Synthesis, structure and oxygen-sensing property of Iridium(III)-containing coordination polymers with different cations.

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Supplementary materials:

Table S1. Selected Bond Length (Å) and Angles (°) for compounds **1**–**4**.[a]

Compound 1				Co-O(3C)	2.087(4)	O(1A)-Co-O(5)	93.33(16)
Zn(1)-O(7A)	1.981(5)	O(7A)-Zn(1)-O(1)	107.7(2)	Co-O(5)	2.155(6)	O(3B)-Co-O(5)	86.05(16)
Zn(1)-O(5)	1.981(5)	O(5)-Zn(1)-O(1)	110.0(2)	Co-O(3B)	2.087(4)	O(1)-Co-O(5)	93.33(16)
Zn(1)-O(1)	1.982(5)	O(7A)-Zn(1)-O(3A)	101.5(2)	Co-O(6)	2.161(5)	O(3C)-Co-O(5)	86.05(16)
Zn(1)-O(3A)	1.985(5)	O(5)-Zn(1)-O(3A)	105.8(2)	O(3)-Co(D)	2.087(4)	O(1)-Co-O(6)	85.76(15)
O(7A)-Zn(1)-O(5)	115.4(2)	O(1)-Zn(1)-O(3A)	116.5(2)	O(1)-Co-O(1A)	87.4(3)	O(1A)-Co-O(6)	85.76(15)
Compound 2				O(1)-Co-O(3B)	93.01(19)	O(3B)-Co-O(6)	94.86(15)
Cd-O(3B)	2.273(5)	O(1)-Cd-O(1A)	85.7(3)	O(1A)-Co-O(3B)	179.26(17)	O(3C)-Co-O(6)	94.86(15)
Cd-O(3C)	2.273(5)	O(3B)-Cd-O(6)	93.05(16)	O(1)-Co-O(3C)	179.26(17)	O(5)-Co-O(6)	178.7(2)
Cd-O(1)	2.293(5)	O(3C)-Cd-O(6)	93.05(16)	C(34)-O(3)-Co(D)	129.7(6)		
				Compound 4			
Cd-O(1A)	2.293(5)	O(1)-Cd-O(6)	88.01(16)	Ni-O(3B)	2.048(4)	O(1)-Ni-O(1A)	87.0(3)
Cd-O(6)	2.341(6)	O(1A)-Cd-O(6)	88.01(16)	Ni-O(3C)	2.048(5)	O(3B)-Ni-O(5)	85.44(19)
Cd-O(5)	2.348(6)	O(3B)-Cd-O(5)	90.35(16)	Ni-O(1)	2.048(5)	O(3C)-Ni-O(5)	85.44(19)
O(3)-Cd(D)	2.273(5)	O(3C)-Cd-O(5)	90.35(16)	Ni-O(1A)	2.049(5)	O(1)-Ni-O(5)	93.69(19)
O(3B)-Cd-O(3C)	84.9(3)	O(1)-Cd-O(5)	88.61(16)	Ni-O(5)	2.096(7)	O(1A)-Ni-O(5)	93.69(19)
O(3B)-Cd-O(1)	94.7(2)	O(1A)-Cd-O(5)	88.61(16)	Ni-O(6)	2.105(6)	O(3B)-Ni-O(6)	95.02(18)
O(3C)-Cd-O(1)	178.89(16)	O(6)-Cd-O(5)	175.4(2)	O(3)-Ni(D)	2.048(4)	O(3C)-Ni-O(6)	95.02(18)
O(3B)-Cd-O(1A)	178.89(16)	C(33)-O(1)-Cd	127.1(5)	O(3B)-Ni-O(3C)	86.3(3)	O(1)-Ni-O(6)	85.86(18)
O(3C)-Cd-O(1A)	94.7(2)	C(34)-O(3)-Cd(D)	122.3(5)	O(3B)-Ni-O(1)	179.07(19)	O(1A)-Ni-O(6)	85.86(18)
Compound 3				O(3C)-Ni-O(1)	93.3(2)	O(5)-Ni-O(6)	179.4(2)
Co-O(1)	2.079(4)	O(1A)-Co-O(3C)	93.01(19)	O(3B)-Ni-O(1A)	93.3(2)	C(33)-O(1)-Ni	131.3(7)
Co-O(1A)	2.079(4)	O(3B)-Co-O(3C)	86.5(3)	O(3C)-Ni-O(1A)	179.07(19)	C(34)-O(3)-Ni(D)	128.7(7)

[a]Symmetry codes for **1**: (A) x+1/2, -y+5/2, z. Symmetry code for **2**: (A) x, -y+1/2, z; (B) x+1/2, y, -z+5/2; (C) x+1/2, -y+1/2, -z+5/2; (D) x-1/2, y, -z+5/2. Symmetry code for **3**: (A) x, -y+1/2, z; (B) x+1/2, y, -z+1/2; (C) x+1/2, -y+1/2, -z+1/2; (D) x-1/2, y, -z+1/2. Symmetry code for **4**: (A) x, -y+1/2, z; (B) x+1/2, -y+1/2, -z+1/2; (C) x+1/2, y, -z+1/2 ; (D) x-1/2, y, -z+1/2.

Table S2. Selected Hydrogen Bonds Data for compounds **1**–**2**.[a]

D–H···A (Å)	D–H (Å)	H···A (Å)	D···A (Å)	∠ D–H···A(°)
Compound 1				
O12–H12A···O3^{i}	0.91	2.05	2.904(8)	157
O12–H12B···O13^{ii}	0.90	1.86	2.750(10)	167
O13–H13A···O5^{iii}	0.91	2.20	2.808(8)	124
O13–H13B···O9^{iv}	0.92	2.08	2.793(12)	133
O14–H14A···O4^{i}	0.89	1.95	2.828(9)	168
O14–H14B···O12^{v}	0.89	1.93	2.828(9)	179
O15–H15A···O10	0.92	2.22	2.887(10)	129
O15–H15B···O14	0.92	1.95	2.843(13)	164
O16–H16A···O9^{iv}	0.91	2.33	2.842(13)	116
C15–H15···O10^{vi}	0.95	2.52	3.393(10)	153
C19–H19···O14^{vi}	0.95	2.44	3.372(9)	169
C21–H21···O11^{v}	0.95	2.57	3.224(12)	126
C29–H29···O12^{v}	0.95	2.36	3.290(10)	168
C45–H45···O11^{vii}	0.95	2.46	3.224(12)	130
C50–H50···O10^{viii}	0.95	2.44	3.299(12)	151
C60–H60···O13^{ix}	0.95	2.38	3.233(9)	150
C73–H73B···O16	0.98	2.41	3.290(8)	149
Compound 2				
O9–H9B···O10^{i}	0.80	2.10	2.825(20)	149
O26–H26···O9^{ii}	0.95	2.45	3.274(2)	145
O11–H11A···O12	0.90	2.55	2.855(20)	100
O11–H11B···O12	0.89	2.40	2.855(20)	112
O12–H12B···O11	0.87	2.40	2.855(20)	113
O12–H12B···O8^{iii}	0.87	2.53	2.851(20)	102
C8–H8···O8^{iv}	0.95	2.46	3.3772(20)	162
C19–H19···O11	0.95	2.49	3.3556(14)	152
C22–H22···O7^{v}	0.95	2.59	3.2707(12)	128
C26–H26···O9^{ii}	0.95	2.45	3.2742(11)	145

[a]Symmetry codes for **1**: (i) x+1/2, -y+1/2, z; (ii) –x+1, -y+1, z+1/2; (iii) –x+1/2, y+1/2, z-1/2; (iv) x+1/2, -y+3/2, z; (v) x-1/2, -y+1/2, z; (vi) x, y-1, z; (vii) x-1/2, -y+3/2, z; (viii) –x, -y+1, z+1/2; (ix) –x+1/2, y-1/2, z+1/2. Symmetry code for **2**: (i) x, y, z-1; (ii) x, y, z+1; (iii) x+1/2, y, -z+1/2; (iv) -x, -y, -z+1; (v) x-1/2, -y+1/2, -z+3/2.

Table S3. Selected Hydrogen Bonds Data for compounds **3**–**4**.[a]

D–H···A (Å)	D–H (Å)	H···A (Å)	D···A (Å)	∠ D–H···A(°)
Compound 3				
O6–H6···O4^{i}	0.85	1.77	2.550(11)	152
O9–H9B···O6^{ii}	0.84	2.34	3.047(10)	142
O10–H10A···O9^{iii}	0.85	2.25	3.093(14)	175
O11–H11A···O13	0.96	2.53	3.052(20)	114
O11–H11B···O12	0.87	2.56	2.958(30)	109
O12–H12A···O2^{iv}	0.86	1.96	2.634(20)	134
O12–H12B···O11	0.78	2.25	2.958(30)	151
O13–H13A···O8^{v}	0.80	2.05	2.731(20)	143
C19–H19···O11	0.95	2.13	2.968(19)	146
C20–H20···O12	0.95	2.50	2.935(20)	108
C26–H26···O11^{iii}	0.95	2.42	2.936(16)	114
C29–H29···O12^{iii}	0.95	2.52	3.312(20)	122
C40–H40A···O8	0.98	2.27	2.643(20)	101
C40–H40B···O12	0.98	2.48	3.309(30)	142
Compound 4				
O9–H9A···O5^{i}	0.78	2.36	3.136(10)	170
O9–H9B···O10^{ii}	0.78	2.40	3.024(15)	138
O11–H11B···O1^{ii}	0.90	2.39	2.876(13)	114
O12–H12A···O3^{ii}	0.85	2.43	2.863(16)	112
O12–H12A···O5^{i}	0.85	2.42	3.184(19)	149
C8–H8···O8^{iii}	0.95	2.46	3.314(30)	150
C19–H19A···O11	0.95	1.98	2.842(20)	150
C20–H20A···O12	0.95	2.38	2.779(20)	105
C26–H26A···O11^{iv}	0.95	2.39	2.838(18)	109
C26–H26B···O10	1.07	2.59	3.313(19)	124
C29–H29A···O12^{iv}	0.95	2.45	3.068(20)	123

[a] Symmetry code for **3**: (i) x+1/2, -y+1/2, -z+5/2; (ii) x, y, -1+z; (iii) x, y, z+1; (iv) x-1/2, y, -z+3/2; (v) x+1/2, y, -z+1/2. Symmetry code for **4**: (i) x-1/2, -y+1/2, -z+3/2; (ii) x, y, z-1; (iii) -x, -y, -z+1; (iv) x, y, z+1.

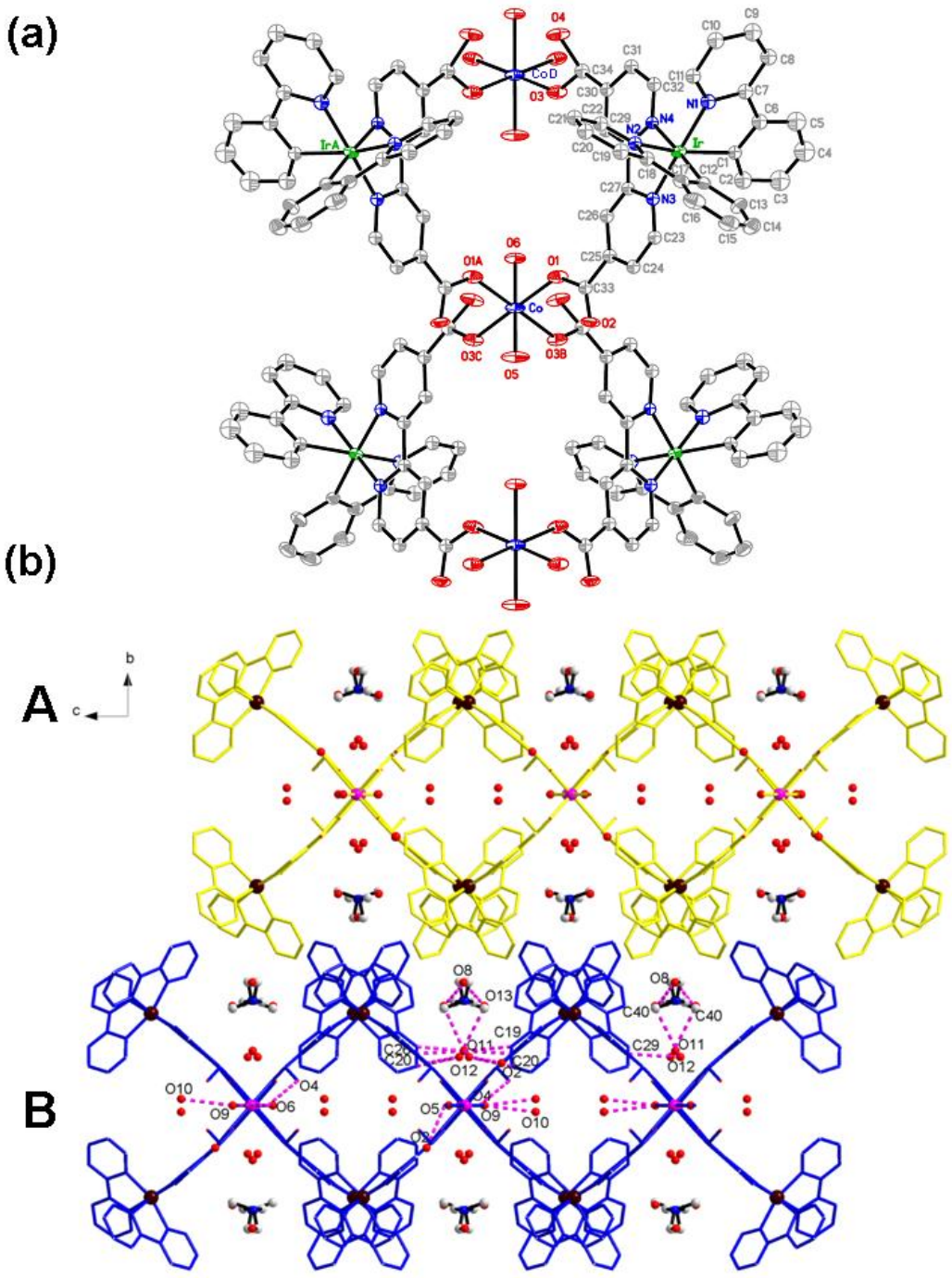

Figure S1. (a) ORTEP view of the coordination environment of Co(II) in **3**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. (b) The 3D cobalt-bridged structure of **3** with open channels. Schematic representation of the alternation in an AB/fashion along the *c* axis (due to the *a*-glide plane), of layers (in blue and yellow) of **3**. Color code: Co, purple; **L**, blue and yellow; Ir, wine; O, red. Hydrogen atoms are omitted for clarity. Magenta dashed lines represent the hydrogen bonding interaction.

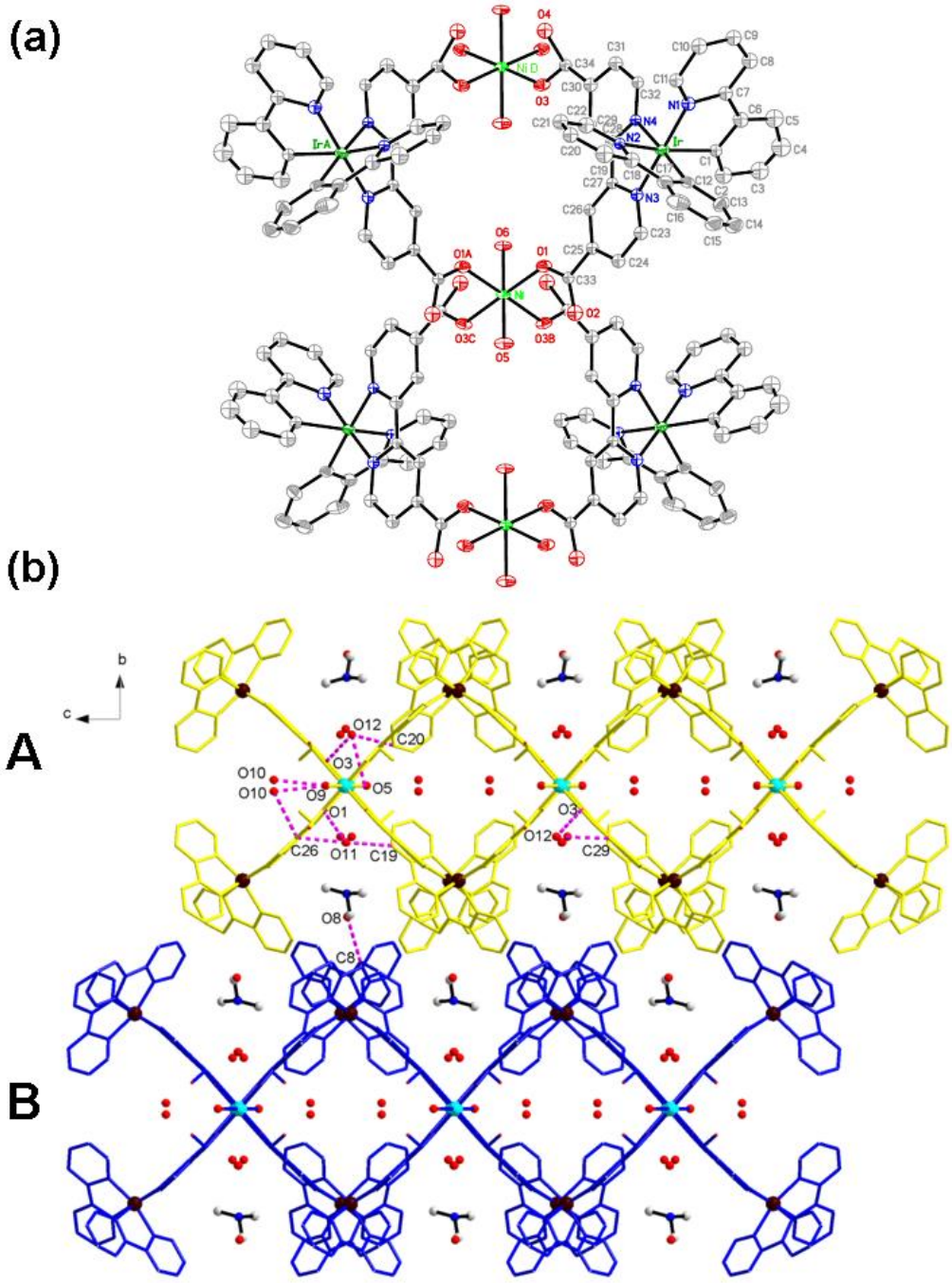

Figure S2. (a) ORTEP view of the coordination environment of Ni(II) in **4**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level. (b) The 3D nickel-bridged structure of **4** with open channels. Schematic representation of the alternation in an AB/fashion along the *c* axis (due to the *a*-glide plane), of layers (in blue and yellow) of **4**. Color code: Co, cyan; **L**, blue and yellow; Ir, wine; O, red. Hydrogen atoms are omitted for clarity. Magenta dashed lines represent the hydrogen bonding interaction.

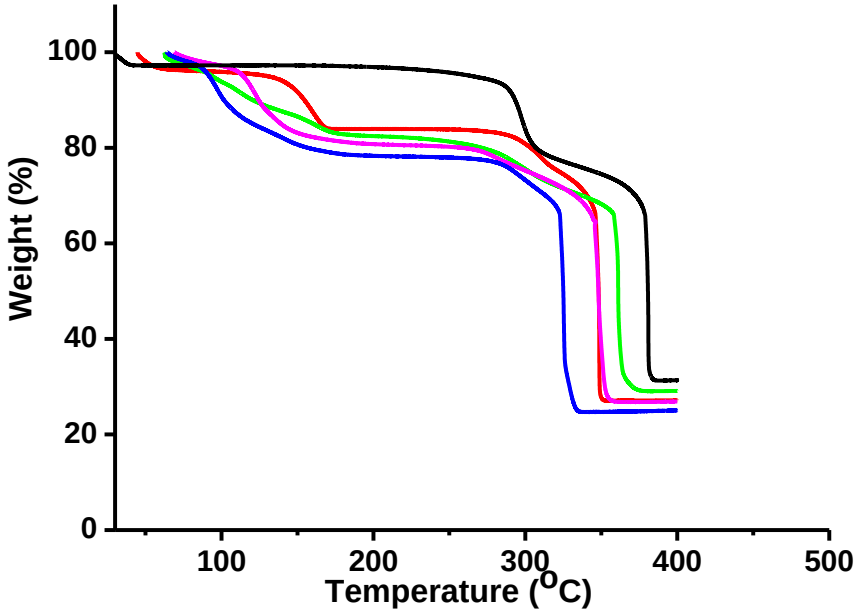

Figure S3. TGA curves for compounds **1**–**4** and **L-H$_2$** (red, **1**; green, **2**; blue, **3**; magenta, **4;** black, **L-H$_2$**).

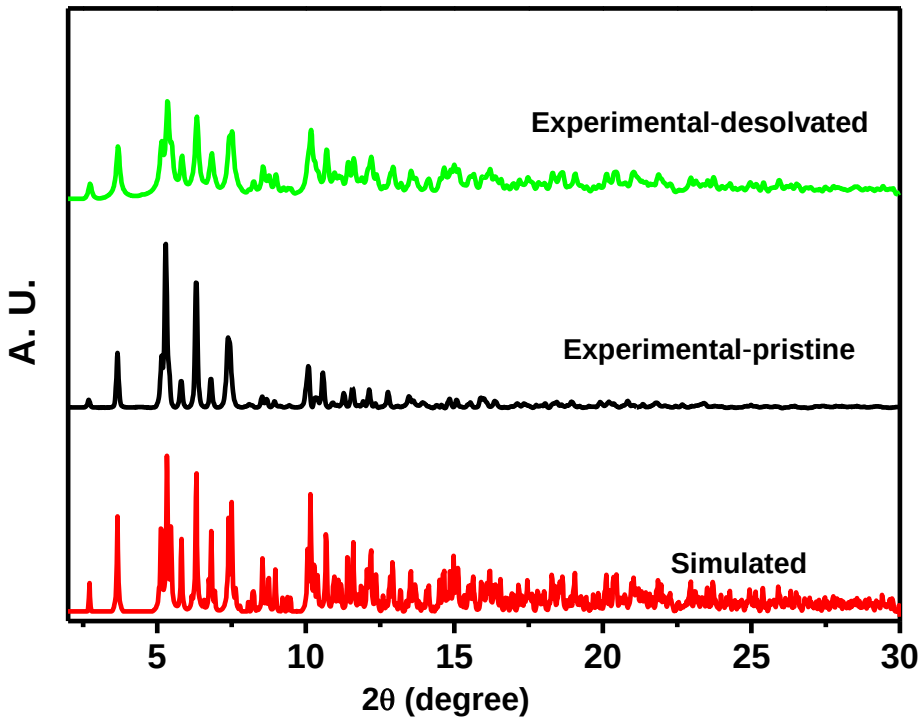

Figure S4. Comparison of simulative (red line), experimental-pristine solid (black line), and experimental-desolvated solid (green line) powder diffraction patterns for **1**.

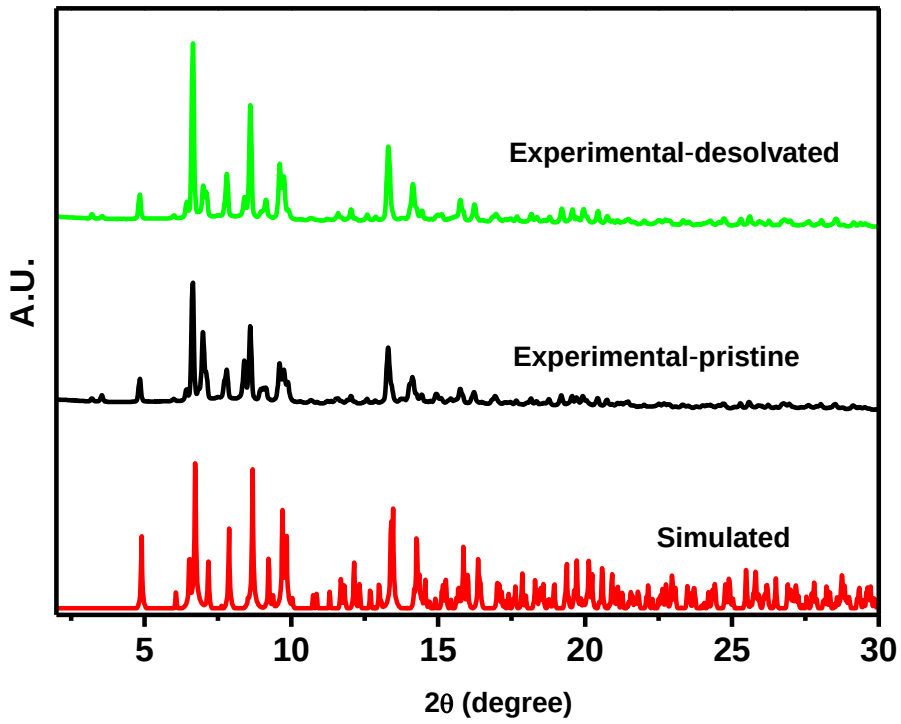

Figure S5. Comparison of simulative (red line), experimental-pristine solid (black line), and experimental-desolvated solid (green line) powder diffraction patterns for **2**.

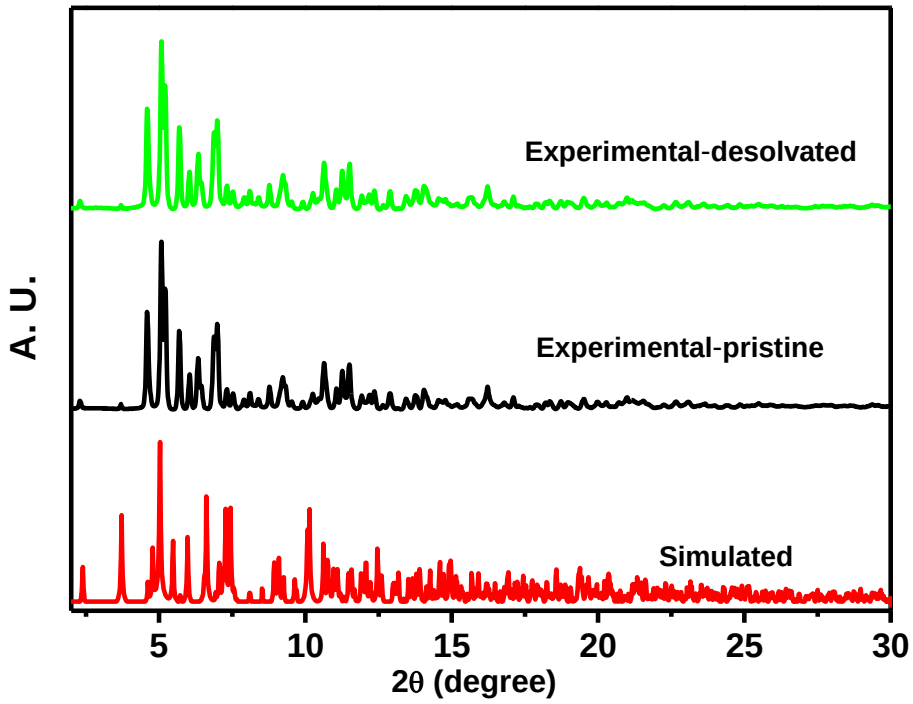

Figure S6. Comparison of simulative (red line), experimental-pristine solid (black line), and experimental-desolvated solid (green line) powder diffraction patterns for **3**.

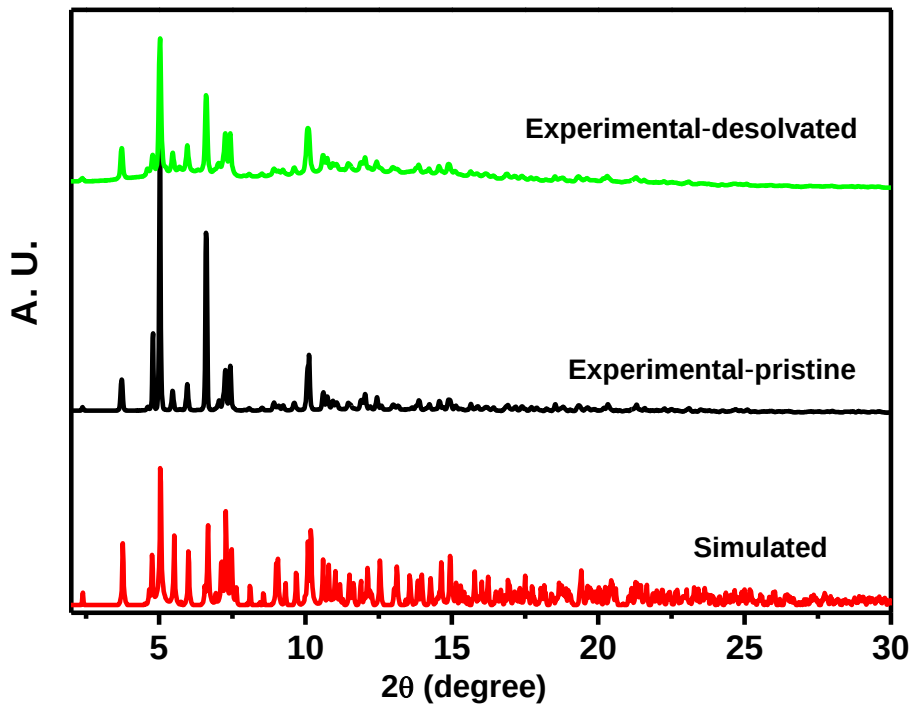

Figure S7. Comparison of simulative (red line), experimental-pristine solid (black line), and experimental-desolvated solid (green line) powder diffraction patterns for **4**.

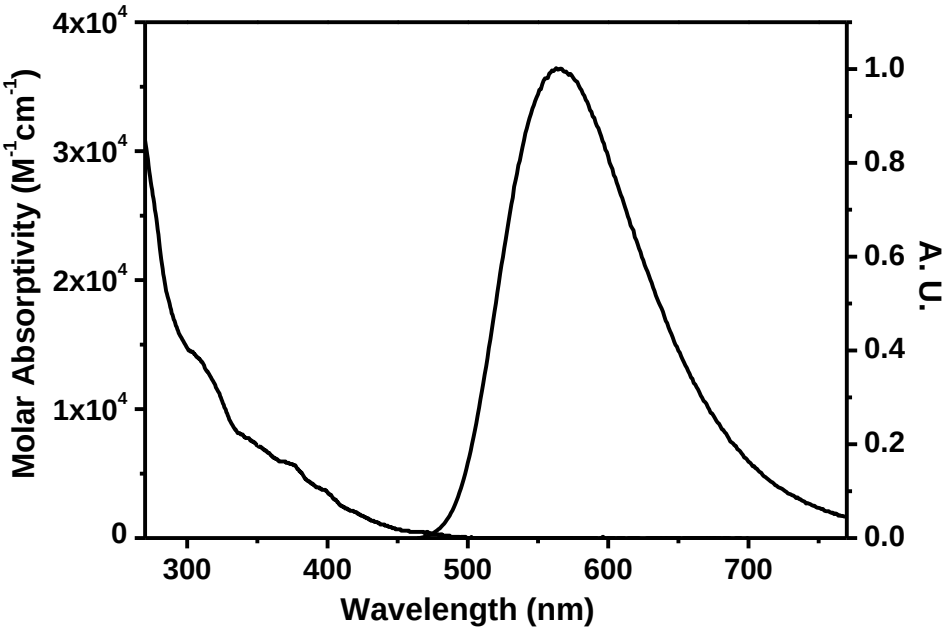

Figure S8. The absorption and emission spectrum of **L-H$_2$** in DMF solution. λ_{ex} = 400 nm.

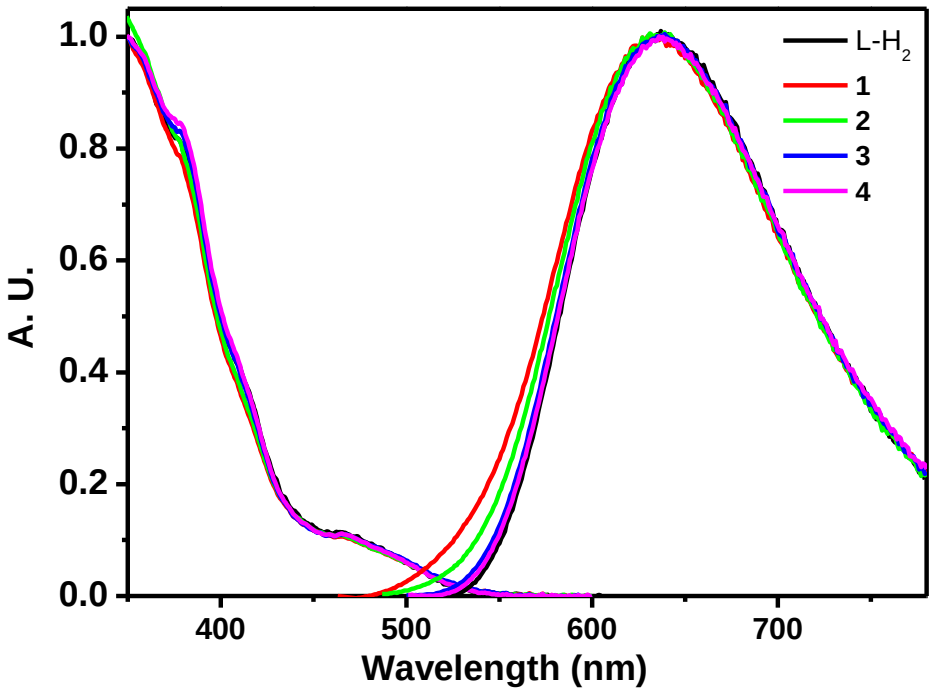

Figure S9. The normalized absorption and emission spectrum of **1–4** and **L-H$_2$** in DMF: H_2O (v/v = 1:1) solution. λ_{ex} = 400 nm.

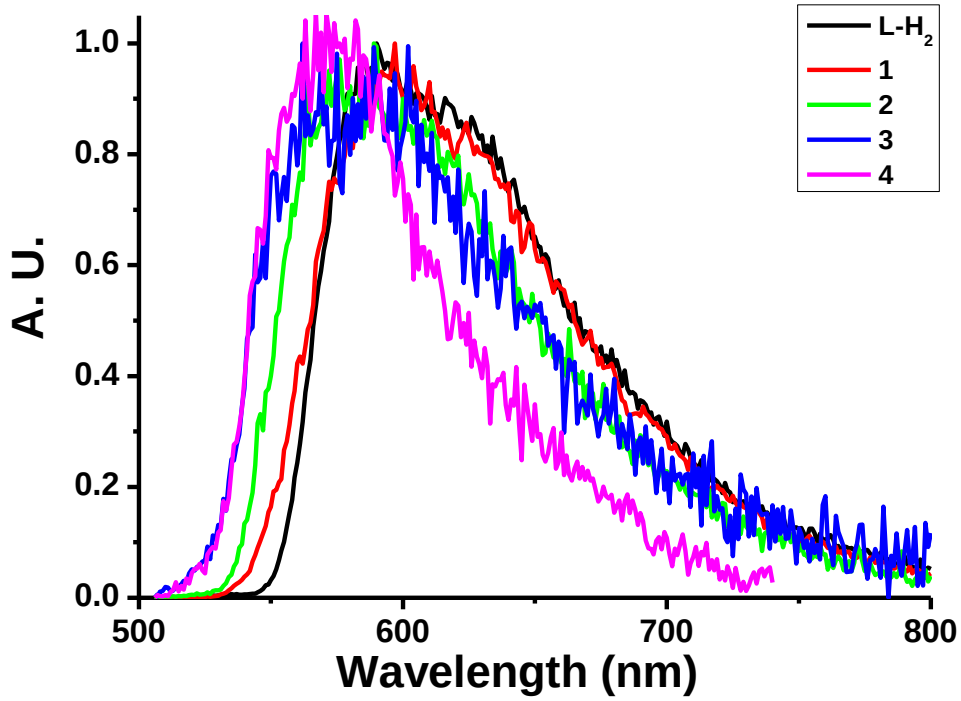

Figure S10. The normalized emission spectrum of **1–4** in single crystal and **L-H$_2$** in powder form in 77K. λ_{ex} = 400 nm.

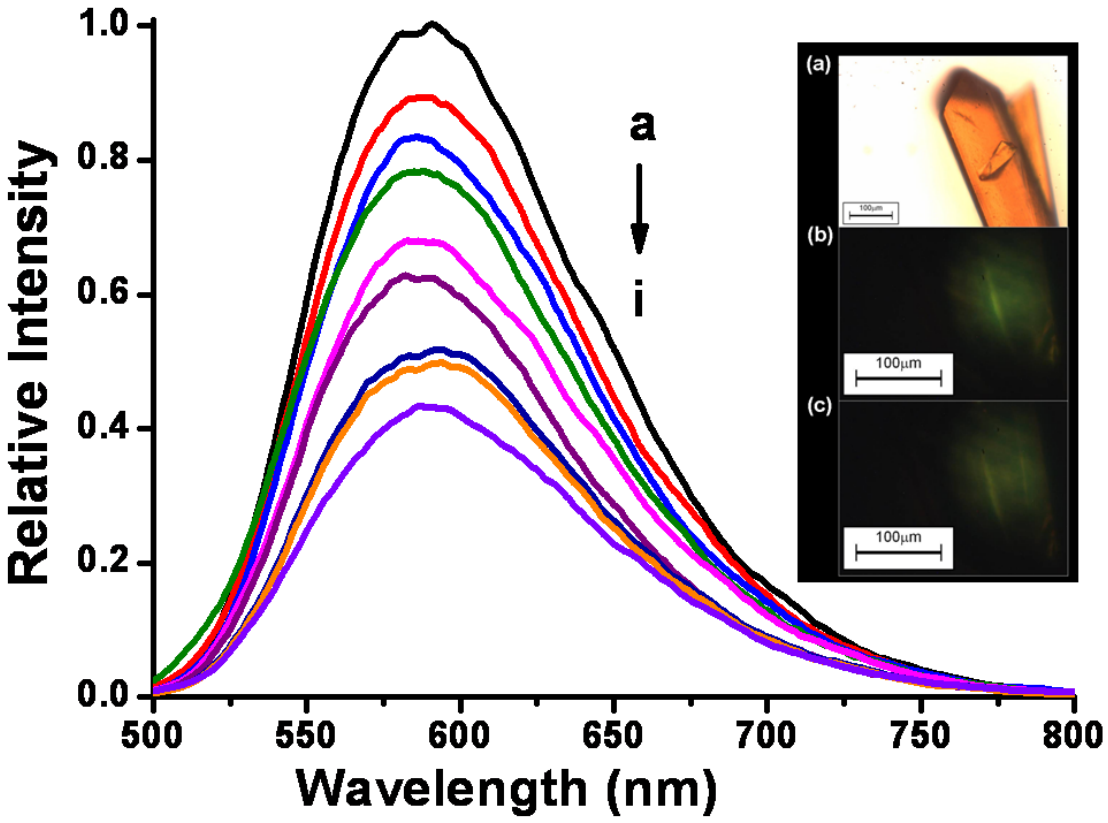

Figure S11. Response of **3** in single crystal to mole fraction of $O_{2(g)}$ in nitrogen (a) 0, (b) 0.06, (c) 0.12, (d) 0.18, (e) 0.33, (f) 0.40, (g) 0.67, (h) 0.71 and (i) 1.0. λ_{ex} = 406 nm. Inset: (a) Color appearance of **3**. (b, c) Luminescence changes of **3** with 100% N_2 and 100% O_2, respectively. Scale bar is 100 μm.

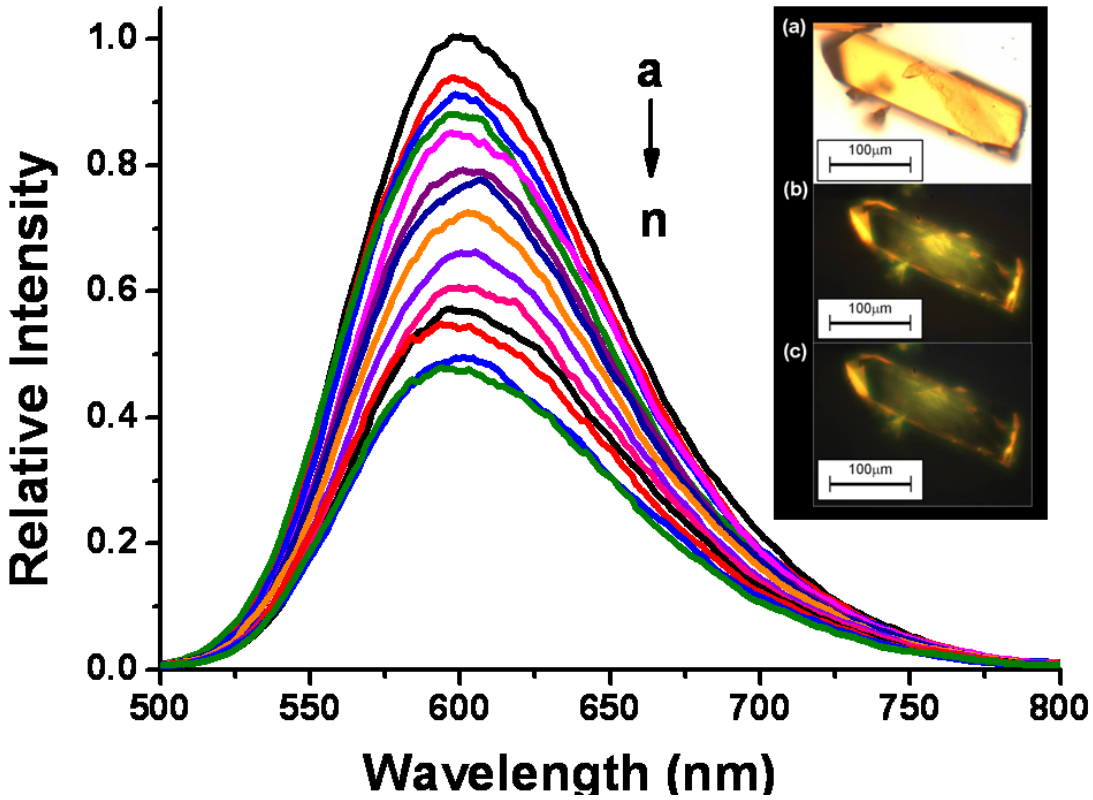

Figure S12. Response of **4** in single crystal to mole fraction of $O_{2(g)}$ in nitrogen (a) 0 (b) 0.05 (c) 0.10 (d) 0.15 (e) 0.20 (f) 0.25 (g) 0.30 (h) 0.40 (i) 0.50 (j) 0.6 (k) 0.7 (l) 0.8 (m) 0.9 (n) 1.0. λ_{ex} = 406 nm. Inset: (a) Color appearance of **4**. (b, c) Luminescence changes of **4** with 100% N_2 and 100% O_2, respectively. Scale bar is 100 μm.

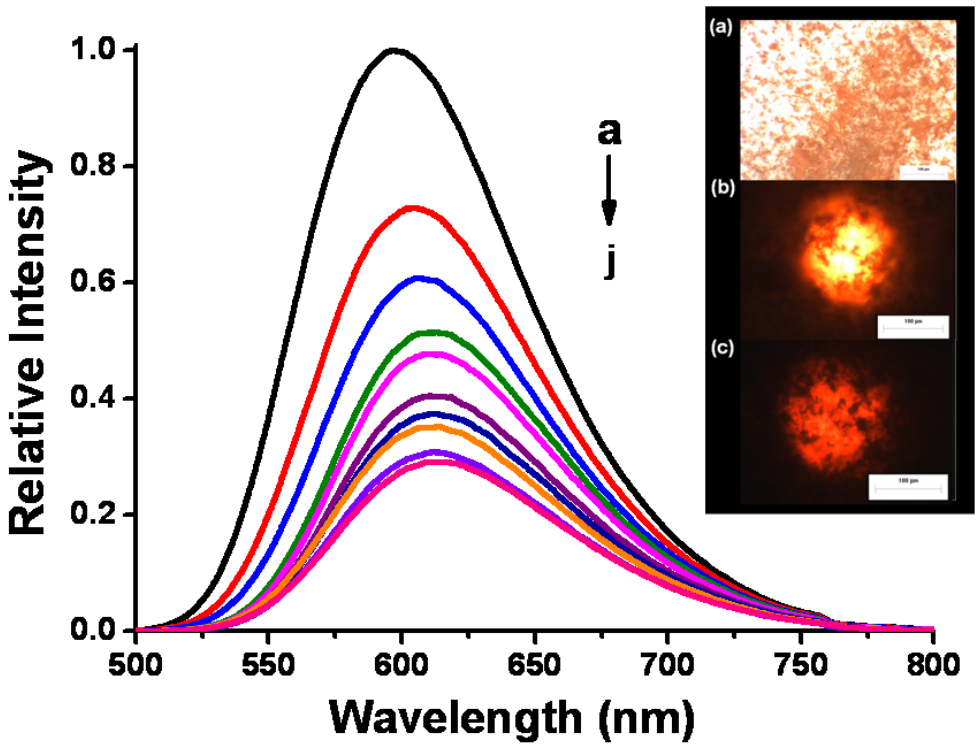

Figure S13. Response of **L-H$_2$** in powder to mole fraction of $O_{2(g)}$ in nitrogen (a) 0, (b) 0.20, (c) 0.30, (d) 0.40, (e) 0.50, (f) 0.60, (g) 0.70, (h) 0.80, (i) 0.90 and (j) 1.0. λ_{ex} = 406 nm. Inset: (a) Color appearance of **L-H$_2$**. (b, c) Luminescence changes of **L-H$_2$** upon with 100% N_2 and 100% O_2, respectively. Scale bar is 100 μm.

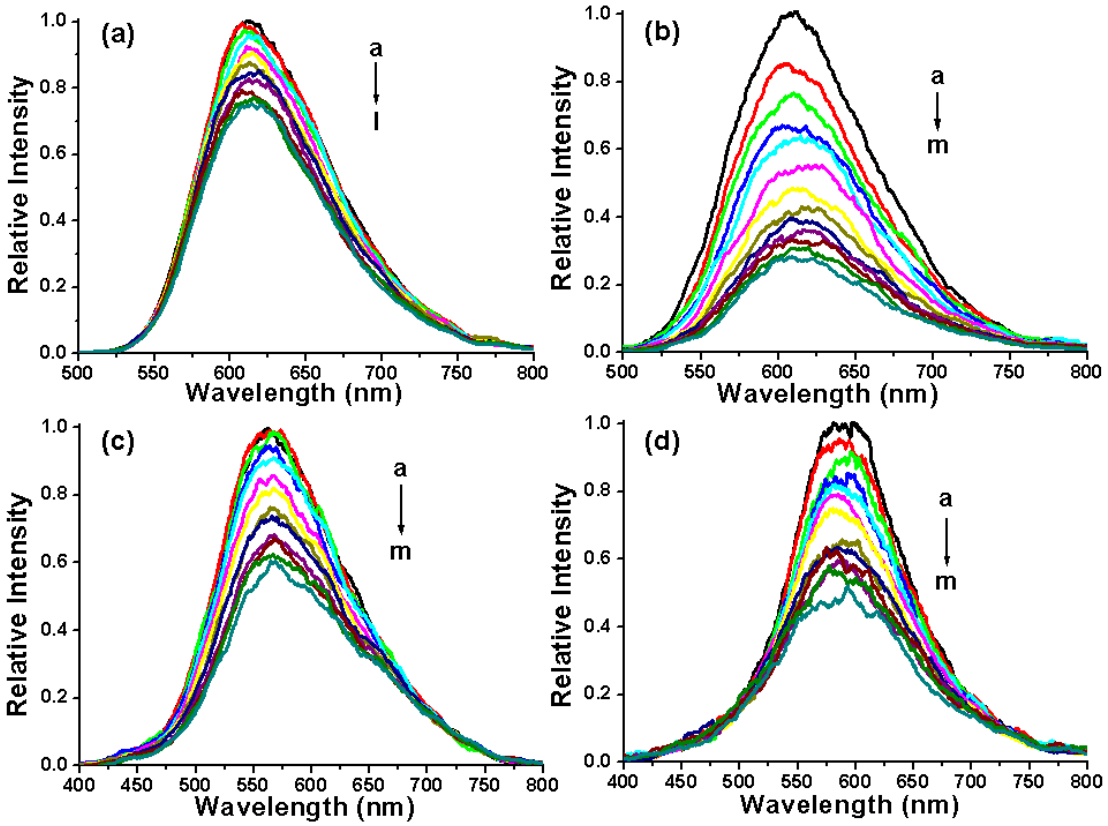

Figure S14. Response of (a) **1**, (b) **2**, (c) **3**, and (d) **4** in powder to mole fraction of $O_{2(g)}$ in nitrogen (a) 0, (b) 0.05, (c) 0.10, (d) 0.15, (e) 0.20, (f) 0.30, (g) 0.40, (h) 0.50, (i) 0.70, (j) 0.80, (k) 0.90 and (l) 1.0 for **1**; (a) 0, (b) 0.05, (c) 0.10, (d) 0.15, (e) 0.20, (f) 0.30, (g) 0.40, (h) 0.50, (i) 0.60, (j) 0.70, (k) 0.80, (l) 0.90 and (m) 1.0 for **2**-**4**. λ_{ex} = 406 nm.

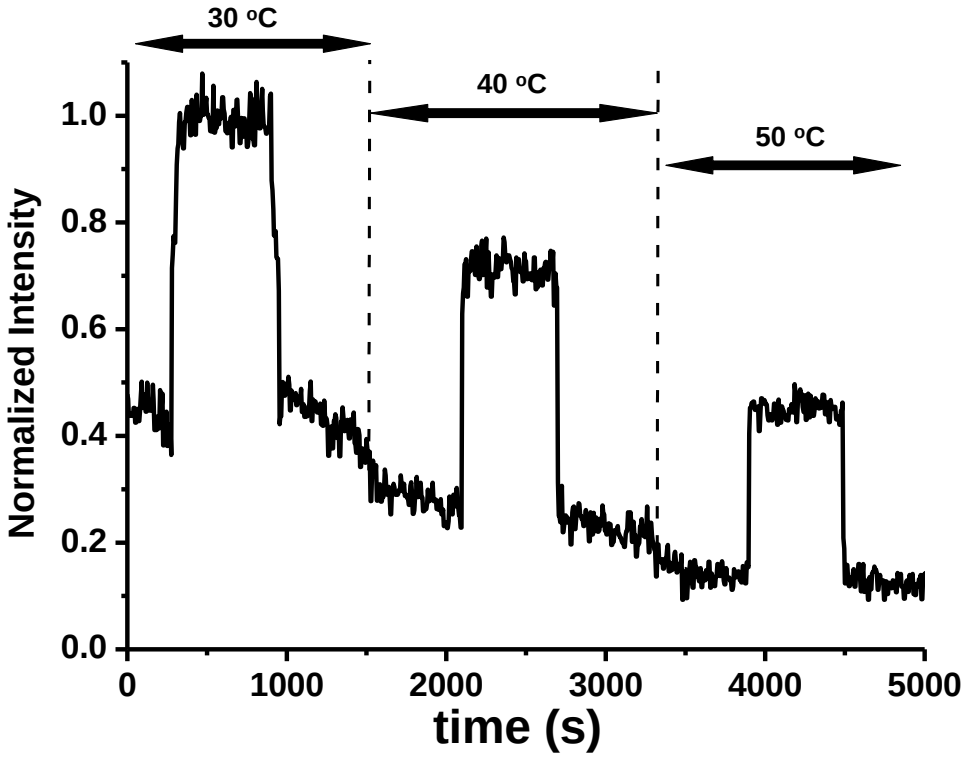

Figure S15. Relative luminescence changes of compound **2** in single crystal at 30, 40 and 50 °C, respectively upon alternating exposure to 100% nitrogen and 100% oxygen atmosphere.