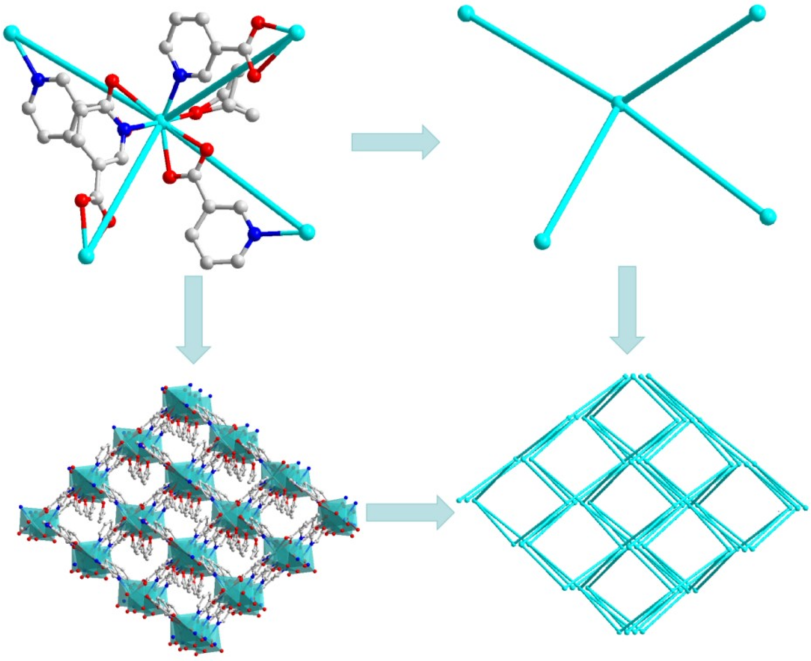

Figure S7. The 3D framework and simplified network of SUST-P2.

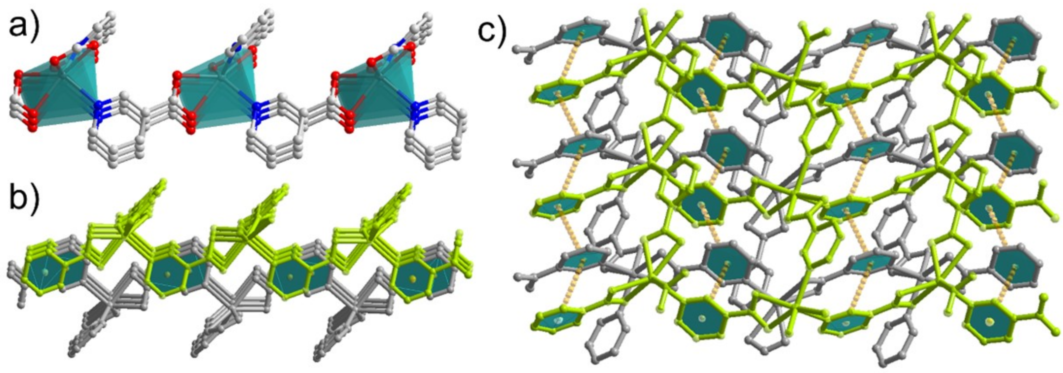

Figure S8. a) 2D framework structure of SUST-P3. b, c) Intermolecular π-π interactions in SUST-P3.

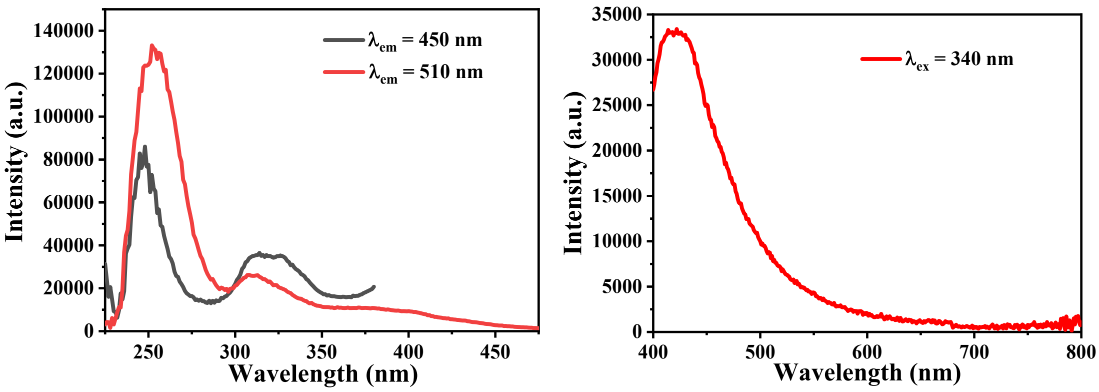

Figure S9. The excitation (λ_{em} = 450 nm or 510 nm) and emission (λ_{ex} =340 nm) spectra of solid HL at room temperature.

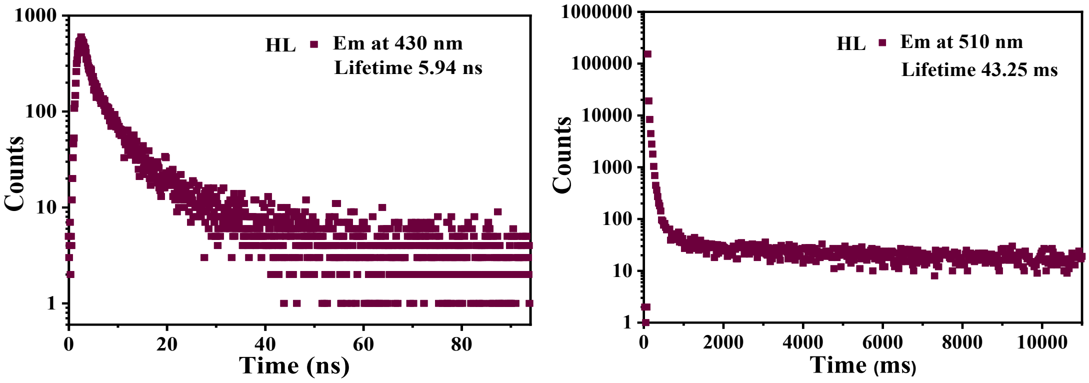

Figure S10. The decay profile for HL in the solid state at room temperature. Emission wavelength were set at 430 nm and 510 nm.

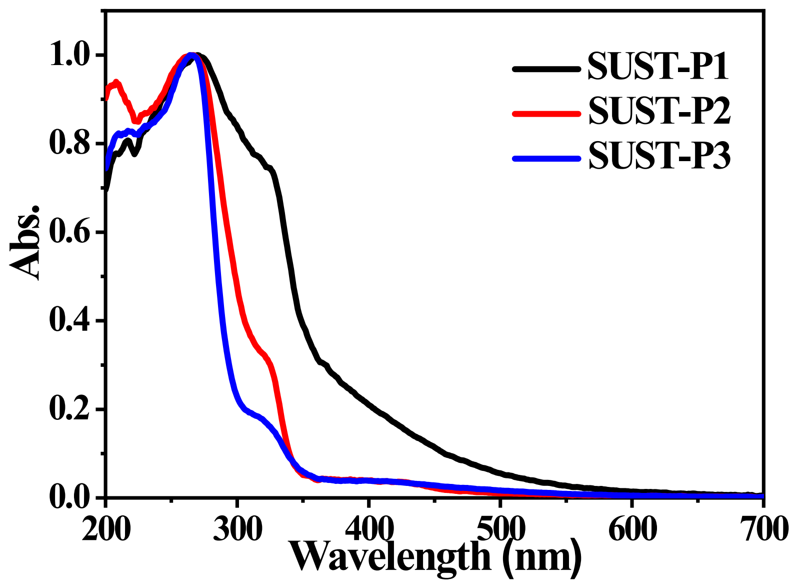

Figure S11. Solid UV-Vis absorption spectra of SUST-P1, SUST-P2 and SUST-P3.

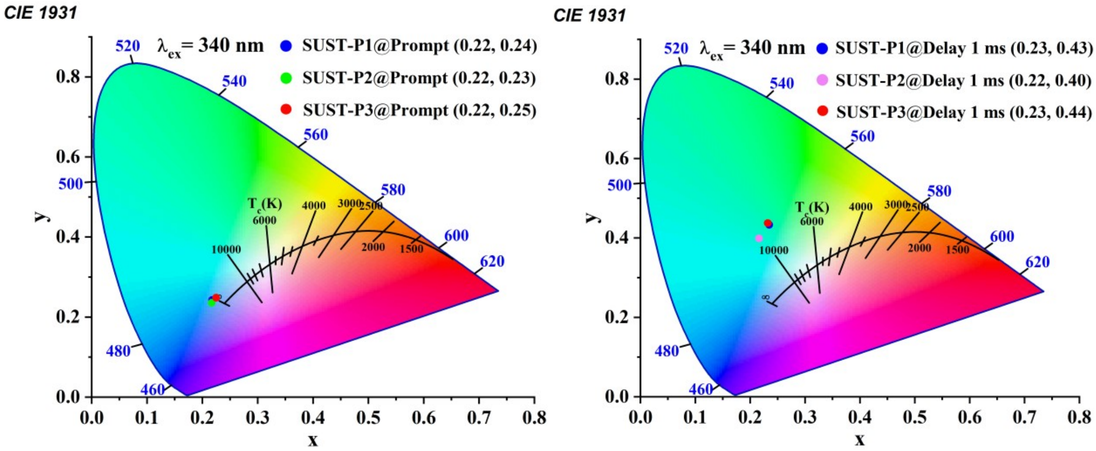

Figure S12. The CIE coordinates corresponding to the prompt and delayed (1 ms) photoluminescence spectra (λ_{ex} = 340 nm).

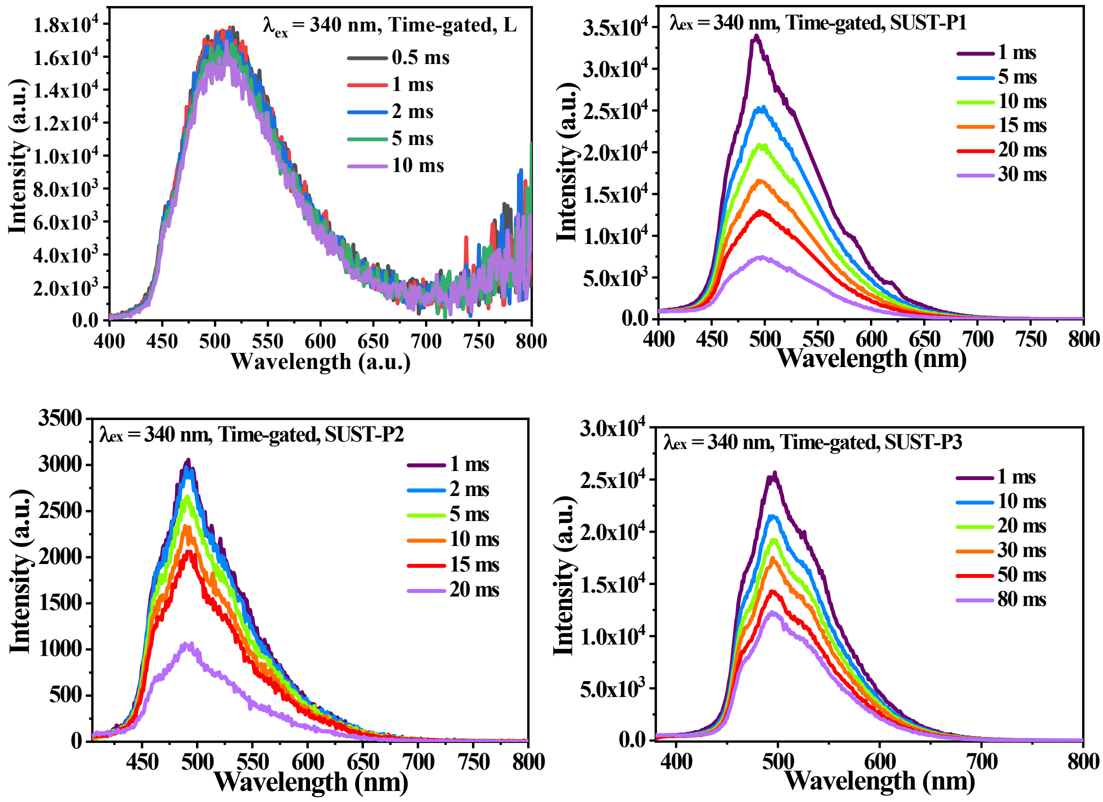

Figure S13. Time-dependent delayed spectra of SUST-P1, SUST-P2 and SUST-P3.

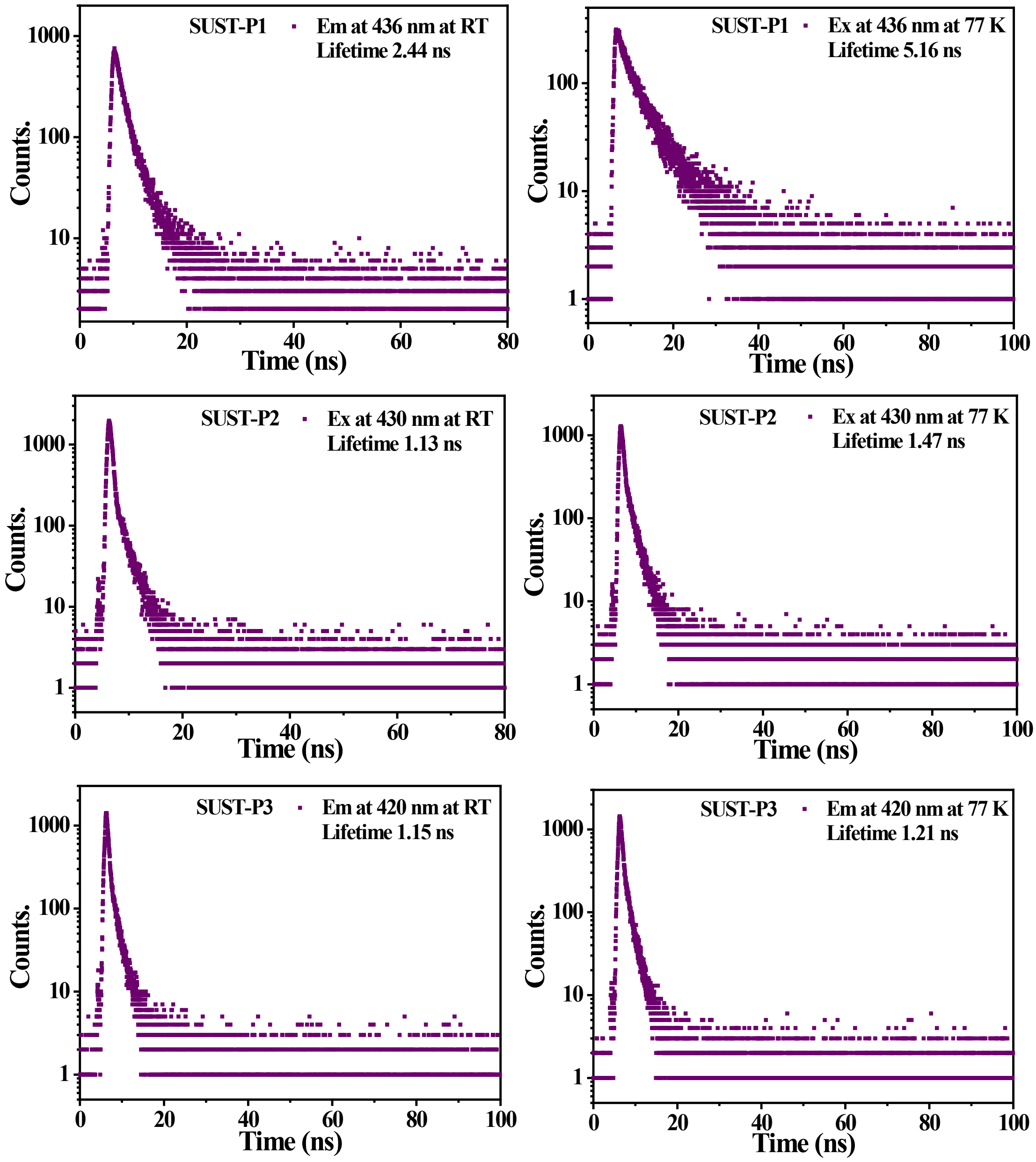

Figure S14. Under RT and 77 K, the decay curves of SUST-P1, SUST-P2 and SUST-P3 at 436, 430 and 420 nm, respectively.

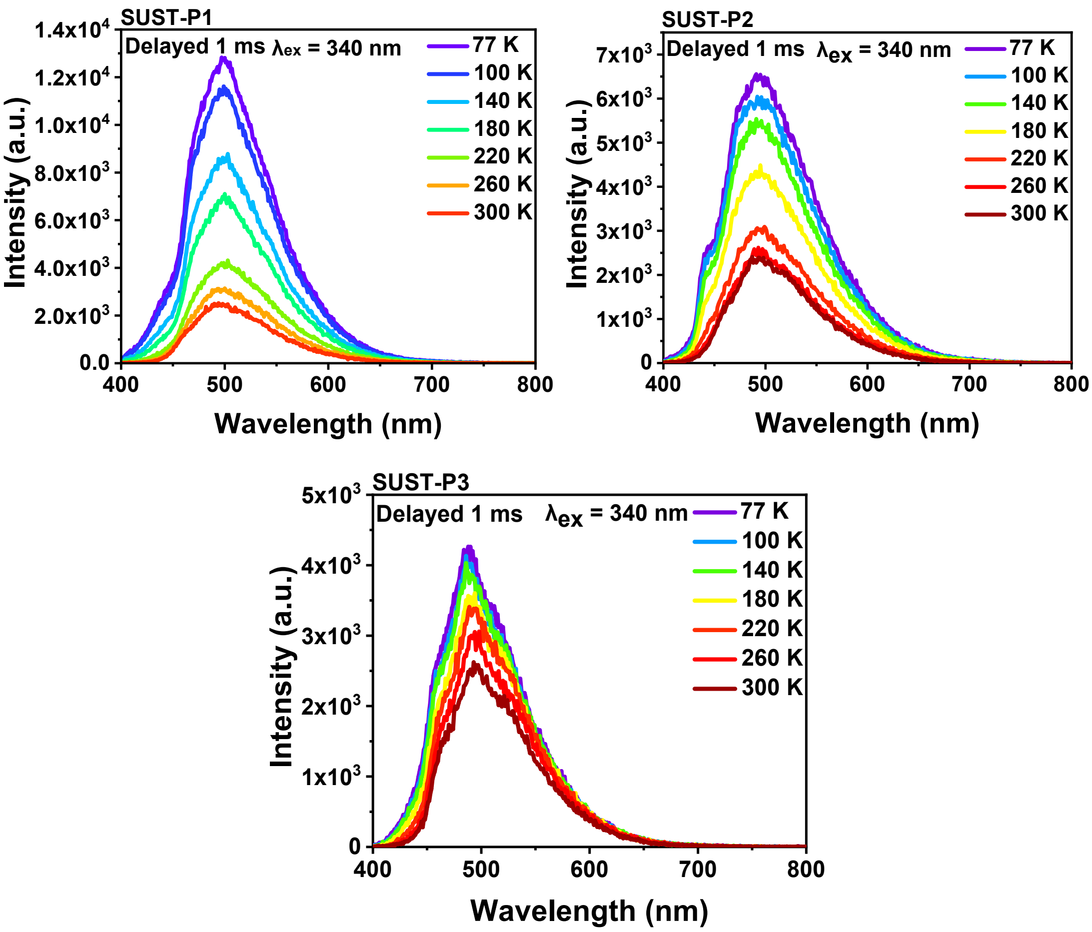

Figure S15. Temperature-dependent delayed spectra (delay 1 ms) of SUST-P1~P3 as the temperature dropped from 300 K to 77 K under 340 nm excitation.

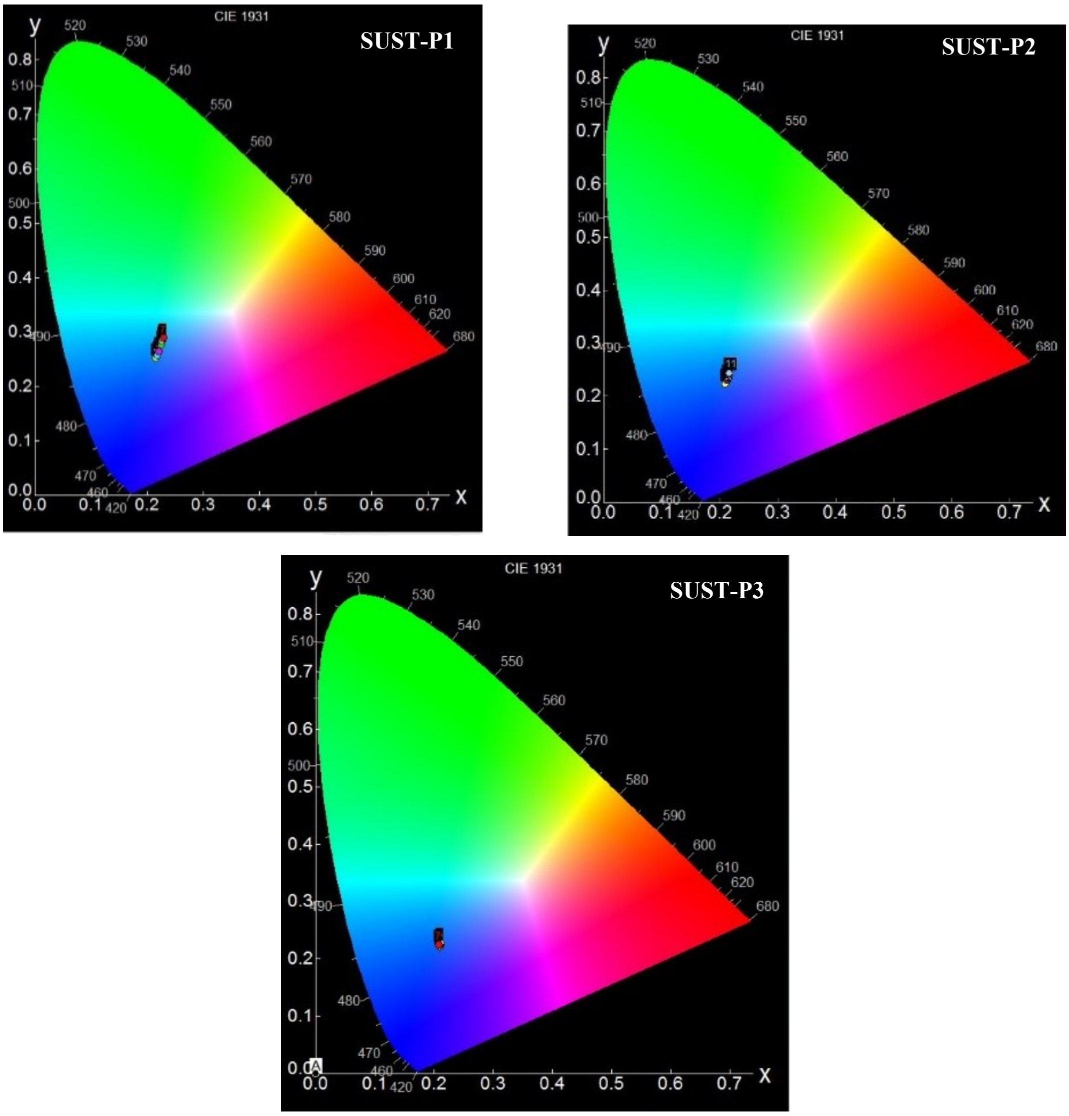

Figure S16. CIE coordinates corresponded to temperature-dependent prompt emissions of SUST-P1, SUST-P2 and SUST-P3 from 77 to 300 K in solid state.

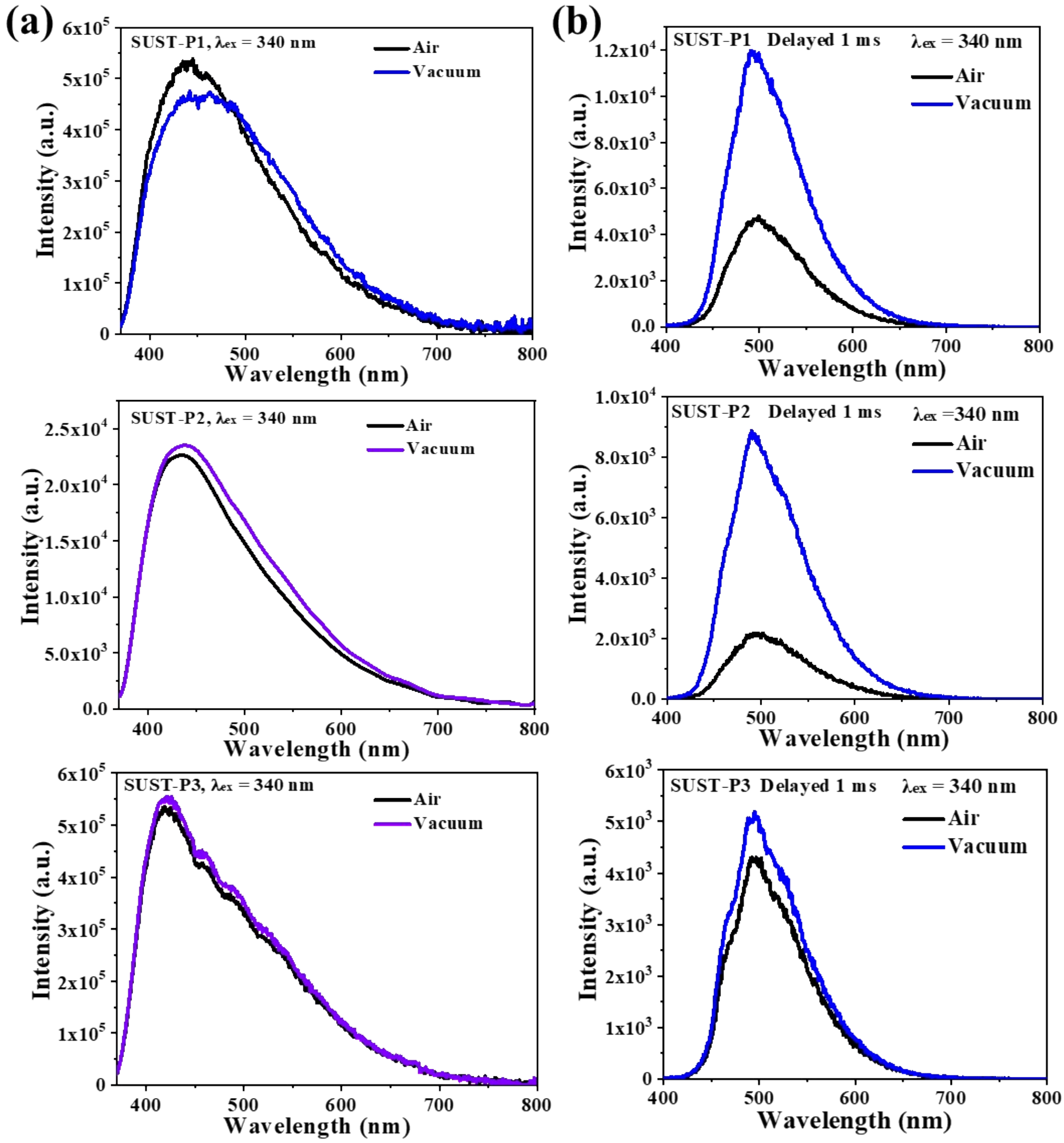

Figure S17. (a) The emission spectra of SUST-P1, SUST-P2 and SUST-P3 in air and vacuum at RT. (b) The delayed spectra of the three MOFs in air and vacuum at RT.

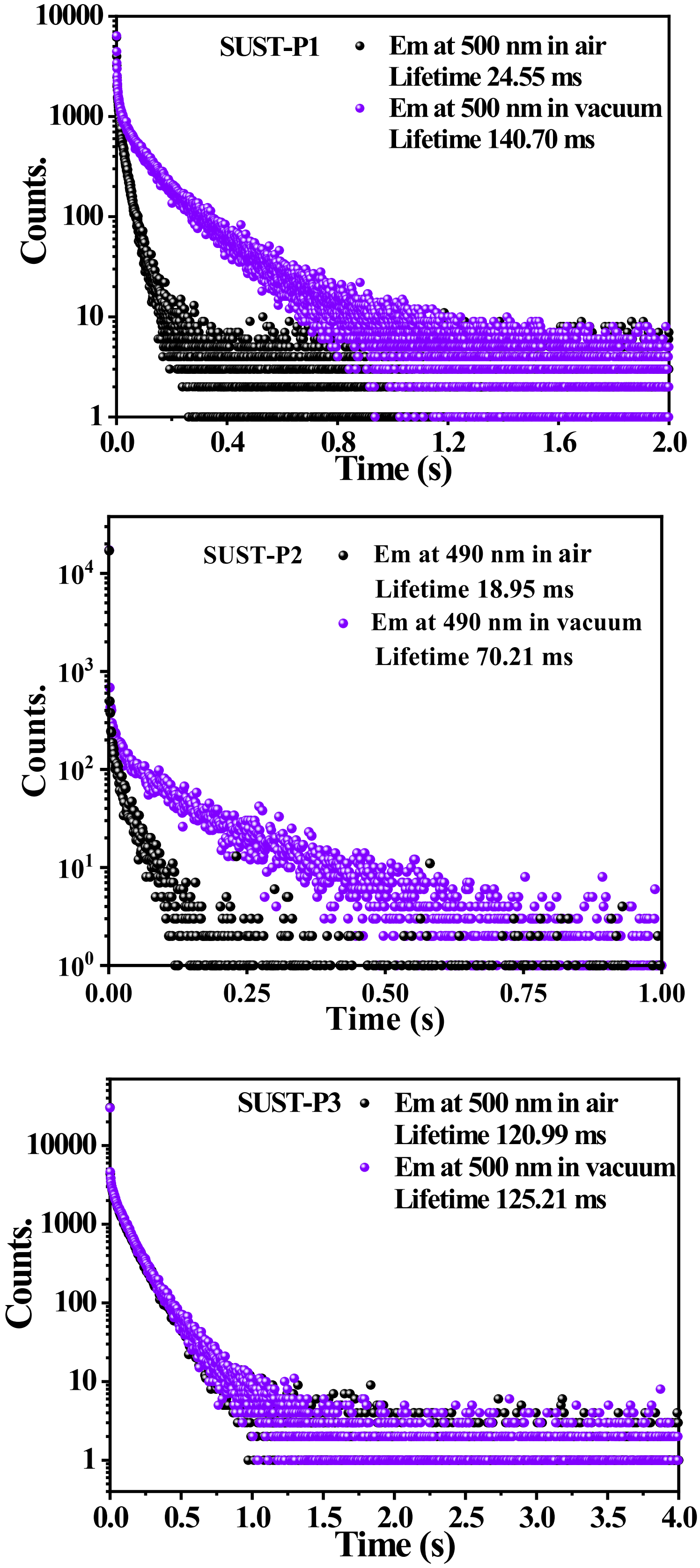

Figure S18. The decay curves of SUST-P1, SUST-P2 and SUST-P3 in air and vacuum at RT.

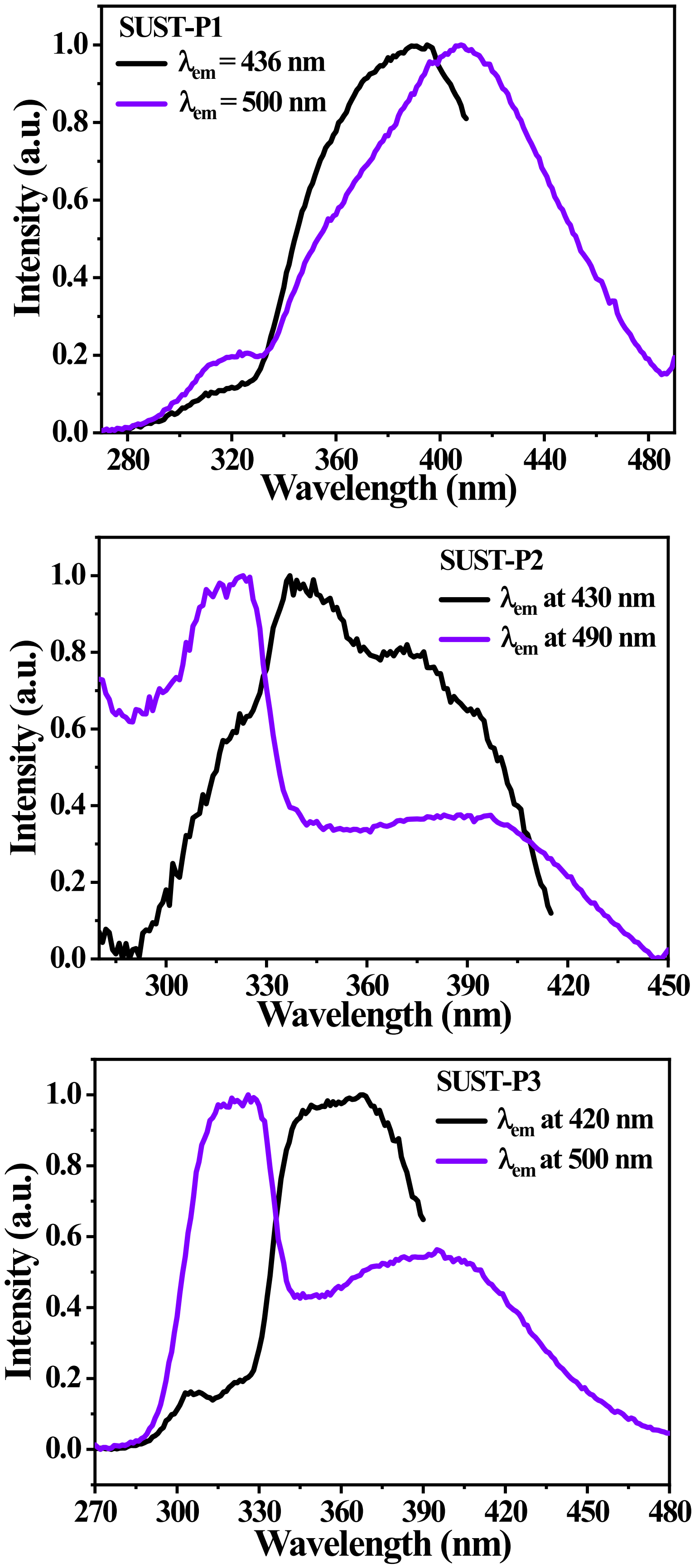

Figure S19. The excitation spectra of SUST-P1, SUST-P2 and SUST-P3 (room temperature, solid state).

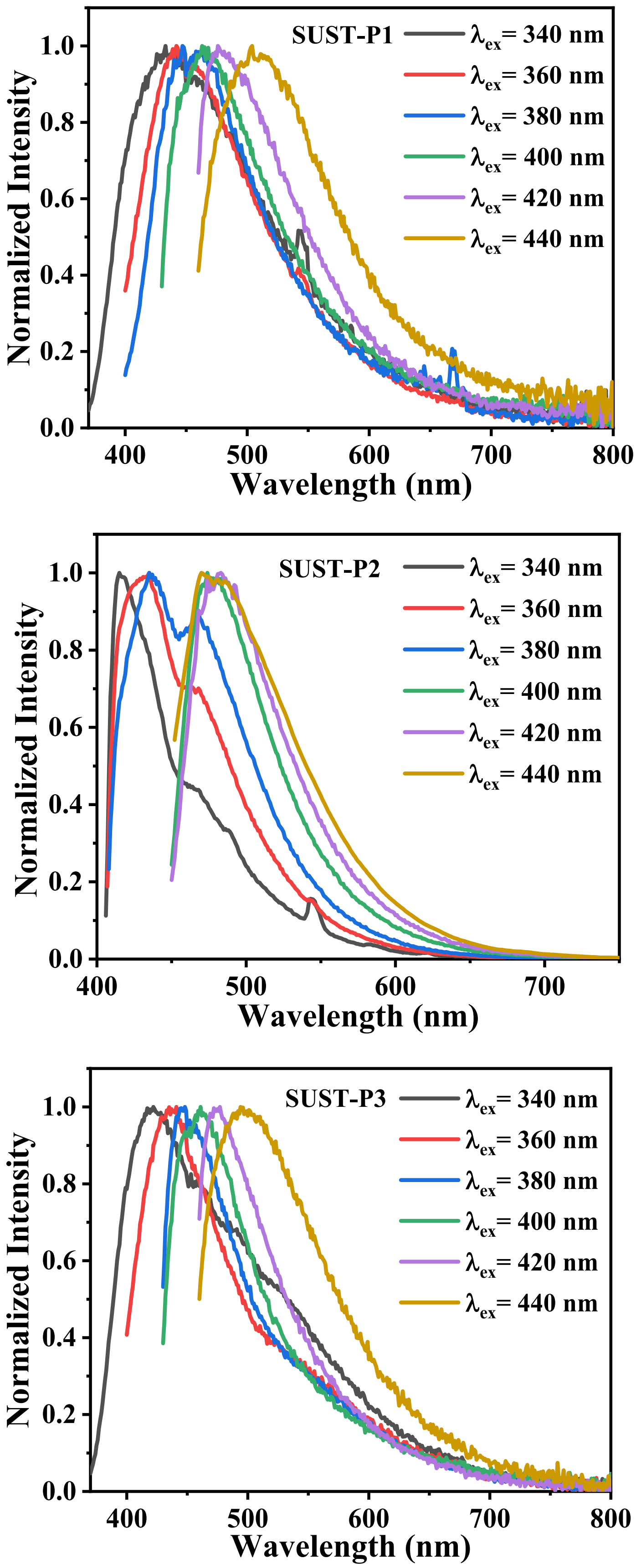

Figure S20. Excitation wavelength-dependent prompt emission spectra of SUST-P1, SUST-P2 and SUST-P3, respectively.

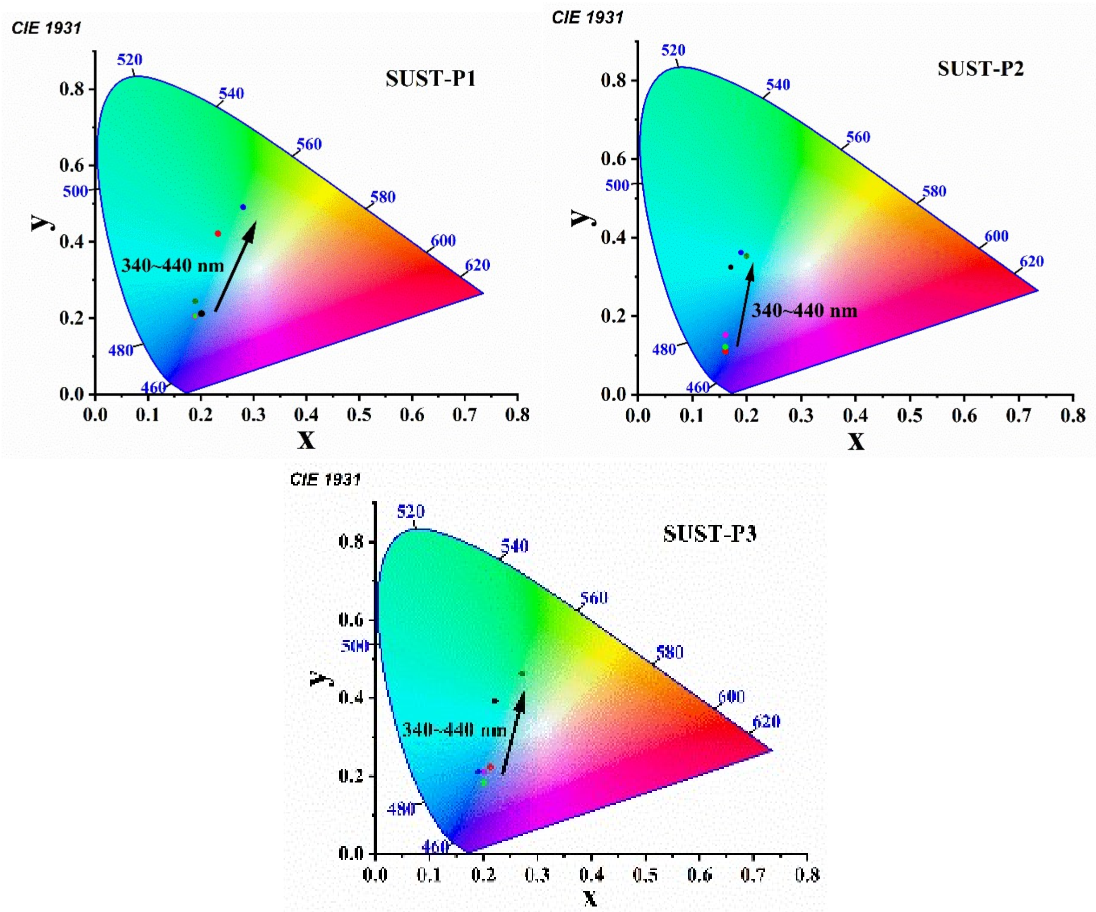

Figure S21. The CIE coordinates of SUST-P1, SUST-P2 and SUST-P3 corresponded to the excitation wavelength-dependent prompt emission spectra.

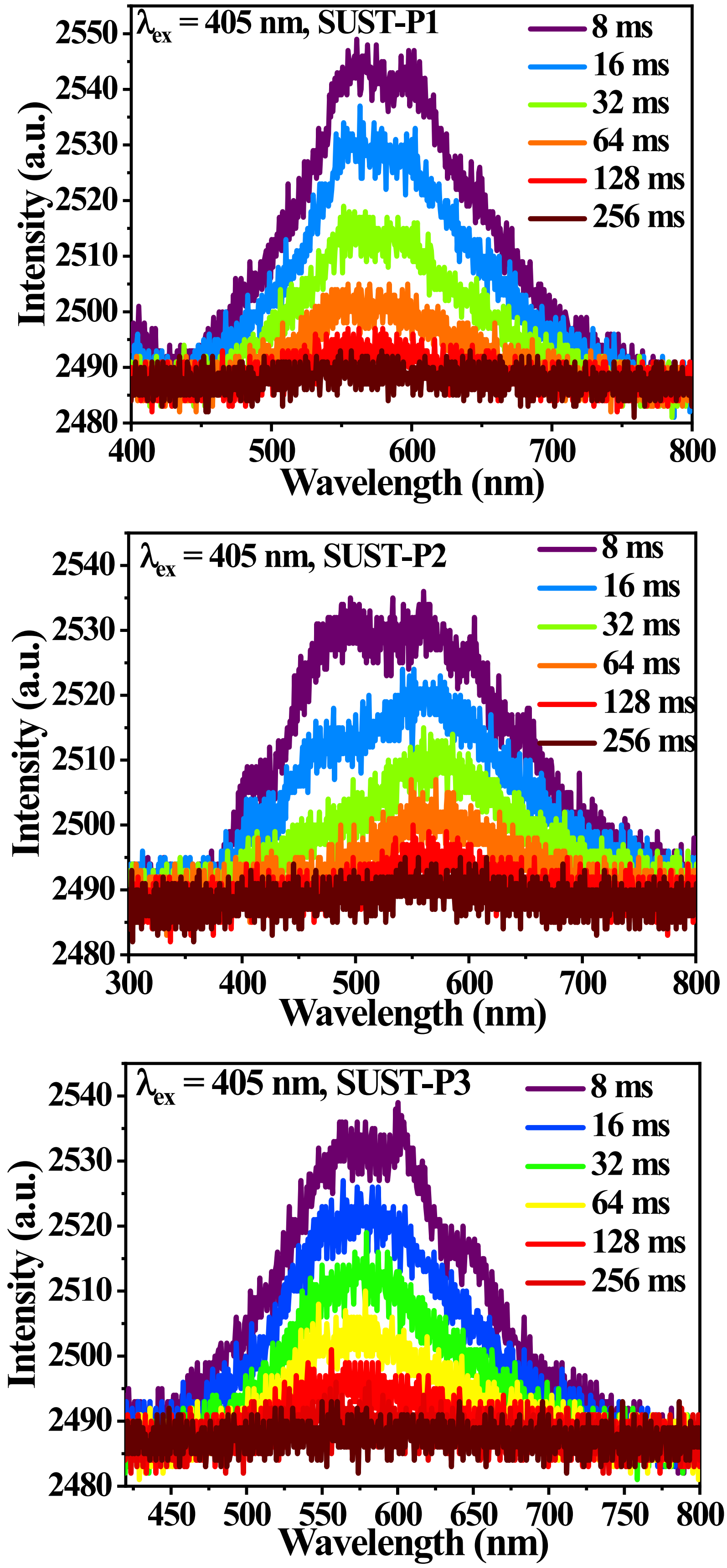

Figure S22. Long persistent luminescence (LPL) of SUST-P1, SUST-P2 and SUST-P3 upon the excitation at 405 nm.

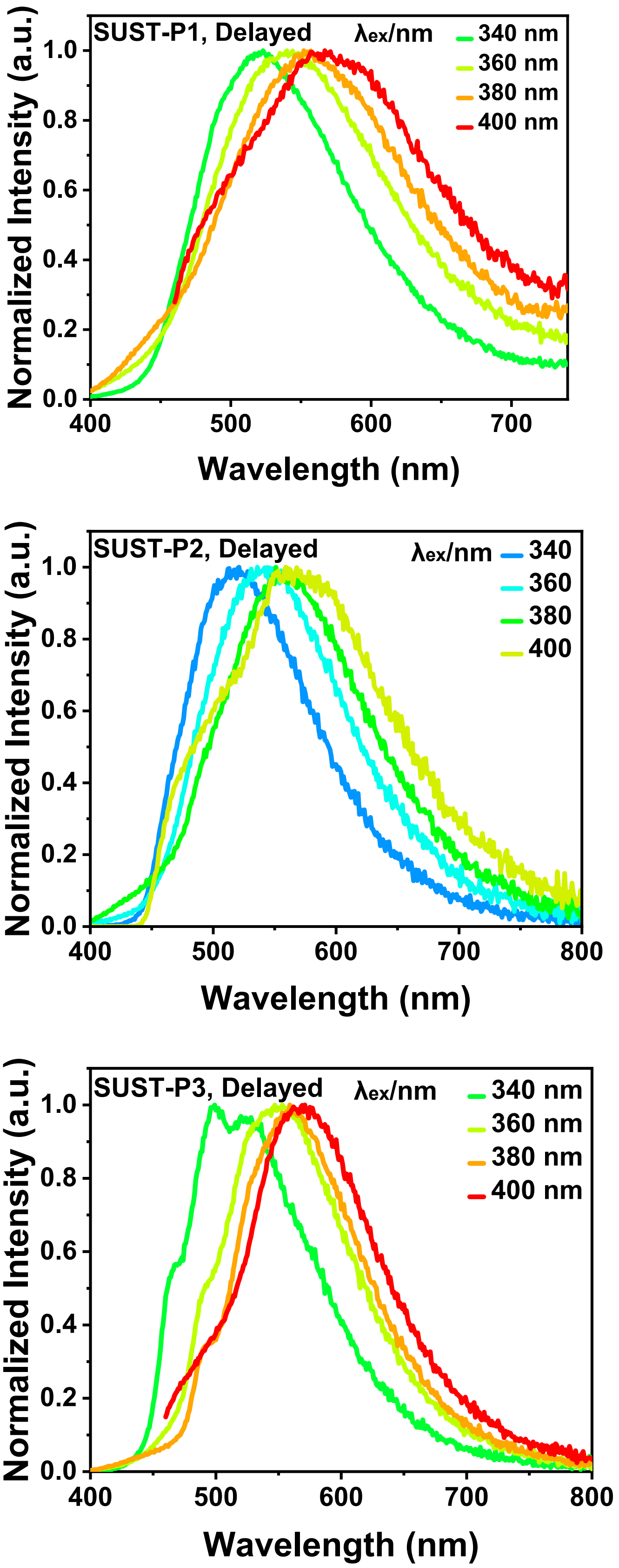

Figure S23. Excitation-dependent delayed emission spectra of SUST-P1, SUST-P2 and SUST-P3, respectively.

Table S1. Summary of X-ray crystallographic data for the three MOFs.

Identification code	**SUST-P1**	**SUST-P2**	**SUST-P3**
Empirical formula	$C_{12}H_8CdN_2O_4$	$C_{17}H_{21}CdN_3O_6$	$C_{12}H_8CdN_2O_4$
Formula weight	356.60	475.77	356.60
Temperature/K	240(2)	240.00(10)	240.00(10)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$Pna2_1$	$P2_1/n$
a/Å	10.2408(19)	16.9934(5)	12.4315(11)
b/Å	10.1860(19)	11.9880(4)	7.7773(5)
c/Å	12.705(2)	9.4740(3)	12.7689(8)
α/°	90	90	90
β/°	106.677(19)	90	104.875(8)
γ/°	90	90	90
Volume/$Å^3$	1269.5(4)	1930.01(10)	1193.17(16)
Z	4	4	4
$\rho_{calc}g/cm^3$	1.866	1.637	1.985
μ/mm^{-1}	13.909	9.406	14.800
F(000)	696.0	960.0	696.0
Crystal size/mm^3	0.170 × 0.120 × 0.080	0.17 × 0.13 × 0.11	0.13 × 0.1 × 0.05
Radiation	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)	CuKα (λ = 1.54184)
2Θ range for data collection/°	11.328 to 133.15	9.028 to 133.184	8.856 to 132.01
Index ranges	$-12 \leq h \leq 12$, $-12 \leq k \leq 11$, $-15 \leq l \leq 10$	$-19 \leq h \leq 20$, $-8 \leq k \leq 14$, $-11 \leq l \leq 7$	$-14 \leq h \leq 14$, $-6 \leq k \leq 9$, $-15 \leq l \leq 13$
Reflections collected	4002	3667	3263
Independent reflections	2215 [R_{int} = 0.0921, R_{sigma} = 0.0830]	2337 [R_{int} = 0.0369, R_{sigma} = 0.0591]	2057 [R_{int} = 0.0318, R_{sigma} = 0.0396]
Data/restraints/parameters	2215/0/172	2337/269/261	2057/0/172
Goodness-of-fit on F^2	1.113	1.022	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0974, wR_2 = 0.2167	R_1 = 0.0364, wR_2 = 0.0860	R_1 = 0.0442, wR_2 = 0.1231
Final R indexes [all data]	R_1 = 0.1134, wR_2 = 0.2246	R_1 = 0.0443, wR_2 = 0.0930	R_1 = 0.0504, wR_2 = 0.1306
Largest diff. peak/hole / e $Å^{-3}$	2.23/-1.71	0.66/-0.69	1.72/-1.17
Flack parameter		0.024(16)	

Table S2. Selected bond distances (Å) and bond angles (°) for the three MOFs.

SUST-P1							
Cd1	O2		2.220(7)	N1	Cd1^{4}		2.321(7)
Cd1	O3		2.293(7)	N2	C7		1.339(12)
Cd1	N1^{1}		2.321(7)	N2	C11		1.356(13)
Cd1	N2^{2}		2.324(8)	N2	Cd1^{5}		2.324(8)
Cd1	O1^{3}		2.392(7)	C1	C2		1.367(16)
Cd1	O4		2.492(8)	C2	C3		1.373(14)
Cd1	C12		2.730(11)	C3	C4		1.445(15)
O1	C6		1.135(12)	C4	C5		1.333(14)
O1	Cd1^{3}		2.392(7)	C4	C6		1.534(13)
O2	C6		1.276(13)	C7	C8		1.323(14)
O3	C12		1.260(13)	C8	C9		1.397(15)
O4	C12		1.225(12)	C9	C10		1.361(12)
N1	C1		1.259(14)	C10	C11		1.370(13)
N1	C5		1.349(12)	C10	C12		1.527(14)
O2	Cd1	O3	146.7(3)	C5	N1	Cd1^{4}	111.5(6)
O2	Cd1	N1^{1}	88.6(3)	C7	N2	C11	116.1(8)
O3	Cd1	N1^{1}	91.3(3)	C7	N2	Cd1^{5}	127.2(7)
O2	Cd1	N2^{2}	92.0(3)	C11	N2	Cd1^{5}	116.7(6)
O3	Cd1	N2^{2}	91.6(3)	N1	C1	C2	128.1(9)
N1^{1}	Cd1	N2^{2}	173.8(3)	C1	C2	C3	116.5(10)
O2	Cd1	O1^{3}	130.4(3)	C2	C3	C4	118.2(10)
O3	Cd1	O1^{3}	82.8(2)	C5	C4	C3	116.1(9)
N1^{1}	Cd1	O1^{3}	88.0(3)	C5	C4	C6	121.8(10)
N2^{2}	Cd1	O1^{3}	86.9(3)	C3	C4	C6	121.8(8)
O2	Cd1	O4	92.8(3)	C4	C5	N1	125.9(10)
O3	Cd1	O4	53.9(2)	O1	C6	O2	123.4(9)
N1^{1}	Cd1	O4	90.7(3)	O1	C6	C4	123.9(10)
N2^{2}	Cd1	O4	95.4(3)	O2	C6	C4	112.7(8)
O1^{3}	Cd1	O4	136.7(2)	C8	C7	N2	125.5(10)
O2	Cd1	C12	119.4(3)	C7	C8	C9	117.6(9)
O3	Cd1	C12	27.3(3)	C10	C9	C8	119.5(10)
N1^{1}	Cd1	C12	90.0(3)	C9	C10	C11	118.9(10)
N2^{2}	Cd1	C12	95.0(3)	C9	C10	C12	121.5(9)
O1^{3}	Cd1	C12	110.1(3)	C11	C10	C12	119.7(8)
O4	Cd1	C12	26.6(3)	N2	C11	C10	122.3(8)
C6	O1	Cd1^{3}	174.4(7)	O4	C12	O3	122.3(10)
C6	O2	Cd1	101.3(6)	O4	C12	C10	121.0(10)
C12	O3	Cd1	96.0(6)	O3	C12	C10	116.6(8)

C12	O4	Cd1	87.6(7)	O4	C12	Cd1	65.8(6)
C1	N1	C5	115.1(8)	O3	C12	Cd1	56.7(5)
C1	N1	Cd1[4]	132.7(6)	C10	C12	Cd1	169.4(6)
			SUST-P2				
Cd1	O2		2.332(5)	N2	C7		1.339(11)
Cd1	O1		2.483(7)	C1	C2		1.358(13)
Cd1	O3		2.244(7)	C11	C10		1.382(12)
Cd1	O5		2.332(8)	C7	C8		1.388(13)
Cd1	N11		2.377(7)	C3	C2		1.388(12)
Cd1	N22		2.322(7)	C3	C4		1.386(12)
Cd1	C6		2.737(9)	C12	C10		1.509(12)
O2	C6		1.263(11)	C8	C9		1.376(12)
O4	C12		1.244(12)	C10	C9		1.393(13)
O1	C6		1.245(11)	C4	C6		1.505(12)
O3	C12		1.259(13)	C4	C5		1.396(13)
O5	C13		1.42(2)	C14	C13		1.50(2)
O5	C13A		1.42(2)	C14A	C13A		1.48(2)
N1	Cd13		2.377(7)	O6	C15		1.199(18)
N1	C1		1.326(11)	N3	C17		1.408(19)
N1	C5		1.328(11)	N3	C16		1.49(2)
N2	Cd14		2.322(7)	N3	C15		1.291(15)
N2	C11		1.337(10)				
O2	Cd1	O1	54.4(2)	C7	N2	Cd14	119.4(5)
O2	Cd1	N11	86.9(3)	N1	C1	C2	123.6(9)
O2	Cd1	C6	27.4(2)	N2	C11	C10	122.7(8)
O1	Cd1	C6	27.0(2)	N2	C7	C8	121.9(8)
O3	Cd1	O2	87.2(3)	C4	C3	C2	117.7(9)
O3	Cd1	O1	140.0(3)	O4	C12	O3	124.9(9)
O3	Cd1	O5	83.3(3)	O4	C12	C10	118.9(9)
O3	Cd1	N11	93.0(3)	O3	C12	C10	116.2(8)
O3	Cd1	N22	132.7(3)	C1	C2	C3	119.5(9)
O3	Cd1	C6	114.1(3)	C9	C8	C7	119.3(9)
O5	Cd1	O2	94.7(3)	C11	C10	C12	121.6(8)
O5	Cd1	O1	88.8(3)	C11	C10	C9	118.5(8)
O5	Cd1	N11	175.9(3)	C9	C10	C12	119.8(8)
O5	Cd1	C6	92.8(3)	C3	C4	C6	121.0(8)
N11	Cd1	O1	95.2(3)	C3	C4	C5	118.6(8)
N11	Cd1	C6	90.4(3)	C5	C4	C6	120.4(8)
N22	Cd1	O2	140.1(2)	O2	C6	Cd1	58.2(4)

N22	Cd1	O1	86.4(2)	O2	C6	C4	117.4(8)
N22	Cd1	O5	91.0(3)	O1	C6	Cd1	65.0(5)
N22	Cd1	N11	90.1(2)	O1	C6	O2	123.1(8)
N22	Cd1	C6	113.0(3)	O1	C6	C4	119.5(8)
C6	O2	Cd1	94.5(5)	C4	C6	Cd1	174.3(6)
C6	O1	Cd1	87.9(5)	C8	C9	C10	118.8(9)
C12	O3	Cd1	106.5(6)	N1	C5	C4	122.7(9)
C13	O5	Cd1	127(2)	O5	C13	C14	117(4)
C13A	O5	Cd1	136(2)	O5	C13A	C14A	109(3)
C1	N1	Cd13	122.2(6)	C17	N3	C16	116.3(11)
C5	N1	Cd13	119.8(6)	C15	N3	C17	123.3(15)
C5	N1	C1	117.9(8)	C15	N3	C16	120.0(14)
C11	N2	Cd14	121.9(6)	O6	C15	N3	123.1(15)
C11	N2	C7	118.7(7)				

SUST-P3

Cd1	O1		2.252(4)	N1	C1		1.352(8)
Cd1	O2		2.469(5)	N1	C5		1.331(8)
Cd1	O3[1]		2.318(5)	N2	C7		1.359(8)
Cd1	O4[1]		2.394(5)	N2	C11		1.336(8)
Cd1	N1[2]		2.310(5)	C1	C2		1.390(9)
Cd1	N2		2.301(5)	C2	C3		1.378(9)
Cd1	C6		2.682(6)	C3	C4		1.389(9)
Cd1	C12[1]		2.685(6)	C4	C5		1.393(8)
O1	C6		1.252(8)	C4	C6		1.503(8)
O2	C6		1.243(8)	C7	C8		1.363(10)
O3	Cd1[3]		2.318(5)	C8	C9		1.382(9)
O3	C12		1.240(8)	C9	C10		1.389(9)
O4	Cd1[3]		2.394(5)	C10	C11		1.379(9)
O4	C12		1.256(8)	C10	C12		1.498(9)
N1	Cd1[4]		2.310(5)	C12	Cd1[3]		2.685(6)
O1	Cd1	O2	55.15(16)	C1	N1	Cd1[4]	122.4(4)
O1	Cd1	O3[1]	102.1(2)	C5	N1	Cd1[4]	118.0(4)
O1	Cd1	O4[1]	97.40(17)	C5	N1	C1	118.5(5)
O1	Cd1	N1[2]	127.88(18)	C7	N2	Cd1	120.5(4)
O1	Cd1	N2	117.2(2)	C11	N2	Cd1	120.4(4)
O1	Cd1	C6	27.68(18)	C11	N2	C7	117.8(6)
O1	Cd1	C12[1]	100.46(18)	N1	C1	C2	121.8(6)
O2	Cd1	C6	27.53(18)	C3	C2	C1	119.2(6)
O2	Cd1	C12[1]	154.96(18)	C2	C3	C4	119.2(5)

O3[1]	Cd1	O2	141.6(2)	C3	C4	C5	118.2(5)
O3[1]	Cd1	O4[1]	55.34(17)	C3	C4	C6	121.0(5)
O3[1]	Cd1	C6	125.0(2)	C5	C4	C6	120.7(5)
O3[1]	Cd1	C12[1]	27.46(18)	N1	C5	C4	123.0(5)
O4[1]	Cd1	O2	146.00(17)	O1	C6	Cd1	56.7(3)
O4[1]	Cd1	C6	122.20(18)	O1	C6	C4	118.6(5)
O4[1]	Cd1	C12[1]	27.89(18)	O2	C6	Cd1	66.7(3)
N1[2]	Cd1	O2	84.33(17)	O2	C6	O1	123.2(6)
N1[2]	Cd1	O3[1]	90.14(19)	O2	C6	C4	118.2(5)
N1[2]	Cd1	O4[1]	129.41(17)	C4	C6	Cd1	172.4(4)
N1[2]	Cd1	C6	107.59(17)	N2	C7	C8	121.8(6)
N1[2]	Cd1	C12[1]	111.32(18)	C7	C8	C9	120.0(6)
N2	Cd1	O2	89.47(19)	C8	C9	C10	118.8(6)
N2	Cd1	O3[1]	128.7(2)	C9	C10	C12	121.2(6)
N2	Cd1	O4[1]	86.55(17)	C11	C10	C9	118.0(6)
N2	Cd1	N1[2]	90.43(19)	C11	C10	C12	120.7(6)
N2	Cd1	C6	103.52(19)	N2	C11	C10	123.6(6)
N2	Cd1	C12[1]	109.11(19)	O3	C12	Cd1[3]	59.6(3)
C6	Cd1	C12[1]	128.07(19)	O3	C12	O4	122.6(6)
C6	O1	Cd1	95.6(4)	O3	C12	C10	119.2(6)
C6	O2	Cd1	85.8(4)	O4	C12	Cd1[3]	63.1(3)
C12	O3	Cd1[3]	93.0(4)	O4	C12	C10	118.2(6)
C12	O4	Cd1[3]	89.1(4)	C10	C12	Cd1[3]	174.9(5)

Table S3. The CIE coordinates of emission of SUST-P1, SUST-P2 and SUST-P3 under different temperatures.

SUST-P1			SUST-P2			SUST-P3		
Temperature (K)	X	Y	Temperature (K)	X	Y	Temperature (K)	X	Y
300	0.22	0.25	300	0.21	0.22	300	0.21	0.22
260	0.22	0.26	260	0.21	0.23	260	0.21	0.22
220	0.22	0.26	220	0.21	0.23	220	0.21	0.22
180	0.23	0.27	180	0.22	0.24	180	0.21	0.23
140	0.23	0.28	140	0.22	0.24	140	0.21	0.23
100	0.23	0.29	100	0.22	0.24	100	0.21	0.22
77	0.23	0.29	77	0.22	0.24	77	0.21	0.22

Table S4. The CIE coordinates of prompt emission of SUST-P1, SUST-P2 and SUST-P3 upon different excitations.

SUST-P1			SUST-P2			SUST-P3		
Wavelength (nm)	X	Y	Wavelength (nm)	X	Y	Wavelength (nm)	X	Y
340	0.20	0.21	340	0.16	0.11	340	0.21	0.22
360	0.19	0.20	360	0.16	0.12	360	0.20	0.18
380	0.19	0.20	380	0.16	0.15	380	0.20	0.21
400	0.19	0.24	400	0.17	0.32	400	0.19	0.21
420	0.23	0.42	420	0.19	0.36	420	0.22	0.39
440	0.28	0.49	440	0.20	0.35	440	0.27	0.46

Table S5. Absolute quantum yield (Φ) of SUST-P1, SUST-P2 and SUST-P3 at different excitation wavelength at RT.

Excitation wavelength (nm)	Quantum Yield (Φ)		
	SUST-P1	SUST-P2	SUST-P3
340	0.045	0.114	0.081
345	0.055	0.151	0.080
350	0.068	0.174	0.074
360	0.082	0.185	0.063
380	0.105	0.166	0.072
400	0.127	0.132	0.066
420	0.119	0.073	0.045
440	0.097	0.041	0.001

Table S6. Quantum yields (Φ) and lifetimes (τ) of the three MOFs at RT in the air.

MOFs	**λ_F (nm)**	**λ_P (nm)**	**τ_F (ns)**	**τ_P (ms)**	**Φ_F (%)**	**Φ_P (%)**
SUST-P1	436	500	2.44	24.55	11.1	1.6
SUST-P2	430	490	1.13	18.95	16.5	2.0
SUST-P3	420	500	1.15	120.99	4.2	3.9
MOFs	**K^F_r (s^{-1})**	**K^F_{nr} (s^{-1})**	**K_{ISC} (s^{-1})**	**K^P_r (s^{-1})**	**K^P_{nr} (s^{-1})**	
SUST-P1	4.55×10^7	3.58×10^8	6.56×10^6	0.65	40.1	
SUST-P2	1.46×10^8	7.21×10^8	1.77×10^7	1.06	51.7	
SUST-P3	3.65×10^7	7.99×10^8	3.39×10^7	0.32	7.94	

$K^F_{nr} = (1- \Phi_F - \Phi_P)/\tau_F$ $K^F_r = \Phi_F/\tau_F$ $K_{ISC} = \Phi_p/\tau_F$

$K^P_r = \Phi_P/\tau_p$ $K^P_{nr} = (1-\Phi_P)/\tau_p$