

Construction of Two Stable Co(II)-Based Hydrogen-Bonded Organic Frameworks as a Luminescent Probe for Recognition of Fe³⁺ and Cr₂O₇²⁻ in H₂O

Qi-Ying Weng ¹, Ya-Li Zhao ^{1,2}, Jia-Ming Li ^{1,*}, Miao Ouyang ^{3,*}

¹ Guangxi Key Laboratory of Green Chemical New Materials and Safety Technology, College of Petroleum and Chemical Engineering, Beibu Gulf University, Qinzhou 535011, China; qy13977735754@163.com (Q.-Y.W.); jmli@bbgu.edu.cn (J.-M.L.)

² College of International Studies, Beibu Gulf University, Qinzhou 535011, China; ylzha@bbgu.edu.cn (Y.-L.Z)

³ School of Chemical and Environmental Engineering, Hanshan Normal University, Chaozhou 521041, China; 442976264@qq.com (M.O)

* Correspondence: jmli@bbgu.edu.cn (J.-M.L); 2557@hstc.edu.cn (M.O)

Contents

Figure S1. IR spectra of compounds **1** (a) and **2** (b).. 2

Figure S2. The simplified 2D HOFs for **2**..2

Figure S3. (a) The 1D chain constructed by $\pi\cdots\pi$ interactions in **2**. (b) The 1D chain constructed by C-H $\cdots\pi$ interactions in **2**..3

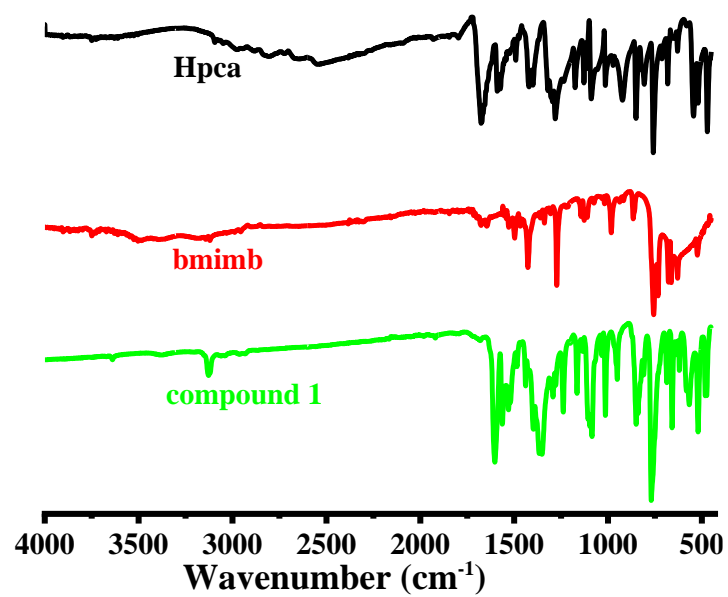
Figure S4. The solid state excitation and emission spectra of **1** and **2** at room temperature.....3

Figure S5. TG curves of compounds **1** and **2**.4

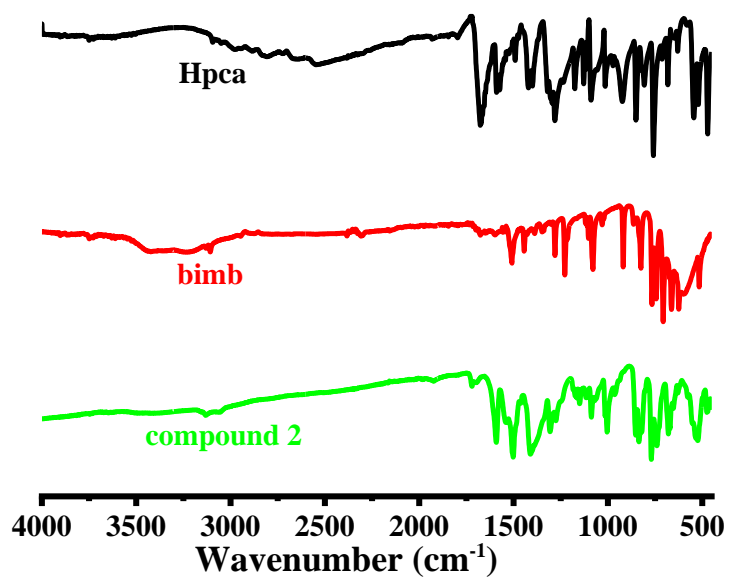
Table S1. Crystal structure data for **1** and **2**^{a,b,c}.....5

Table S2. Selected bond lengths/Å and bond angles/° for compounds **1** and **2**.6

Table S3. Selected bond lengths (Å) and angles (deg) for **1** and **2** with estimated standard deviations in parentheses.7



(a)



(b)

Figure S1. IR spectra of compounds 1 (a) and 2 (b).

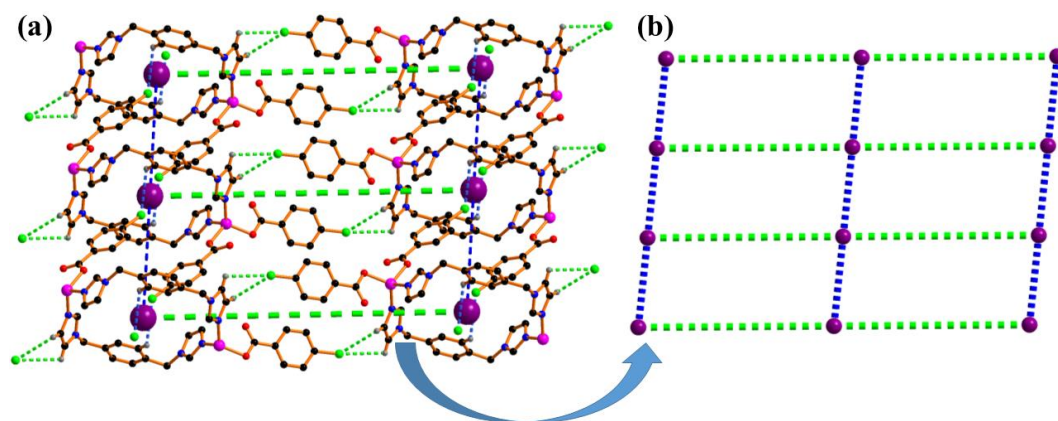


Figure S2. The simplified 2D HOFs for 2.

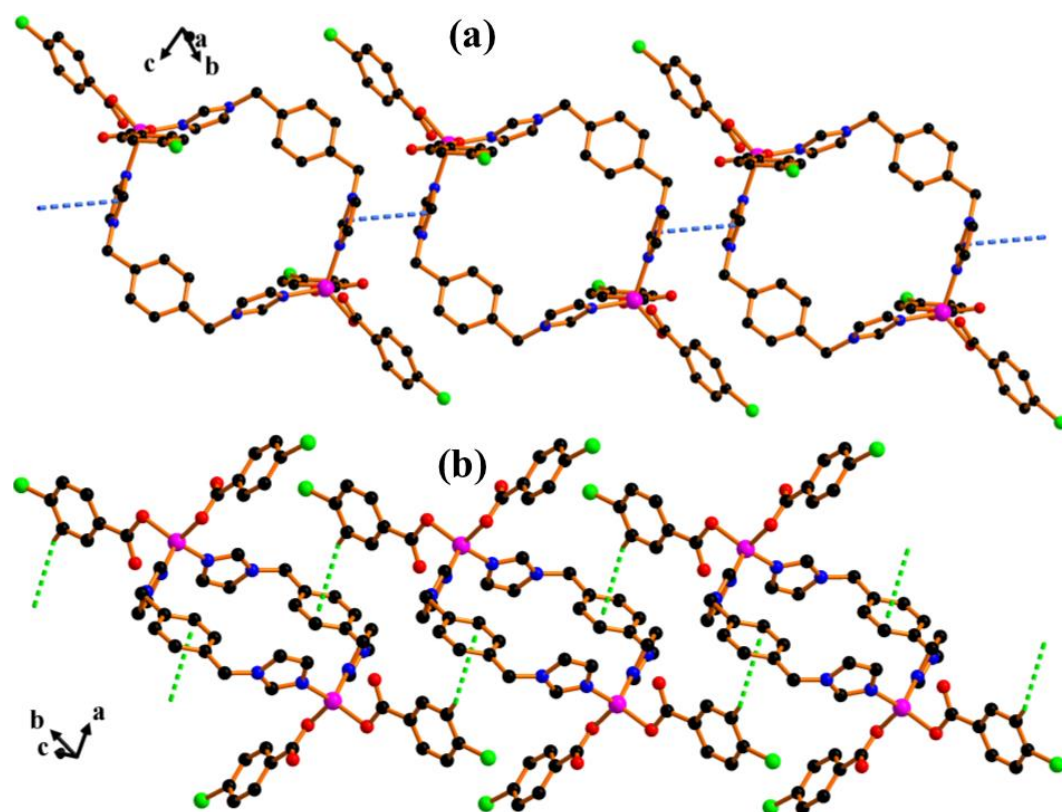


Figure S3. (a) The 1D chain constructed by $\pi \cdots \pi$ interactions in 2. (b) The 1D chain constructed by C-H \cdots π interactions in 2.

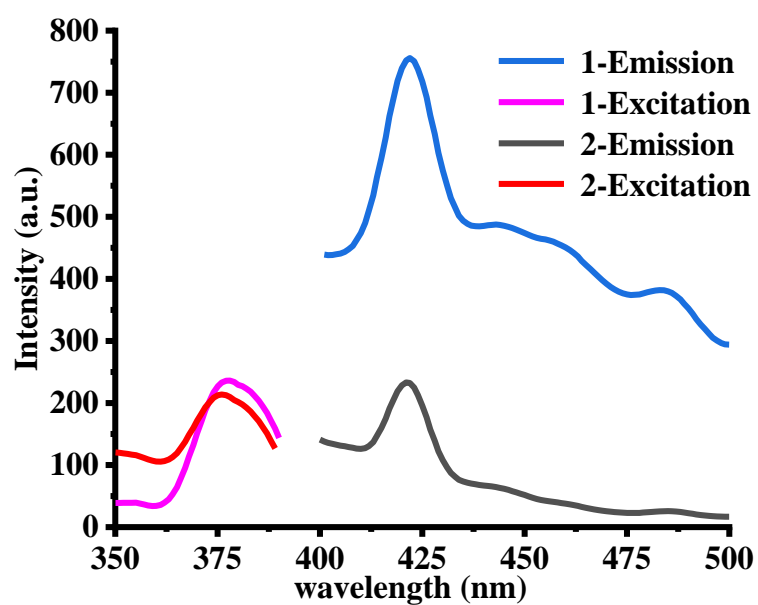


Figure S4. The solid state excitation and emission spectra of 1 and 2 at room temperature.

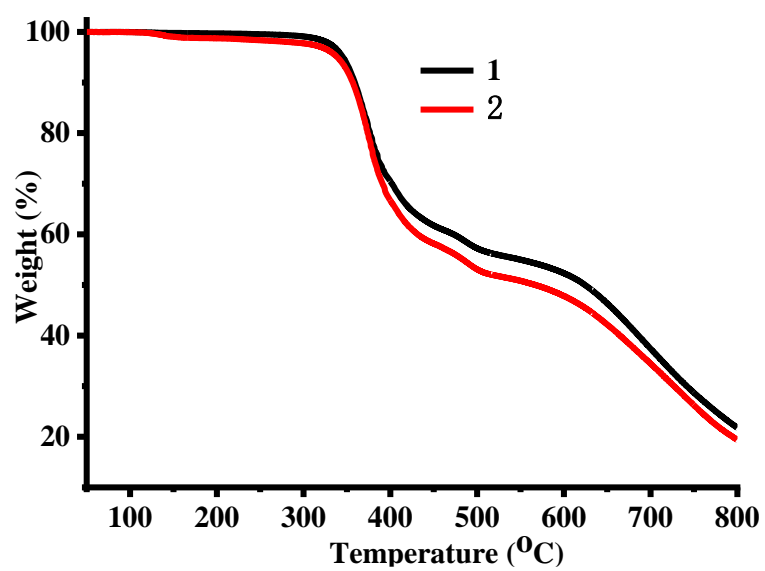


Figure S5. TG curves of compounds 1 and 2.

Table S1. Crystal structure data for **1** and **2**^{a,b,c}.

Compound	1	2
Empirical formula	C ₃₀ H ₂₆ Cl ₂ CoN ₄ O ₄	C ₅₆ H ₄₄ Cl ₄ Co ₂ N ₈ O ₈
Formula weight	636.38	1216.65
Crystal system	hexagonal	triclinic
Space group	<i>P</i> 6 ₄	<i>P</i> -1
<i>a</i> , Å	14.0240(6)	10.0331(8)
<i>b</i> , Å	14.0240(6)	12.8050(11)
<i>c</i> , Å	12.6288(6)	13.1684(14)
α , deg	90	63.495(10)
β , deg	90	80.368(8)
γ , deg	120	67.362(8)
<i>V</i> , Å ³	2151.0(2)	1397.3(3)
<i>Z</i>	3	1
<i>D</i> _{calcd} , g cm ⁻³	1.474	1.446
μ (MoK α), mm ⁻¹	0.828	0.846
<i>F</i> (000), e	981	622
<i>hkl</i> range	-17→16, \pm 17, \pm 15	\pm 11, \pm 15, -13→15
((sin θ)/ λ) _{max} , Å ⁻¹	0.617	0.597
Refl. measured	15400	8706
Refl. unique	2827	4961
<i>R</i> _{int}	0.0525	0.0503
Param. refined	188	352
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0400/0.0697	0.0690/0.1252
<i>R</i> ₁ ^a / <i>wR</i> ₂ ^b (all data)	0.0606/0.0799	0.1366/0.1671
GoF (<i>F</i> ²) ^c	1.057	1.047
$\Delta\rho_{\text{fin}}$ (max/min), e Å ⁻³	0.25/-0.34	0.54/-0.59

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$, where $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$; ^c GoF = $[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

Table S2. Selected bond lengths/Å and bond angles/° for compounds **1** and **2**.

Compound 1 ^a			
Co1-N1	2.048 (4)	Co1-N1 ⁱ	2.048 (4)
Co1-O1	1.948 (4)	Co1-O1 ⁱ	1.948 (4)
N1-Co1-N1 ⁱ	111.5 (2)	O1-Co1-N1	117.81 (16)
O1-Co1-N1 ⁱ	92.58 (15)	O1i-Co1-N1 ⁱ	117.81 (16)
O1 ⁱ -Co1-N1	92.58 (15)	O1-Co1-O1 ⁱ	126.0 (2)
Compound 2 ^b			
Co1-O1	1.978 (3)	Co1-O3	1.961 (3)
Co1-N1	2.013 (4)	Co1-N4 ⁱ	2.028 (5)
O1-Co1-N1	111.84 (16)	O1-Co1-N4 ⁱ	116.81 (16)
O3-Co1-O1	110.89 (15)	O3-Co1-N1	95.96 (16)
O3-Co1-N4 ⁱ	105.53 (17)	N1-Co1-N4 ⁱ	113.56 (17)

^aSymmetry codes: i $-x+2, -y+1, z$; ii $-x+1, -y+1, z$.^bSymmetry codes: i $-x+1, -y, -z+1$.

Table S3. Selected bond lengths (Å) and angles (deg) for **1** and **2** with estimated standard deviations in parentheses.

D-H...A	d(D-H)	d(H...A)	d(D...A)	∠(DHA)
Compound 1 ^a				
C16-H16...O2 ⁱⁱⁱ	0.93	2.95	3.728 (8)	142
C16-H16...O2 ^{iv}	0.93	2.95	3.728 (8)	142
C15-H15...N1 ^v	0.93	2.89	3.682 (7)	144
C15-H15...N1 ^{vi}	0.93	2.89	3.682 (7)	144
C4-H4...Cl1 ^{vii}	0.93	2.95	3.743 (6)	144
C8-H8A...Cl1 ^{viii}	0.96	2.84	3.676 (7)	147
Compound 2 ^b				
C15-H15...O1 ⁱⁱ	0.93	2.47	3.261 (6)	142
C17-H17...O2 ⁱⁱⁱ	0.93	2.51	3.417 (7)	165
C18-H18B...O1 ⁱⁱ	0.97	2.60	3.491 (7)	152
C23-H23...O1 ^{iv}	0.93	2.91	3.798 (6)	161
C25-H25A...O4 ^{iv}	0.97	2.65	3.539 (7)	153
C27-H27...O4 ^{iv}	0.93	2.79	3.425 (8)	126
C27-H27...Cl1 ^v	0.93	3.175	3.522 (6)	104
C28-H28...Cl1 ^v	0.93	3.125	3.511 (6)	107
C20-H20...Cl2 ^{vi}	0.93	3.308	3.884 (6)	122

^aSymmetry codes: iii $-y+1, x-y, z-2/3$; iv $y, -x+y+1, z-2/3$; v $-y+1, x-y, z+1/3$; vi $y, -x+y+1, z+1/3$; vii $-x+2, -y+2, z$; viii $-x+y+1, -x+2, z-1/3$.

^bSymmetry codes: ii $-x+1, -y+1, -z+1$; iii $-x, -y+1, -z+1$; iv $x, y-1, z+1$; v $x+1, y-2, z+1$; vi $x-1, y, z$.