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

Supplementary Information

Taking cuprophilicity as a multi-responsive chromphore switching colors responsive to temperature, mechanical force and solvent vapors

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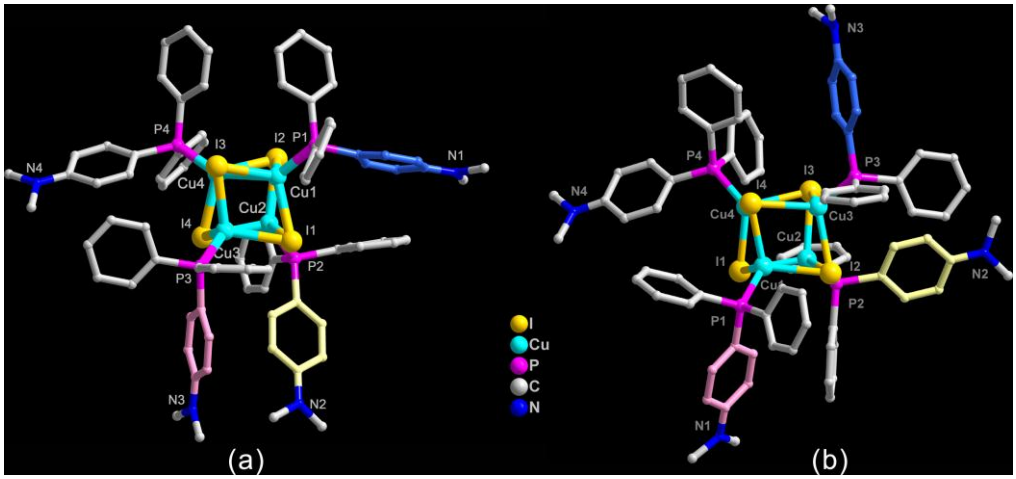

Fig. S1 The asymmetric unit of compound **1**·CH_3CN (a) and **1c**·$0.5CH_2Cl_2$. The solvent molecules are omitted for clarity

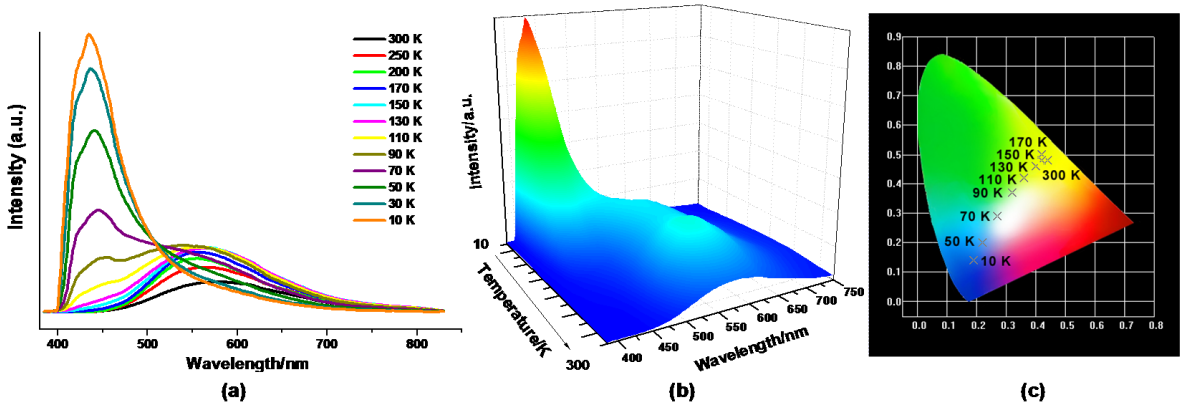

Fig. S2 (a) 2D and (b) 3D temperature-dependent emission spectra (λ_{ex} = 355 nm) of compound **1b** from 300 K to 10 K in solid state; (c) CIE-1931 chromaticity diagram showing the tunable colors from orange emission to blue step by step as temperature decreasing.

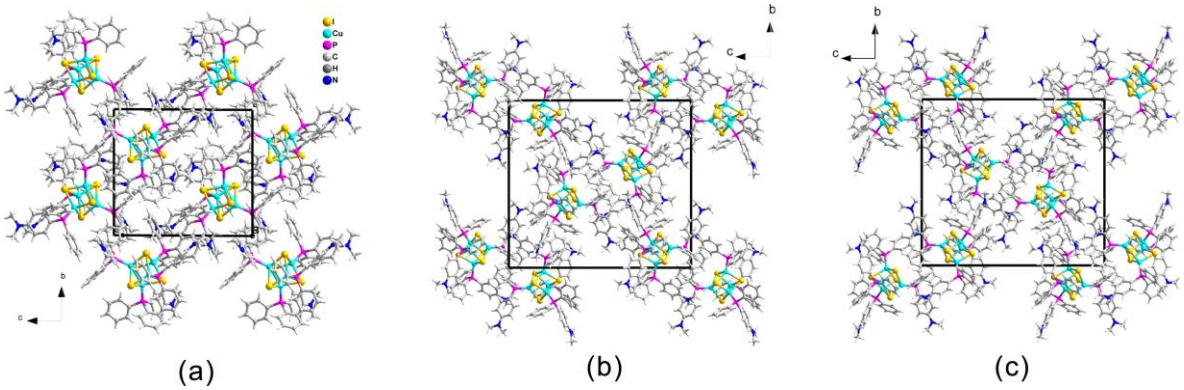

Fig. S3 Different packing modes of crystal **1**·CH_3CN (a), **1c**·$0.5CH_2Cl_2$ (b) and **1d**·$CHCl_3$ (c) along a axis. The solvent molecules are omitted for clarity.

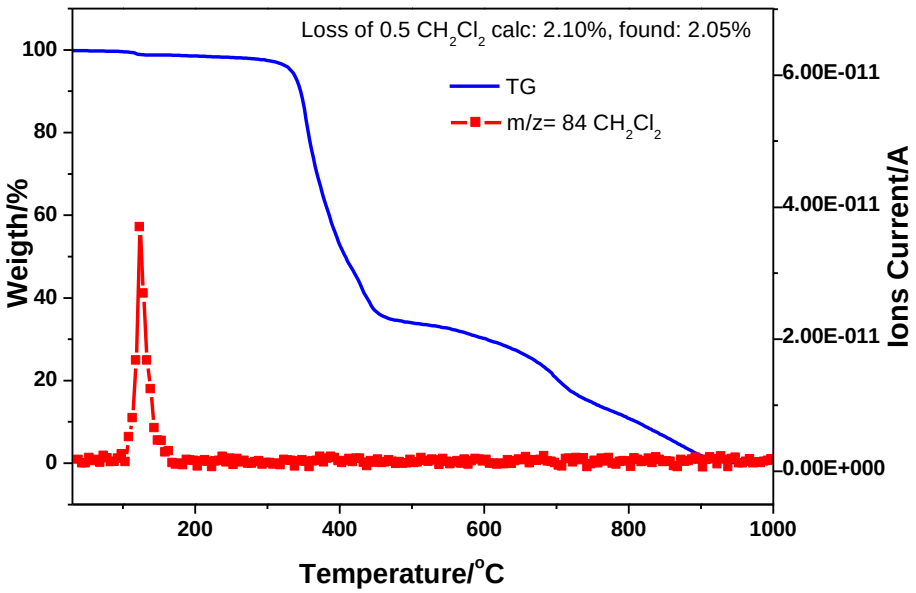

Fig. S4 TG-MS curves of complex **1c**·0.5CH_2Cl_2. The TG curve of complex **1c**·0.5CH_2Cl_2 has one weight loss (2.05%) in the temperature range of 90-160 °C, corresponding to the loss (calculated: 2.10%) of 0.5 molecule of CH_2Cl_2. It reaches a plateau until 300 °C before the decomposition reaction takes place. The only observed species (m/z: 84) show strong flux signals in the MS spectra when the temperature rises, which can be assigned to CH_2Cl_2 only.

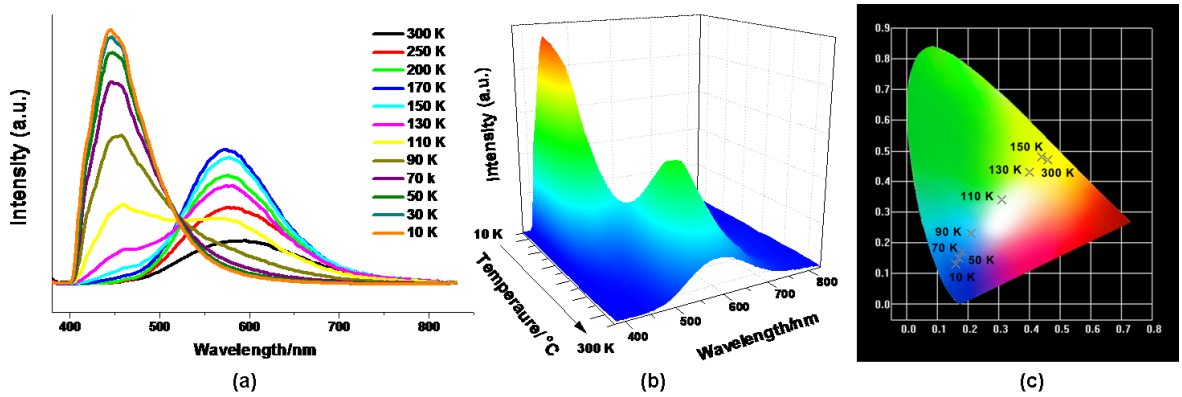

Fig. S5 (a) 2D and (b) 3D temperature-dependent emission spectra (λ_{ex} = 365 nm) of compound **1c**·0.5CH_2Cl_2 from 300 K to 10 K in solid state; (c) CIE-1931 chromaticity diagram showing the tunable colors from yellow emission to blue step by step as temperature decreasing.

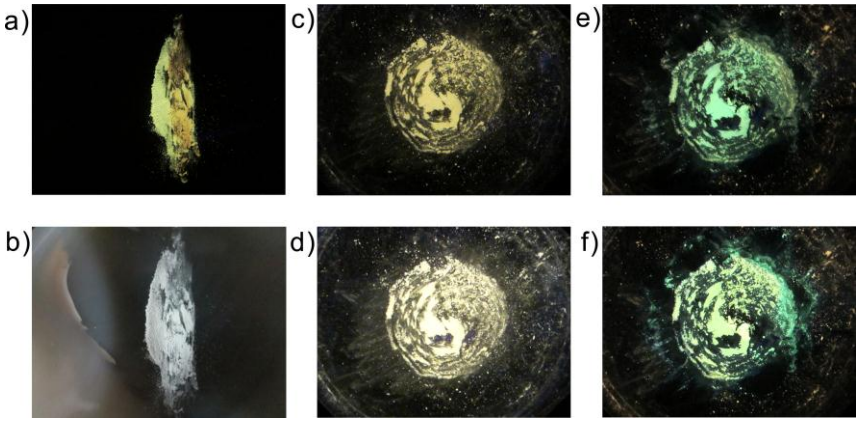

Fig. S6 Photographs showing compound **1c**·0.5CH_2Cl_2 on an agate mortar under UV irradiation with black light (365 nm): (a) **1c**·0.5CH_2Cl_2 powder after grinding the right-half with a pestle, (b) the same sample under ambient light, (c) entirely ground powder of **1c**·0.5CH_2Cl_2, (d) entirely reversion to the yellow luminescence by exposing the ground sample in the atmosphere of CH_2Cl_2, (e) change emission color from yellow to yellow-green by treatment the sample in (d) with CH_3CN atmosphere, (f) partial reversion to the yellow luminescence by dropwise addition of CH_2Cl_2 onto the center of the sample.

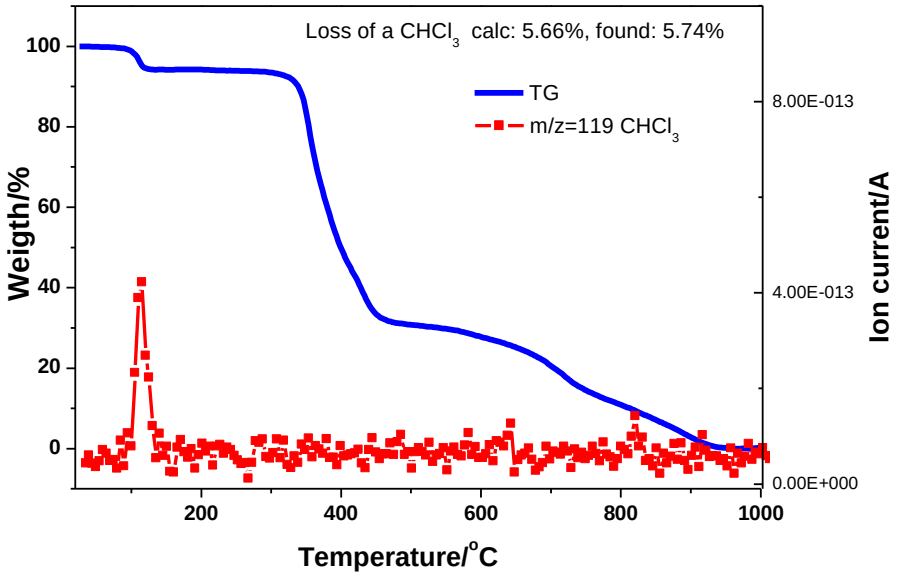

Fig. S7 TG-MS curves of complex **1d**·$CHCl_3$. The TG curve of complex **1d**·$CHCl_3$ has one weight loss (5.74%) in the temperature range of 80-140 °C, corresponding to the loss (calculated: 5.66%) of a molecule of $CHCl_3$. It reaches a plateau until 320 °C before the decomposition reaction takes place. The only observed species (m/z: 119) show flux signals in the MS spectra when the temperature rises, which can be assigned to $CHCl_3$ only.

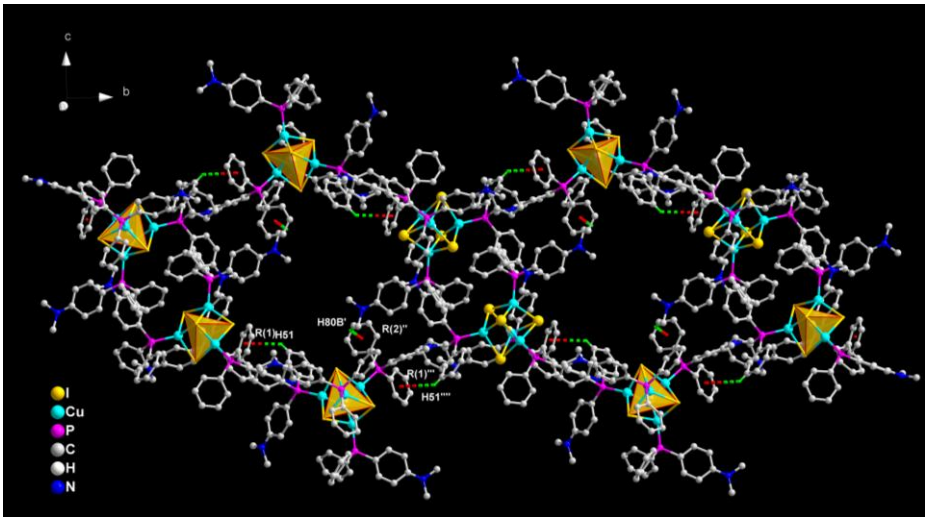

Fig. S8 The C-H…π interactions in **1d**·$CHCl_3$ that extend monomers to 1D chains and then to a 2D sheet. The solvent molecules are omitted for clarity. Symmetry codes: H51: -x, -y, -z; H80B′: -x, -0.5+y, 0.5-z; R2″: -1-x, -1-y, -z; R1‴: -1-x, 0.5+y, -0.5-z.

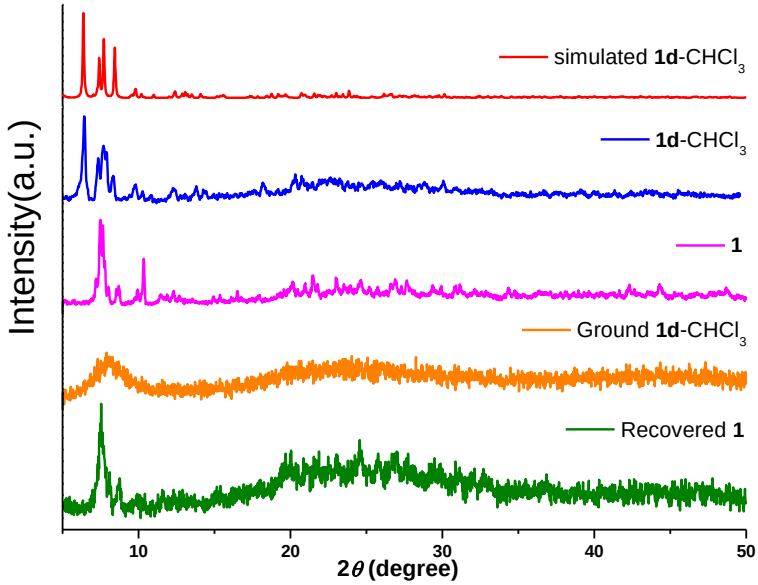

Fig. S9 PXRD pattern of compound **1d**·$CHCl_3$ at different state: sample of **1d**·$CHCl_3$ (blue), observed data of unground **1** (pink), ground sample of **1d**·$CHCl_3$ (orange), recovered sample of **1** by CH_3CN (green).

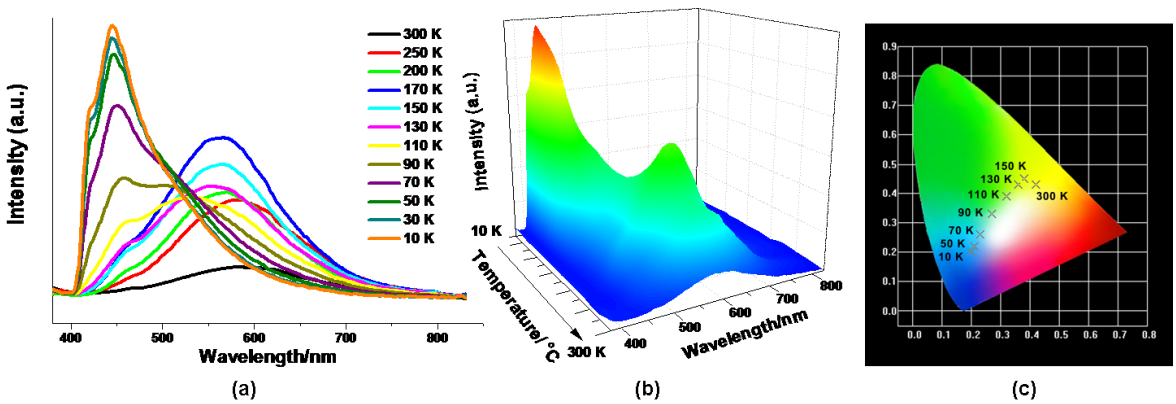

Fig. S10 (a) 2D and (b) 3D temperature-dependent emission spectra (λ_{ex} = 365 nm) of compound **1d**·$CHCl_3$ from 300 K to 10 K in solid state; (c) CIE-1931 chromaticity diagram showing the tunable colors from orange emission to blue step by step as temperature decreasing.

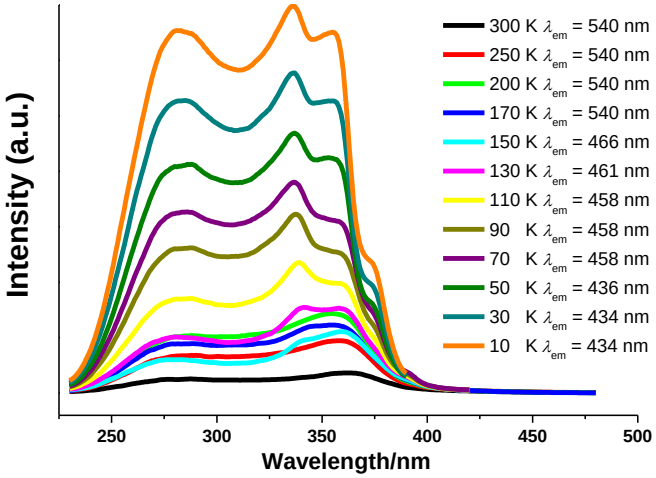

Fig. S11 Temperature-dependent excitation spectra of compound **1**·CH_3CN from 300 K to 10 K in solid state.

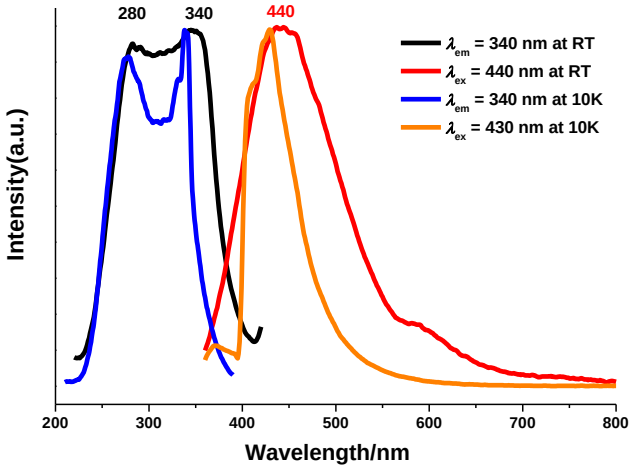

Fig. S12 Excitation and emission spectra of organic ligand 4-dpda at room temperature and 10 K, respectively. At room temperature, the maximum of emission band is at 440 nm, and of excitation band is at 280 and 340 nm.

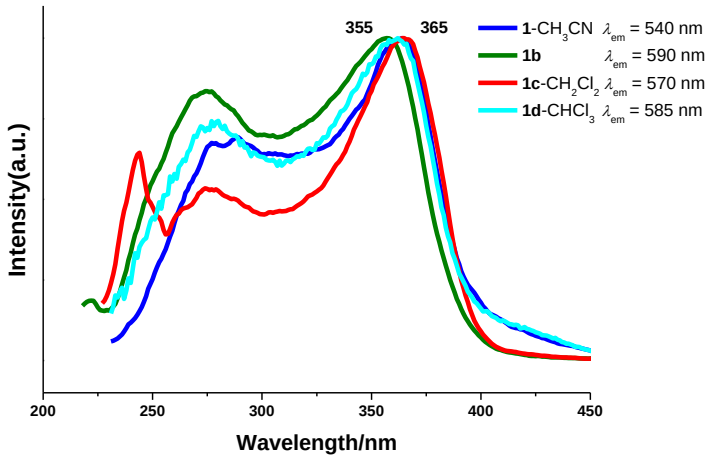

Fig. S13 Excitation spectra of sample **1**·CH_3CN, **1b**, **1c**·$0.5CH_2Cl_2$ and **1d**·$CHCl_3$ at room temperature in solid state.

Table S1. Different Cu-Cu distances in **1**·CH_3CN, **1c**·$0.5CH_2Cl_2$ and **1d**·$CHCl_3$

	1•CH_3CN	**1c**•$0.5CH_2Cl_2$	**1d**•$CHCl_3$
Cu1-Cu2/Å	3.028	3.035	3.042
Cu1-Cu3/Å	3.125	3.232	3.207
Cu1-Cu4/Å	2.996	3.152	3.157
Cu2-Cu3/Å	3.174	3.137	3.120
Cu2-Cu4/Å	3.081	3.252	3.270
Cu3-Cu4/Å	3.131	3.356	3.398
average/Å	3.089	3.194	3.199
Space group	*P*-1	$P2_1/c$	$P2_1/c$
Cell volumes/$Å^3$	4128	9596	9522

Table S2. Elemental analyses of compound **1**·CH_3CN, **1c**·$0.5CH_2Cl_2$ and **1d**·$CHCl_3$ at varied states.

	Calculated			Found		
Element	C	H	N	C	H	N
1·CH_3CN	48.65	4.13	3.45	48.64	4.16	3.32
1	48.45	4.06	2.83	48.46	4.10	2.82
Ground **1**·CH_3CN	48.45	4.06	2.83	48.54	4.14	2.87
1c·$0.5CH_2Cl_2$	47.73	4.03	2.76	47.75	4.13	2.75
1d·$CHCl_3$	46.27	3.88	2.66	46.37	3.95	2.71

Table S3. PL data of compound **1c**·0.5CH_2Cl_2 and **1d**·$CHCl_3$

sample	Temperature/K	λ_{ex}/nm	λ_{em}/nm	Lifetime τ/s	Φ/%	color
1c·0.5CH_2Cl_2	300	365	570	5.03×10^{-6} (34% [a]) 2.11×10^{-6} (44% [a]) 6.95×10^{-7} (22% [a])	14.88	Yellow
	10	365	445	1.67×10^{-3} (58% [a]) 3.55×10^{-4} (28% [a]) 6.42×10^{-5} (14% [a])	41.98	Blue
1d·$CHCl_3$	300	365	585	4.36×10^{-6} (49% [a]) 1.57×10^{-6} (42% [a]) 3.67×10^{-7} (9% [a])	1.93	Organe
	10	365	445	2.81×10^{-3} (26% [b]) 8.99×10^{-4} (30% [b]) 1.41×10^{-4} (26% [b]) 4.07×10^{-5} (18% [b])	7.87	blue

[a]Triexponential decays. [b]Quarticexponential decays.

Table S4. Color coordinates based on CIE (Commission International de L'Eclairage) 1931 chromaticity calculated results of compound **1** at varied state from 300 K to 10 K

	1·CH_3CN		**1b**		**1c**·0.5CH_2Cl_2		**1d**·$CHCl_3$	
Temperature / K	X	Y	X	Y	X	Y	X	Y
300	0.34	0.46	0.44	0.48	0.46	0.47	0.42	0.43
250	0.34	0.49	0.43	0.50	0.46	0.49	0.43	0.46
200	0.32	0.48	0.42	0.51	0.46	0.50	0.40	0.47
170	0.28	0.40	0.42	0.50	0.45	0.50	0.39	0.46
150	0.26	0.34	0.42	0.48	0.44	0.48	0.38	0.45
130	0.23	0.30	0.40	0.46	0.40	0.43	0.36	0.43
110	0.22	0.27	0.36	0.42	0.31	0.34	0.32	0.39
90	0.20	0.24	0.32	0.37	0.21	0.23	0.27	0.33
70	0.20	0.21	0.27	0.29	0.18	0.17	0.23	0.26
50	0.19	0.18	0.22	0.20	0.17	0.15	0.21	0.22
30	0.18	0.16	0.19	0.15	0.16	0.14	0.20	0.20
10	0.18	0.15	0.19	0.14	0.16	0.13	0.19	0.20

Table S5. C-H···π interactions in compound **1d**·$CHCl_3$

C-H···π interactions	H···R/Å	∠C-H···π/°	C···R/ Å
C51-H51···R1‴	2.989	133.28	3.689
C80′-H80B′···R2″	3.322	120.09	3.893

Table S6. Crystallographic data and structure refinement details for **1** at six different temperatures

T (K)	113 K	160 K	170 K	200 K	230 K	260 K
Empirical formula	$C_{82}H_{83}Cu_4I_4N_5P_4$	$C_{80}H_{80}Cu_4I_4N_4P_4$	$C_{80}H_{80}Cu_4I_4N_4P_4$	$C_{80}H_{80}Cu_4I_4N_4P_4$	$C_{80}H_{80}Cu_4I_4N_4P_4$	$C_{80}H_{80}Cu_4I_4N_4P_4$
Formula weight	2024.17	1983.12	1983.12	1983.12	1983.12	1983.12
Crystal system	triclinic	triclinic	triclinic	triclinic	triclinic	triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1	*P*-1
a (Å)	15.3088(5)	15.3491(4)	15.3594(4)	15.3915(3)	15.4242(3)	15.4577(3)
b (Å)	15.5278(7)	15.4845(4)	15.4883(4)	15.5053(4)	15.5207(4)	15.5354(4)
c (Å)	16.9897(8)	16.9896(4)	16.9959(5)	17.0242(4)	17.0532(4)	17.0827(4)
α (deg)	89.042(5)	88.448(2)	88.447(2)	88.460(2)	88.460(2)	88.465(2)
β (deg)	85.531(6)	85.496(2)	85.484(2)	85.486(2)	85.455(2)	85.427(2)
γ (deg)	81.924(4)	81.231(2)	81.238(2)	81.260(2)	81.274(2)	81.285(2)
V (Å^3)	3986.4(3)	3977.98(17)	3983.11(19)	4002.73(16)	4022.04(16)	4041.54(16)
Z	2	2	2	2	2	2
D_c (g/cm^{-3})	1.686	1.656	1.654	1.645	1.638	1.630
μ (mm^{-1})	2.728	14.487	14.468	14.397	14.328	14.259
F (000)	1996	1952	1952	1952	1952	1952
Parameters	856	873	873	873	873	873
θ range (deg)	2.3–27.5	2.6–74.0	2.6–74.1	2.6–74.1	2.6–74.0	2.6–74.0
GOF on F^2	1.073	0.987	1.072	0.984	1.030	0.989
R_1,[a] wR_2[b]	0.0491,	0.0229,	0.0257,	0.0238,	0.0258,	0.0273,
($I > 2\sigma(I)$)	0.1673	0.0549	0.0659	0.0571	0.0601	0.0611
R_1,[a] wR_2[b]	0.0508,	0.0289,	0.0321	0.0307	0.0339	0.0375
(all data)	0.1690	0.0582	0.0760	0.0610	0.0690	0.0668
Reflns. Collected	39819	42748	42805	43074	43334	43410
Reflns. Unique	17716	14036	14062	14131	14223	14282
(R_{int})	(0.0202)	(0.0297)	(0.0310)	(0.0304)	(0.0310)	(0.0396)

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

Table S7. Crystallographic data and structure refinement details for **1**·CH_3CN, **1c**·$0.5CH_2Cl_2$ and **1d**·$CHCl_3$ at 293 K

Compound	**1**	**1c**	**1d**
Empirical formula	$C_{80}H_{80}Cu_4I_4N_4P_4$	$C_{80}H_{80}Cu_4I_4N_4P_4$	$C_{80}H_{80}Cu_4I_4N_4P_4$
Formula weight	1983.12	1983.12	1983.12
Crystal system	triclinic	monoclinic	monoclinic
Space group	*P*-1	$P2_1/c$	$P2_1/c$
a (Å)	15.5322(5)	13.722(3)	13.663(2)
b (Å)	15.6498(5)	25.304(6)	25.134(4)
c (Å)	17.2181(9)	27.966(7)	28.011(5)
α (deg)	88.714(6)	90	90
β (deg)	85.179(6)	98.810(6)	98.145(3)
γ (deg)	81.898(5)	90	90
V (Å^3)	4128.6(3)	9596(4)	9522(3)
Z	2	4	4
D_c (g/cm^{-3})	1.595	1.373	1.383
μ (mm^{-1})	2.632	2.265	2.282
F (000)	1952	3904	3904
Parameters	873	873	870
θ range (deg)	2.6–27.5	2.3–27.5	2.4–27.5
GOF on F^2	0.997	1.011	0.947
R_1,[a] wR_2[b] ($I > 2\sigma(I)$)	0.0403, 0.1179	0.0653, 0.1838	0.0494, 0.1523
R_1,[a] wR_2[b] (all data)	0.0483, 0.1256	0.0955, 0.2097	0.0645, 0.1686
Reflns. Collected	43677	71682	74734
Reflns. Unique, (R_{int})	18793, (0.0228)	21825, (0.0639)	21675, (0.0552)

Table S8. Selected bonds length (Å) and angles (°) in compound **1**·CH_3CN, **1c**·0.5CH_2Cl_2 and **1d**·$CHCl_3$ at 293 K

	1·CH_3CN	**1c**·0.5CH_2Cl_2	**1d**·$CHCl_3$
Length/ Å			
Cu-Cu	Cu4—Cu1 2.9953 (8) Cu1—Cu2 3.0278 (8)	Cu2—Cu1 3.0357 (8)	Cu2—Cu1 3.0409 (11)
Cu-I	I3—Cu1 2.6901 (7) I3—Cu4 2.6934 (7) I3—Cu3 2.6976 (6) I2—Cu2 2.6493 (7) I2—Cu4 2.6628 (7) I2—Cu1 2.6778 (7) I4—Cu4 2.6848 (6) I4—Cu3 2.6850 (6) I4—Cu2 2.7087 (7) I1—Cu2 2.6809 (7) I1—Cu1 2.6928 (7) I1—Cu3 2.7071 (6)	I1—Cu4 2.6701 (6) I1—Cu2 2.7144 (6) I1—Cu1 2.7382 (6) I3—Cu3 2.6315 (7) I3—Cu2 2.7184 (7) I3—Cu4 2.7632 (6) I2—Cu2 2.6763 (6) I2—Cu1 2.6978 (6) I2—Cu3 2.7118 (7) I4—Cu1 2.6677 (6) I4—Cu4 2.6846 (7) I4—Cu3 2.8440 (6)	I1—Cu4 2.6513 (8) I1—Cu2 2.6962 (9) I1—Cu1 2.7410 (9) I2—Cu2 2.6703 (9) I2—Cu1 2.6859 (10) I2—Cu3 2.6919 (9) I3—Cu3 2.6280 (9) I3—Cu2 2.7029 (9) I3—Cu4 2.7831 (9) I4—Cu1 2.6567 (9) I4—Cu4 2.6738 (8) I4—Cu3 2.8261 (9)
Cu-P	Cu4—P4 2.2521 (12) Cu1—P1 2.2523 (12) Cu2—P2 2.2475 (12) Cu3—P3 2.2519 (12)	Cu2—P2 2.2582 (9) Cu1—P1 2.2559 (10) Cu4—P4 2.2439 (10) Cu3—P3 2.2600 (9)	Cu2—P2 2.2522 (16) Cu4—P4 2.2378 (16) Cu3—P3 2.2476 (16)
Angles			
I-Cu-I	I2—Cu1—I1 107.50 (2) I3—Cu1—I1 106.10 (2) I2—Cu4—I3 109.31 (2) I2—Cu4—I4 106.40 (2) I4—Cu4—I3 105.86 (2) I2—Cu2—I4 106.10 (2) I1—Cu2—I4 104.97 (2) I2—Cu2—I1 108.69 (2) I4—Cu3—I1 104.91 (2) I3—Cu3—I1 105.49 (2) I4—Cu3—I3 105.74 (2)	I2—Cu2—I3 105.89 (2) I1—Cu2—I3 103.19 (2) I4—Cu1—I2 106.83 (2) I4—Cu1—I1 105.15 (2) I2—Cu1—I1 108.68 (2) I3—Cu3—I2 107.356 (19) I1—Cu4—I3 103.16 (2) I4—Cu4—I3 102.424 (19) I1—Cu4—I4 106.599 (17) I3—Cu3—I4 101.65 (2) I2—Cu3—I4 101.67 (2)	I2—Cu2—I3 106.06 (3) I1—Cu2—I3 103.13 (3) I1—Cu4—I4 106.84 (3) I1—Cu4—I3 102.16 (3) I4—Cu4—I3 100.64 (3) I3—Cu3—I2 107.60 (3) I2—Cu2—I1 109.73 (3) I3—Cu3—I4 100.67 (3) I2—Cu3—I4 102.35 (3) I4—Cu1—I1 104.78 (3) I2—Cu1—I1 107.93 (3)
Cu-I-Cu	Cu1—I3—Cu4 67.613 (19) Cu1—I3—Cu3 70.911 (19) Cu4—I3—Cu3 71.023 (18) Cu2—I2—Cu4 70.90 (2) Cu2—I2—Cu1 69.27 (2) Cu4—I2—Cu1 68.23 (2) Cu4—I4—Cu3 71.348 (19) Cu4—I4—Cu2 69.668 (19) Cu3—I4—Cu2 72.092 (19) Cu2—I1—Cu1 68.589 (19)	Cu4—I1—Cu2 74.35 (2) Cu4—I1—Cu1 71.258 (18) Cu2—I1—Cu1 67.660 (18) Cu3—I3—Cu2 71.790 (17) Cu3—I3—Cu4 76.914 (18) Cu2—I3—Cu4 72.819 (19) Cu2—I2—Cu1 68.787 (19) Cu2—I2—Cu3 71.222 (19) Cu1—I2—Cu3 73.44 (2) Cu1—I4—Cu4 72.132 (18)	Cu4—I1—Cu2 75.44 (3) Cu4—I1—Cu1 71.69 (2) Cu2—I1—Cu1 68.01 (3) Cu2—I2—Cu1 69.19 (3) Cu2—I2—Cu3 71.17 (3) Cu1—I2—Cu3 73.22 (3) Cu3—I3—Cu2 71.63 (2) Cu3—I3—Cu4 77.75 (3) Cu2—I3—Cu4 73.21 (2) Cu1—I4—Cu4 72.67 (3)

	Cu2—I1—Cu3	72.180 (19)	Cu1—I4—Cu3	71.78 (2)	Cu1—I4—Cu3	71.52 (3)
	Cu1—I1—Cu3	70.727 (19)	Cu4—I4—Cu3	74.706 (19)	Cu4—I4—Cu3	76.26 (3)
I-Cu-Cu	I2—Cu1—Cu2	54.920 (18)				
	I3—Cu1—Cu2	105.35 (2)				
	I1—Cu1—Cu2	55.519 (17)				
	I2—Cu1—Cu4	55.646 (18)	I2—Cu2—Cu1	55.941 (16)	I4—Cu1—Cu2	103.70 (3)
	I3—Cu1—Cu4	56.246 (18)	I1—Cu2—Cu1	56.544 (12)	I2—Cu1—Cu2	55.16 (2)
	I1—Cu1—Cu4	104.39 (2)	I3—Cu2—Cu1	101.709 (15)	I1—Cu1—Cu2	55.30 (2)
	I2—Cu4—Cu1	56.123 (18)	I4—Cu1—Cu2	104.292 (19)	I2—Cu2—Cu1	55.65 (2)
	I4—Cu4—Cu1	103.15 (2)	I2—Cu1—Cu2	55.272 (13)	I1—Cu2—Cu1	56.70 (2)
	I3—Cu4—Cu1	56.141 (17)	I1—Cu1—Cu2	55.796 (17)	I3—Cu2—Cu1	101.30 (3)
	I2—Cu2—Cu1	55.808 (18)				
	I1—Cu2—Cu1	55.892 (18)				
	I4—Cu2—Cu1	101.73 (2)				
P-Cu-Cu	P2—Cu2—Cu1	146.06 (4)				
	P1—Cu1—Cu4	143.49 (4)	P2—Cu2—Cu1	149.33 (3)	P2—Cu2—Cu1	149.71 (5)
	P4—Cu4—Cu1	152.25 (4)	P1—Cu1—Cu2	141.02 (3)	P1—Cu1—Cu2	141.51 (5)
	P1—Cu1—Cu2	143.50 (4)				
P-Cu-I	P1—Cu1—I2	110.81 (4)	P2—Cu2—I2	113.11 (3)	P3—Cu3—I3	117.92 (5)
	P1—Cu1—I3	111.14 (4)	P2—Cu2—I1	114.80 (2)	P3—Cu3—I2	111.74 (5)
	I2—Cu1—I3	108.96 (2)	I2—Cu2—I1	110.031 (18)	P4—Cu4—I1	121.02 (5)
	P1—Cu1—I1	112.13 (4)	P2—Cu2—I3	108.96 (3)	P4—Cu4—I4	117.24 (5)
	P2—Cu2—I2	116.90 (4)	P1—Cu1—I4	114.67 (3)	P2—Cu2—I2	112.58 (5)
	P2—Cu2—I1	107.80 (4)	P1—Cu1—I2	109.36 (3)	P2—Cu2—I1	115.52 (5)
	P2—Cu2—I4	111.71 (4)	P3—Cu3—I3	117.24 (3)	P1—Cu1—I4	114.78 (5)
	P4—Cu4—I2	111.63 (4)	P3—Cu3—I2	111.82 (3)	P1—Cu1—I2	109.55 (5)
	P4—Cu4—I4	104.36 (4)	P4—Cu4—I3	105.42 (2)	I4—Cu1—I2	107.18 (3)
	P4—Cu4—I3	118.35 (4)	P4—Cu4—I1	119.90 (3)	P1—Cu1—I1	112.26 (5)
	P3—Cu3—I4	113.30 (3)	P4—Cu4—I4	116.96 (2)	P2—Cu2—I3	108.96 (5)
	P3—Cu3—I3	113.73 (3)	P1—Cu1—I1	111.86 (3)	P4—Cu4—I3	105.81 (4)
	P3—Cu3—I1	112.88 (3)	P3—Cu3—I4	115.49 (3)	P3—Cu3—I4	114.93 (5)
C-P-Cu	C53—P3—Cu3	114.40 (13)			C7—P1—Cu1	113.7 (2)
	C47—P3—Cu3	114.71 (14)			C1—P1—Cu1	115.0 (2)
	C41—P3—Cu3	116.42 (14)	C73—P4—Cu4	117.70 (10)	C13—P1—Cu1	114.9 (2)
	C33—P2—Cu2	115.68 (15)	C61—P4—Cu4	113.51 (10)	C61—P4—Cu4	113.3 (2)
	C27—P2—Cu2	112.79 (16)	C67—P4—Cu4	111.79 (10)	C67—P4—Cu4	111.28 (19)
	C21—P2—Cu2	116.16 (15)	C13—P1—Cu1	114.74 (10)	C73—P4—Cu4	119.18 (18)
	C73—P4—Cu4	115.39 (15)	C1—P1—Cu1	114.07 (12)	C33—P2—Cu2	115.46 (19)
	C67—P4—Cu4	115.18 (17)	C7—P1—Cu1	114.14 (11)	C21—P2—Cu2	116.24 (19)
	C61—P4—Cu4	111.72 (16)	C41—P3—Cu3	116.41 (10)	C27—P2—Cu2	114.43 (19)
	C13—P1—Cu1	114.07 (15)	C53—P3—Cu3	116.51 (10)	C53—P3—Cu3	117.35 (17)
	C1—P1—Cu1	117.11 (17)	C47—P3—Cu3	112.49 (9)	C47—P3—Cu3	112.67 (18)
	C7—P1—Cu1	112.92 (16)			C41—P3—Cu3	117.02 (18)
Cu-Cu-Cu	Cu4—Cu1—Cu2	61.52 (2)				