

Sensitive Luminescent Mechanochromism and Unique Luminescent Thermochromism Tuned by Bending P–O–P Skeleton in Diphosphonium/[Cu₂I₄] Hybrid

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Table S1 Crystal data and structure refinements in this work

	1–RT	1–175K	2
Empirical formula	C ₂₄ H ₄₈ Cu ₂ I ₄ N ₆ OP ₂	C ₂₄ H ₄₈ Cu ₂ I ₄ N ₆ OP ₂	C ₂₄ H ₄₈ Cu ₄ I ₆ N ₆ OP ₂
Crystal system	Orthorhombic	Orthorhombic	Triclinic
Formula mass	1133.3	1133.3	1514.18
Space group	<i>Pbca</i>	<i>Pbca</i>	<i>P</i> $\bar{1}$
a[Å]	12.9110(7)	12.7246(7)	9.7863(7)
b[Å]	14.3489(8)	14.1746(7)	10.7597(8)
c[Å]	19.9832(11)	19.8726(11)	11.0969(8)
α /°	90	90	70.945(3)
β /°	90	90	79.753(3)
γ /°	90	90	72.218(3)
Volume/Å ³	3702.1(4)	3584.3(3)	1047.71(13)
<i>Z</i>	4	4	1
<i>D</i> _c [g/cm ³]	2.033	2.100	2.400
μ /mm ⁻¹	4.598	4.749	6.526
F(000)	2168	2168	706
Reflections, total	117980	62067	28837
Reflections, unique	3290 [<i>R</i> (int) = 0.0787]	3169 [<i>R</i> (int) = 0.0368]	3669 [<i>R</i> (int) = 0.0423]
Reflections, observed	2644	2853	3044
Goodness-of-fit on <i>F</i> ²	1.113	1.040	1.102
No. of parameters refined	179	179	215
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0343	0.0192	0.0304
w <i>R</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.074	0.0403	0.0714

residual extremes ($\epsilon/\text{\AA}^3$)	0.876,-0.618	0.766,-0.728	0.794,-0.655
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Table S2 Selected bond lengths (\AA) and angles($^\circ$) of $(\text{Py}_3\text{P-O-PPy}_3)(\text{Cu}_2\text{I}_4)$ (1)

Room temperature							
Cu(1)-I(1)	2.4850(6)	Cu(1)-I(2)	2.5758(7)	Cu(1)-I(2) ^{#1}	2.5757(7)	Cu(1)-Cu(1) ^{#1}	2.6519(11)
P(1)-O(1)	1.5713(11)	P(1)-N(1)	1.600(4)	P(1)-N(2)	1.584(4)	P(1)-N(3)	1.591(3)
I(1)-Cu(1)-I(2) ^{#1}	120.58(3)	I(1)-Cu(1)-I(2)	121.38(3)	I(2) ^{#1} -Cu(1)-I(2)	118.03(2)	P(1) ^{#2} -O(1)-P(1)	180.0
Low temperature							
Cu(1)-I(1)	2.4898(4)	Cu(1)-I(2)	2.5746(4)	Cu(1)-I(2) ^{#1}	2.5778(4)	Cu(1)-Cu(1) ^{#1}	2.5970(7)
P(1)-O(1)	1.5746(7)	P(1)-N(1)	1.597(2)	P(1)-N(2)	1.590(3)	P(1)-N(3)	1.599(2)
I(1)-Cu(1)-I(2)	120.426(16)	I(1)-Cu(1)-I(2) ^{#1}	120.108(16)	I(2)-Cu(1)-I(2) ^{#1}	119.464(14)	P(1)-O(1)-P(1) ^{#2}	180.0

Symmetry codes: #1 -x+1,-y+1,-z; #2 -x+1,-y+1,-z+1

Table S3 Selected bond lengths (\AA) and angles($^\circ$) of $(\text{Py}_3\text{P-O-PPy}_3)(\text{Cu}_4\text{I}_6)$ (2)

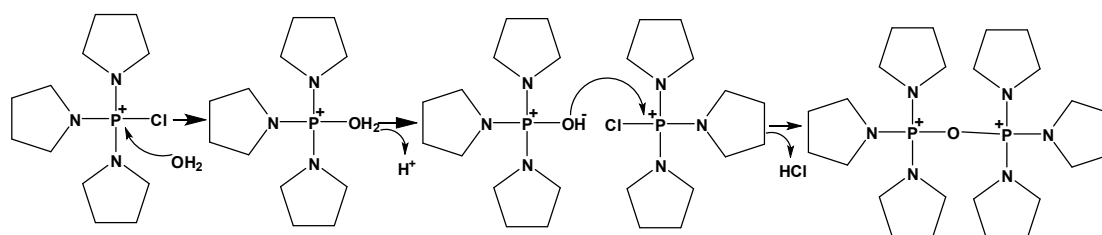
Cu(1)-I(1)	2.5682(14)	Cu(1)-I(2)	2.5752(14)	Cu(1)-I(3)	2.5677(14)	Cu(2)-I(1) ^{#1}	2.5834(14)
Cu(2)-I(3)	2.5546(14)	Cu(2)-I(2)	2.5567(15)	Cu(3)-I(1)	2.5389(15)	Cu(3)-I(2) ^{#1}	2.6024(15)
Cu(3)-I(3)	2.5613(15)	Cu(4)-I(1)	2.5593(14)	Cu(4)-I(2)	2.5388(14)	Cu(4)-I(3) ^{#1}	2.6006(14)
Cu(1)-Cu(2) ^{#1}	2.7603(18)	Cu(1)-Cu(3) ^{#1}	2.7856(19)	Cu(1)-Cu(4) ^{#1}	2.7410(19)	Cu(2)-Cu(3)	2.7444(19)
Cu(2)-Cu(4)	2.7981(19)	Cu(3)-Cu(4)	2.7906(19)				
I(3)-Cu(1)-I(1)	120.58(5)	I(3)-Cu(1)-I(2)	119.68(5)	I(1)-Cu(1)-I(2)	118.56(5)	I(3)-Cu(2)-I(2)	120.92(5)
I(3)-Cu(2)-I(1) ^{#1}	120.12(6)	I(2)-Cu(2)-I(1) ^{#1}	118.41(5)	I(1)-Cu(3)-I(3)	122.00(6)	I(1)-Cu(3)-I(2) ^{#1}	118.36(6)
I(3)-Cu(3)-I(2) ^{#1}	119.13(6)	I(2)-Cu(4)-I(1)	120.29(5)	I(2)-Cu(4)-I(3) ^{#1}	120.06(5)	I(1)-Cu(4)-I(3) ^{#1}	119.28(5)

Symmetry codes: #1 -x+2,-y,-z+1; #2 -x+1,-y+1,-z

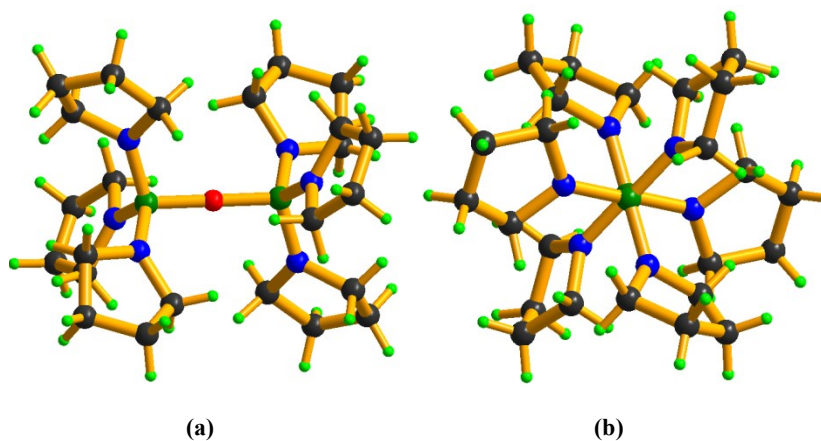
Table S4 The coordinates of optimized $(\text{Py}_3\text{P-O-PPy}_3)^{2+}$ cation at B3LPY/6-31g(d) level

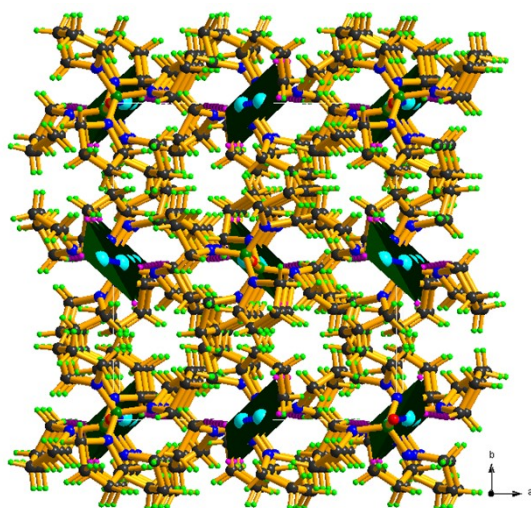
Atom	x	y	z	Atom	x	y	z
P	-1.62038100	0.02737100	-0.03446000	C	1.58536200	-2.30864800	-1.58059500
N	-2.08507300	1.51778300	0.43209200	C	3.17545300	-2.24391000	0.30612600
N	-1.83303700	-1.02680400	1.19186500	C	1.60180600	2.34193800	-1.57252200
O	-0.03000200	0.04469600	-0.45139300	C	3.58632000	0.87668900	-1.69991700
N	-2.31195500	-0.44737900	-1.43127700	C	2.66325300	1.60342300	1.87028200
C	-1.53169500	2.25415400	1.60911600	C	1.46068300	-0.40054000	2.66938300
C	-2.95783500	2.41312800	-0.40039400	H	-3.25762800	-2.50281300	-3.09413100
C	-1.37484700	-2.45109600	1.11065500	H	-4.80409100	-1.65809200	-3.26188200
C	-2.79648000	-0.84328200	2.33025600	H	-2.71483200	-0.71892200	-4.70808200
P	1.56320700	-0.01568200	-0.08192000	H	-3.67771600	0.45515100	-3.80346700
C	-3.65619300	-1.10597800	-1.48425100	H	0.50119000	-2.44786800	-1.58540300
C	-1.82919100	-0.09547000	-2.80512700	H	1.86660700	-1.74443700	-2.47787500
H	-0.45310500	2.08764700	1.69746600	C	2.36221700	-3.62892700	-1.48566600
H	-2.01339700	1.90140400	2.52730100	H	3.94148800	-1.52281200	0.60039700
C	-1.89121400	3.71920100	1.32087100	H	2.83291000	-2.77024100	1.20384500
H	-3.87945500	1.89942100	-0.68120900	C	3.65625800	-3.23402100	-0.76060900
H	-2.43137100	2.71625800	-1.31282600	C	2.49877400	2.76469700	-2.74305900
C	-3.19818100	3.61272200	0.52263400	H	0.55926000	2.18982500	-1.86146400
C	-1.90063600	-3.07489600	2.41167200	H	1.63644500	3.08210300	-0.76253000
H	-0.28598900	-2.49924500	1.02174800	H	4.30961700	0.61344300	-0.92239600

H	-1.81327100	-2.93683300	0.23084400	H	3.57486400	0.07848800	-2.45012400
H	-3.64730100	-0.22999900	2.02741100	C	3.88375600	2.24326700	-2.33413500
H	-2.28553000	-0.34506300	3.16156200	H	3.70753100	1.47300700	1.56825400
C	-3.18069900	-2.27899300	2.70221400	H	2.27508300	2.50765700	1.39625300
N	2.00682600	-1.56404600	-0.34951500	C	2.52366000	1.63045500	3.39800100
N	2.20795600	1.05302500	-1.13132700	H	1.60367600	-1.46938900	2.49565800
N	1.86353900	0.39355800	1.46832400	H	0.40096700	-0.22503500	2.88993600
H	-4.44642400	-0.38970900	-1.22746600	C	2.36289200	0.15219800	3.77922300
H	-3.70322300	-1.94059200	-0.78017500	H	2.53824400	-4.06622400	-2.47139900
C	-3.76358900	-1.54183500	-2.94942200	H	1.79842500	-4.35714700	-0.89195100
H	-1.53685400	0.95716800	-2.86659100	H	4.17636600	-4.08587300	-0.31557900
H	-0.95675400	-0.71034700	-3.04814400	H	4.34908100	-2.74070800	-1.45144100
C	-3.03064500	-0.42316800	-3.70465300	H	2.16346100	2.28041200	-3.66675900
H	-1.99645500	4.30015000	2.24032200	H	2.47891700	3.84571200	-2.90143300
H	-1.10978600	4.18900900	0.71262400	H	4.57514900	2.15440500	-3.17546000
H	-3.42962200	4.51758400	-0.04448200	H	4.33936100	2.91012500	-1.59410300
H	-4.04096900	3.40989000	1.19220100	H	1.63239800	2.19887500	3.68762200
H	-1.17341900	-2.93541400	3.21958800	H	3.38748400	2.10395200	3.87075000
H	-2.07634900	-4.14784300	2.30278400	H	1.92530700	0.00888600	4.77025700
H	-3.50517300	-2.35376300	3.74305200	H	3.33296800	-0.35647300	3.76331800
H	-4.00362100	-2.62825200	2.06841000				



Scheme S1 The possible in - situ generation route of $(\text{Py}_3\text{P-O-PPy}_3)^{2+}$ under hydrothermal condition





(c)

Fig. S1 (a) the structure of $(\text{Py}_3\text{P-O-PPy}_3)^{2+}$ cations showing P-O-P backbone; (b) the structure of $(\text{Py}_3\text{P-O-PPy}_3)^{2+}$ cations showing its staggered form; (c) packing diagram of 1

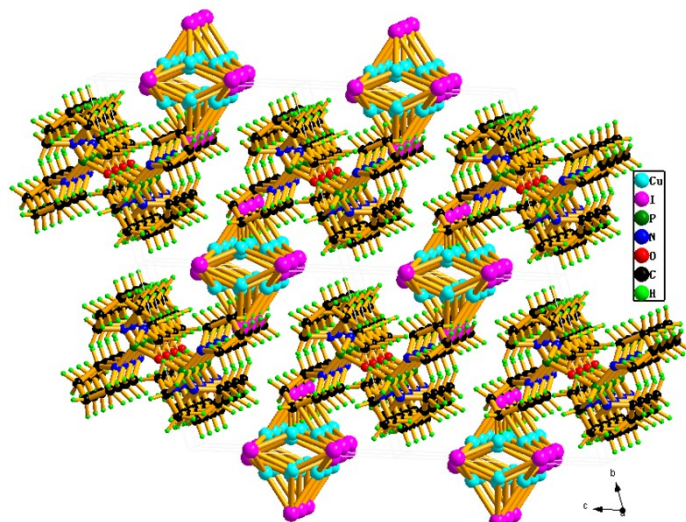
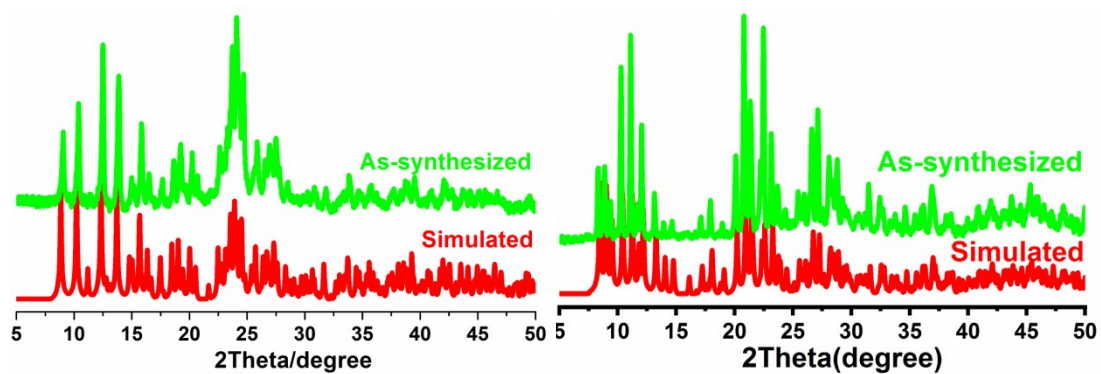
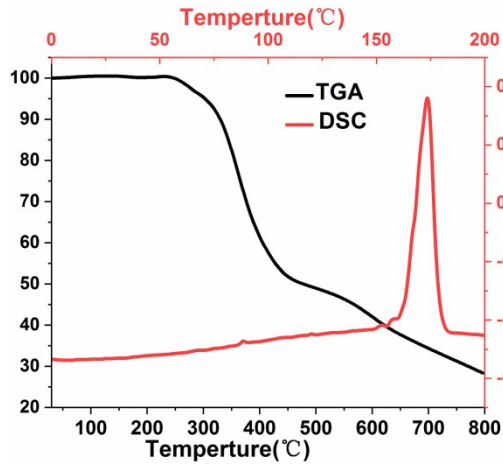


Fig. S2 Packing diagram of 2 without hydrogen bonds

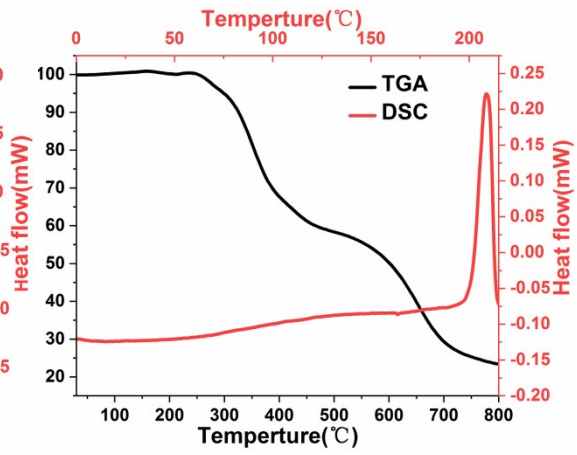


(a)

(b)

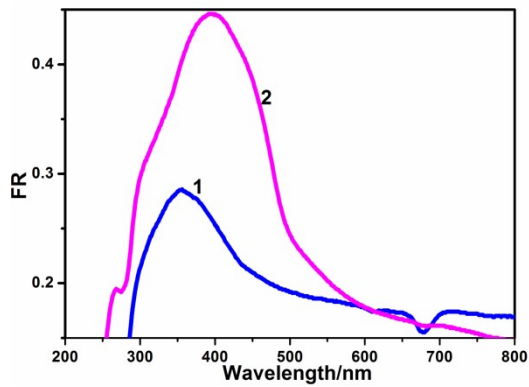


(c)

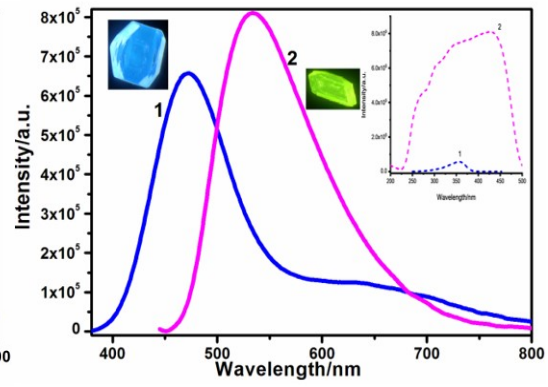


(d)

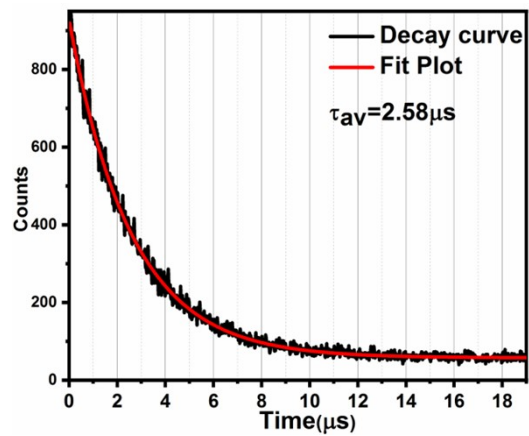
Fig. S3 The simulated (red) and experimental (green) PXRD of (a) 1; and (b) 2; TGA-DSC curves of (c) 1 and (d) 2



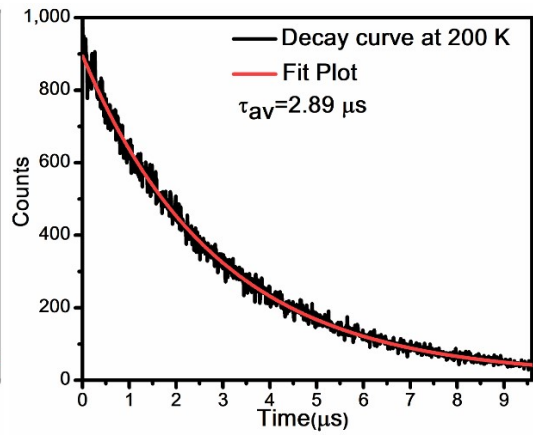
(a)



(b)



(c)



(d)

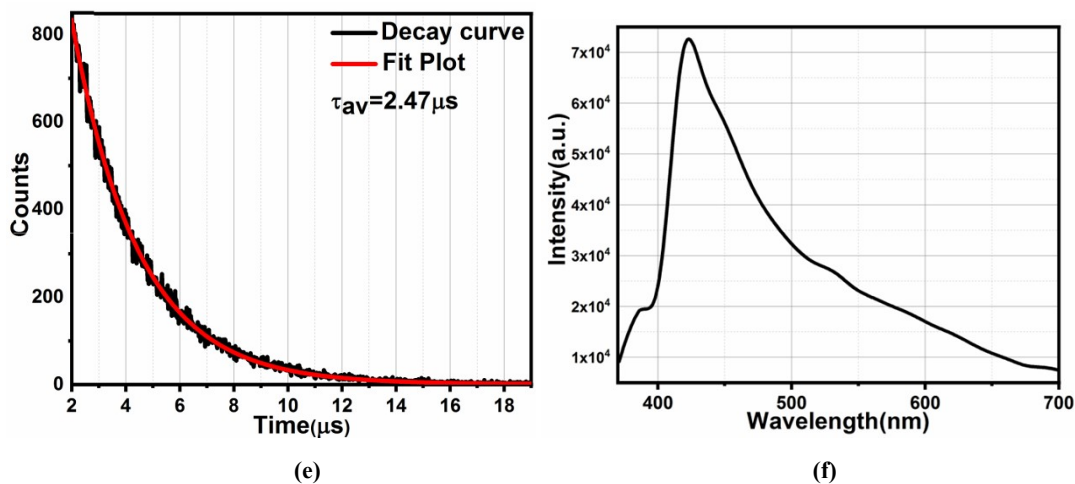


Fig. S4 (a) UV-Vis spectra; (b) emission spectra of two hybrids with inserted excitation spectra: 1-blue ($\lambda_{ex}=355$ nm); 2-magenta ($\lambda_{ex}=425$ nm); (c, d) the photoluminescence decay curves (left: 1; right: 1 at 200 K); (e) the photoluminescence decay curve of 2; (f) the luminescent spectrum of $Py_3PCl \cdot PF_6$ ($\lambda_{ex}=350$ nm)

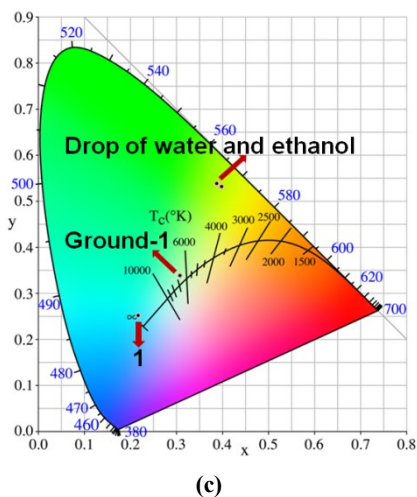
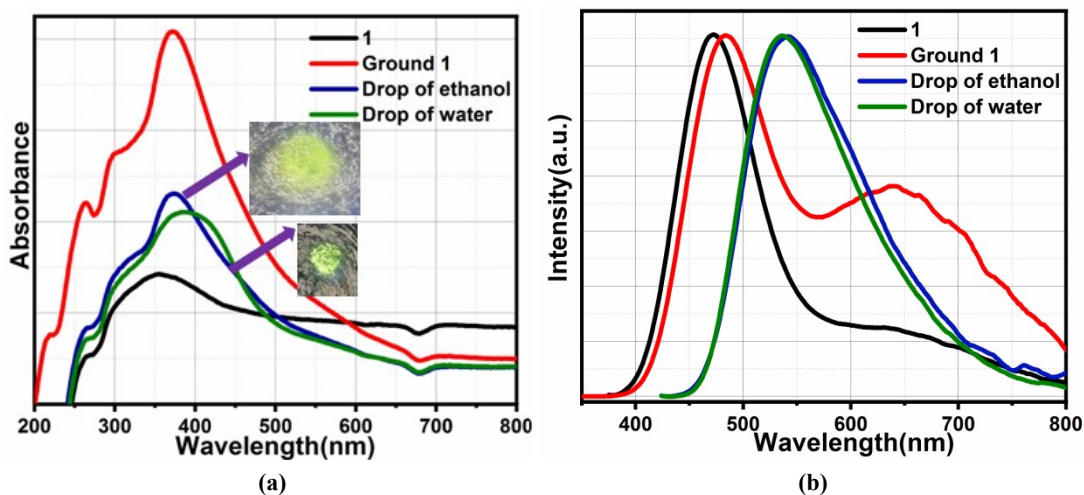


Fig. S5 (a) UV-Vis spectra showing the ground sample treated by adding ethanol and water; (b, c) emission spectra and CIE chromaticity coordinates on various states

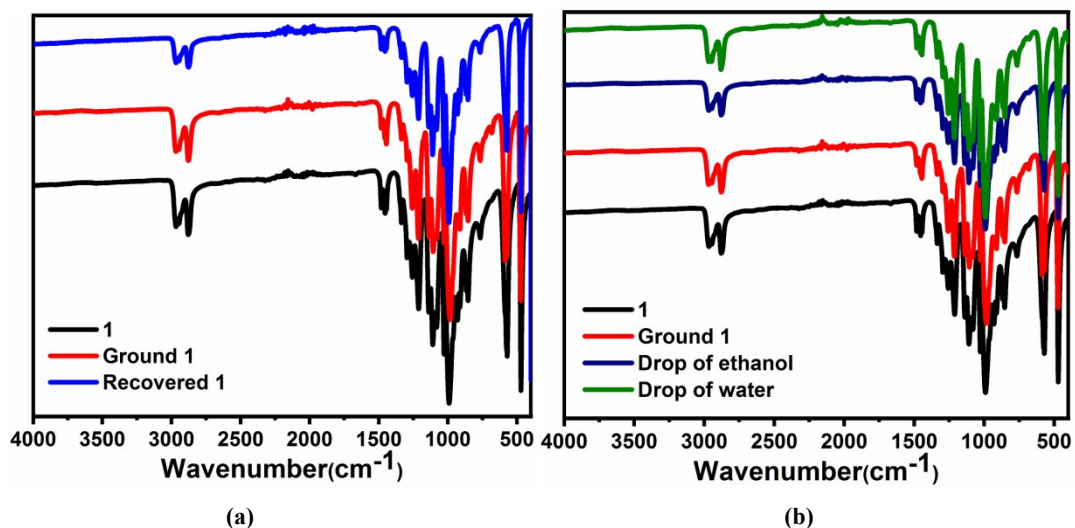


Fig. S6 (a) FT-IR spectra of 1, ground 1 and its recovered one; (b) FT-IR spectra of 1, ground 1 and treated with ethanol and water

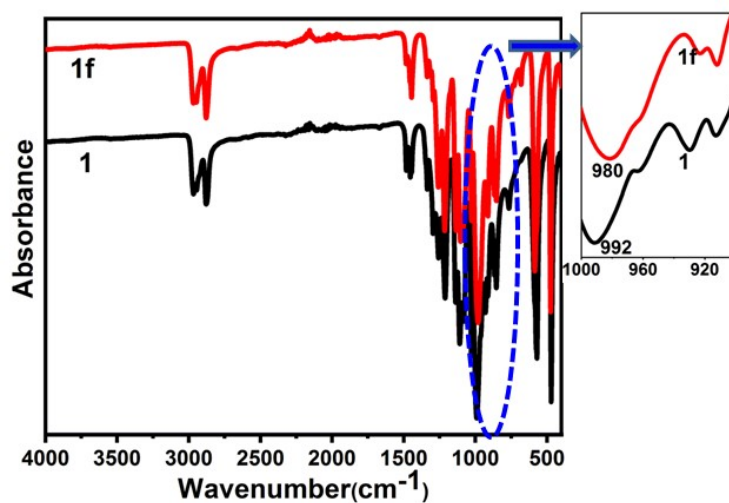
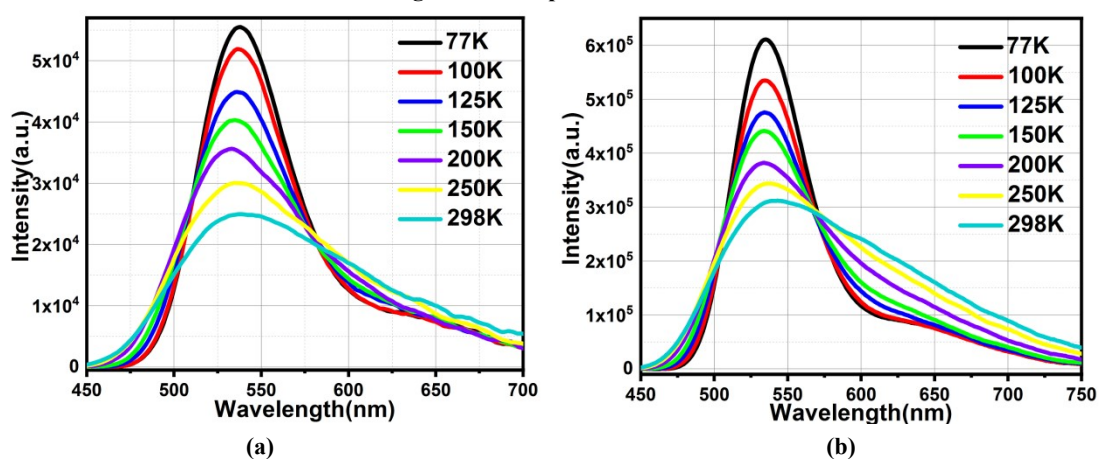


Fig. S7 FT-IR spectra of 1 and 1f



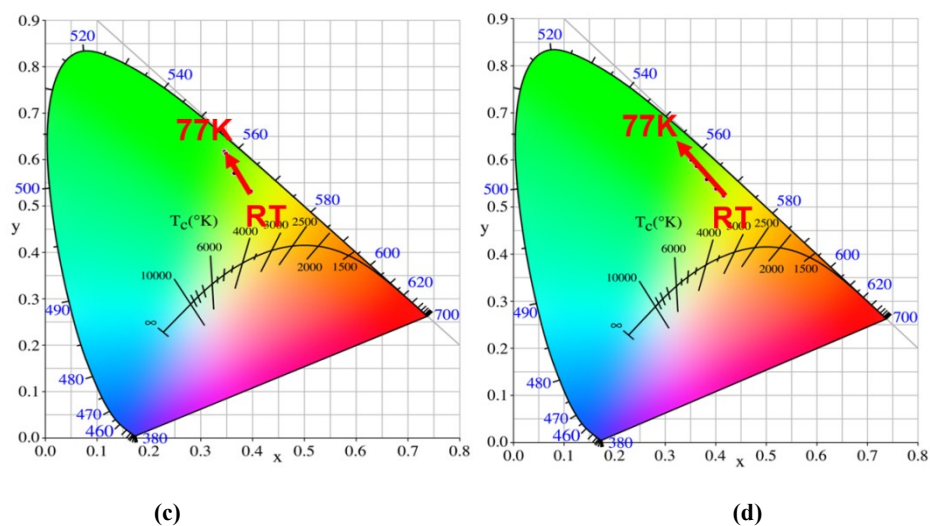


Fig. S8 Temperature dependent fluorescence and CIE chromaticity coordinate of ground 1 treated by solvents: (a, c) ethanol; (b, d) water