Electronic supplementary information (ESI)

Construction of Cd(II)-Based Metal-Organic Frameworks incorporating SiF_6^{2-} as Fluorescence Sensor for Arginine†

Xue Wu,[a] Ding Li, [a] Lei Xu,[b] Yu-Fei Jiang,[a] Yue Zhao* [a] and Jing Zhao* [a]

[a] *Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China.*

[b] *Jiangsu Key Lab of Data Engineering and Knowledge Service, School of Information Management, Nanjing University, Nanjing 210023, China.*

Email address: zhaoyue@nju.edu.cn (Y. Zhao), jingzhao@nju.edu.cn (J. Zhao).

X-ray crystallography

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The SC-XRD data of complex **1** was collected on a Bruker D8 Venture diffractometer with graphite-monochromated Mo K_α radiation (λ = 0.71073 Å) using the φ–ω scan technique at 296 K, while that of complex **2** was on a Bruker D8 Venture Photon II diffractometer with graphite-monochromated Ga K_α radiation (λ = 1.34139 Å) using the φ–ω scan technique at 193K. The integration of the diffraction data and intensity corrections for the Lorentz and polarization effects were performed by using SAINT program and semiempirical absorption corrections were applied using the SADABS program.[1] The structures were solved by direct methods with SHELXT-2018, expanded by subsequent Fourier-difference synthesis, and all the nonhydrogen atoms were refined anisotropically on F^2 using the full-matrix least-squares technique with the SHELXL-2019 crystallographic software package.[2,3] The free solvent molecules in the unit cell of complex **2** were taken into account in the SQUEEZE option of the PLATON program.[4] Hydrogen atoms were introduced at the calculated positions. The final chemical formulas were obtained based on volume/count electron analysis and TG analysis. The reported refinements of complex **2** were of the guest-free structures obtained by the SQUEEZE routine and the results were attached to the CIF files. The details of crystal parameters, data collection, and refinements are listed in Table S1, and the selected bond lengths and angles are given in Table S2.

Table S1. Crystal Data and Structure Refinements for **1** and **2**.

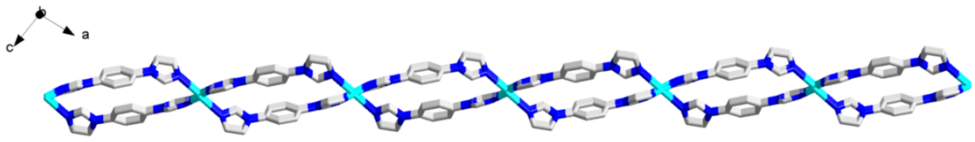
Compound	**1**	**2**
Chemical formula	$C_{24}H_{20}CdF_6N_8Si$	$C_{24}H_{20}CdF_6N_8Si$
Formula weight	674.97	674.97
λ (Å)	0.71073	1.34139
T (K)	296(2)	193(2)
Crystal system	Monoclinic	Monoclinic
Space group	*C*2/*c*	*C*2/*c*
a /Å	19.017(4)	18.5204(11)
b /Å	10.115(2)	18.0376(10)
c /Å	13.080(3)	12.4569(7)
β /°	97.672(8)	125.092(2)
Volume /Å^3	2493.5(9)	3405.0(3)
Z	4	4
D_c /g cm^{-3}	1.798	1.317
μ /mm^{-1}	1.002	4.050
F(000)	1344	1344
Theta range	2.690-27.531°	3.314-60.366
Reflections collected	11525	21133
Independent reflections	2847	3793
Data / restraints / parameters	2847 / 0 / 183	3793 / 0 / 201
GOF	1.017	1.385
R_1,	0.0328	0.0698
wR_2 [$I > 2\sigma(I)$][a,b]	0.1134	0.2575
R_1,	0.0404	0.0733
wR_2 (all data)	0.1293	0.2611

[a]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$

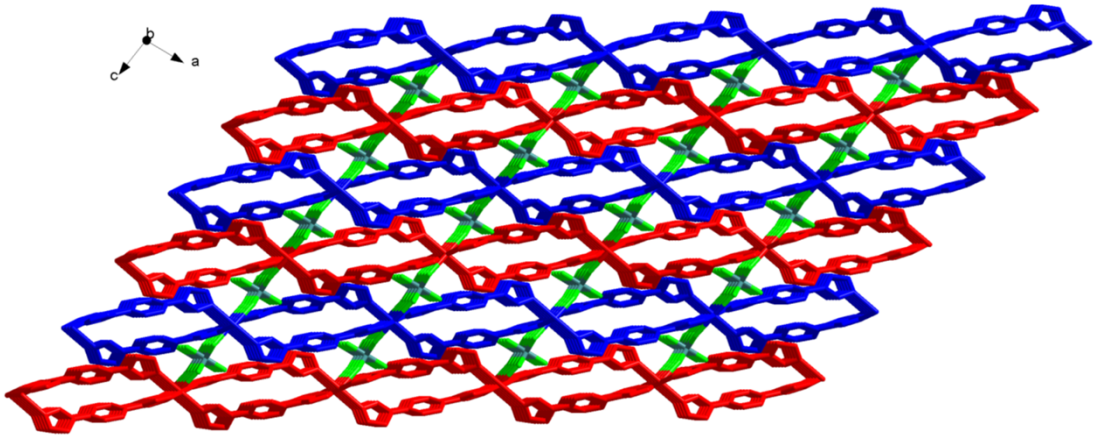
Table S2. Selected Bond Lengths (Å) and Angles (°) for **1** and **2**.

1			
Cd(1)-F(1)	2.2997(18)	Cd(1)-F(1)#1	2.2996(18)
Cd(1)-N(1)#2	2.309(2)	Cd(1)-N(4)	2.315(3)
F(1)#1-Cd(1)-F(1)	180.0	F(1)-Cd(1)-N(1)#3	99.08(8)
F(1)-Cd(1)-N(1)#2	80.92(8)	N(1)#2-Cd(1)-N(1)#3	180.00(7)
F(1)-Cd(1)-N(4)	94.64(9)	F(1)-Cd(1)-N(4)#1	85.36(9)
N(1)#2-Cd(1)-N(4)#1	82.94(10)	N(1)#2-Cd(1)-N(4)	97.06(10)
N(4)#1-Cd(1)-N(4)	180.0		
2			
Cd(1)-F(1)	2.279(4)	Cd(1)-N(1)	2.276(4)
Cd(1)-N(3)	2.284(4)		
F(1)-Cd(1)-F(1)#1	180.0	F(1)-Cd(1)-N(1)#1	85.82(19)
F(1)-Cd(1)-N(1)	94.18(19)	N(1)#1-Cd(1)-N(1)	180.0
F(1)-Cd(1)-N(3)	90.40(18)	F(1)#1-Cd(1)-N(3)	89.60(18)
N(1)#1-Cd(1)-N(3)	88.58(17)	N(1)-Cd(1)-N(3)	91.42(17)
N(1)-Cd(1)-N(3)#1	88.59(17)	N(3)-Cd(1)-N(3)#1	180.0(2)

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y+1, -z+1, #2 x-1/2, -y+1/2, z+1/2, #3 -x+3/2, y+1/2, -z+1/2 for **1**; #1 -x+1/2, -y+1/2, -z+1 for **2**.

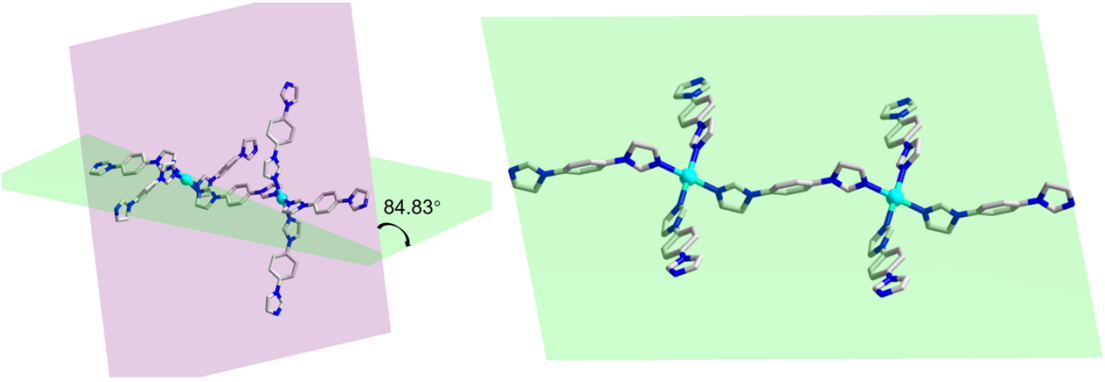


(a)

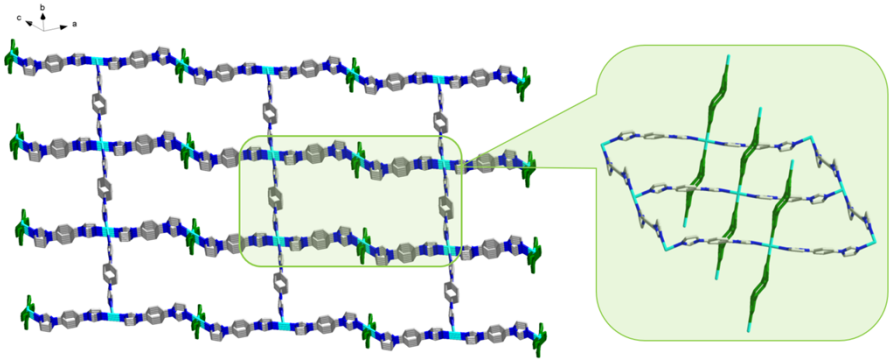


(b)

Fig. S1. (a) Structure of the Cd-bib coordination networks along b-axis. (b) The 3D framework structure of complex **1** along b-axis.



(a)



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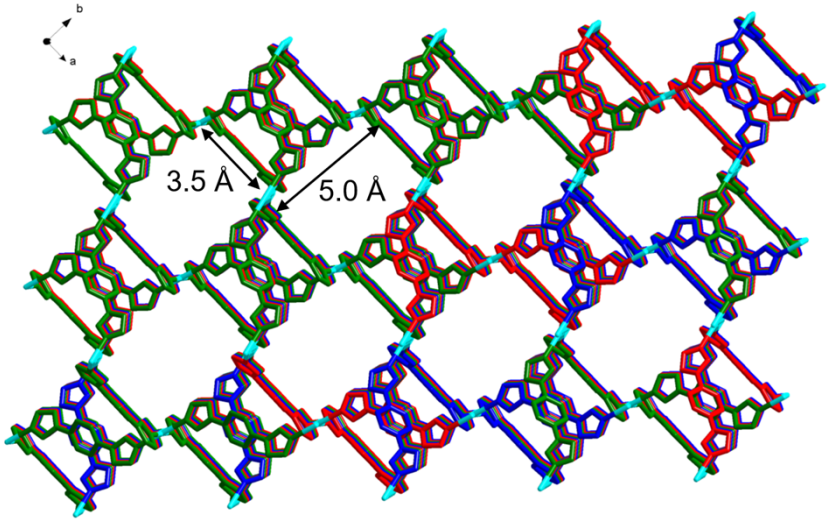
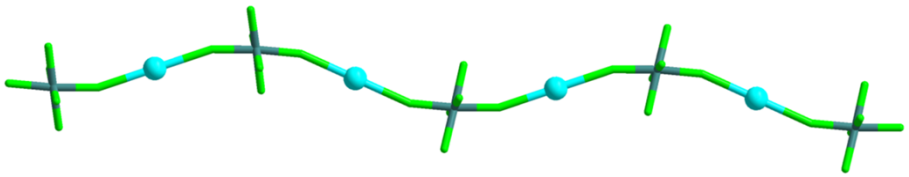
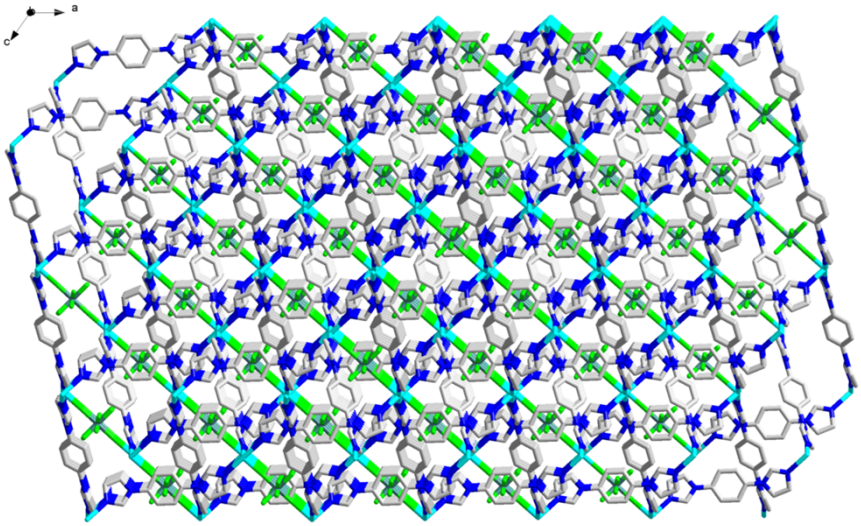


(c)



(d)



(e)

Fig. S2. (a) The angles between the adjacent planes formed by the four benzene ring centers coordinated to the same Cd^{2+} cations. (b) The coordination between Cd^{2+} cations and the ligand at vertical direction. (c) The 3-fold interpenetrated coordination networks along c-axis. (d) 1D coordination chains constructed from SiF_6^{2-} and Cd^{2+}. (e) The final 3D framework structure of complex **2** along b-axis.

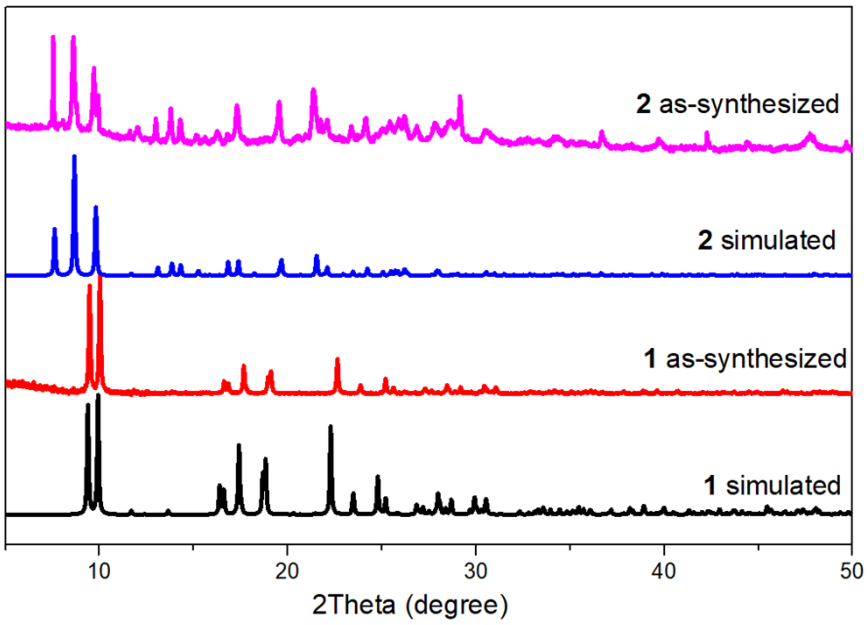


Fig. S3. PXRD spectra of complexes **1** and **2**.

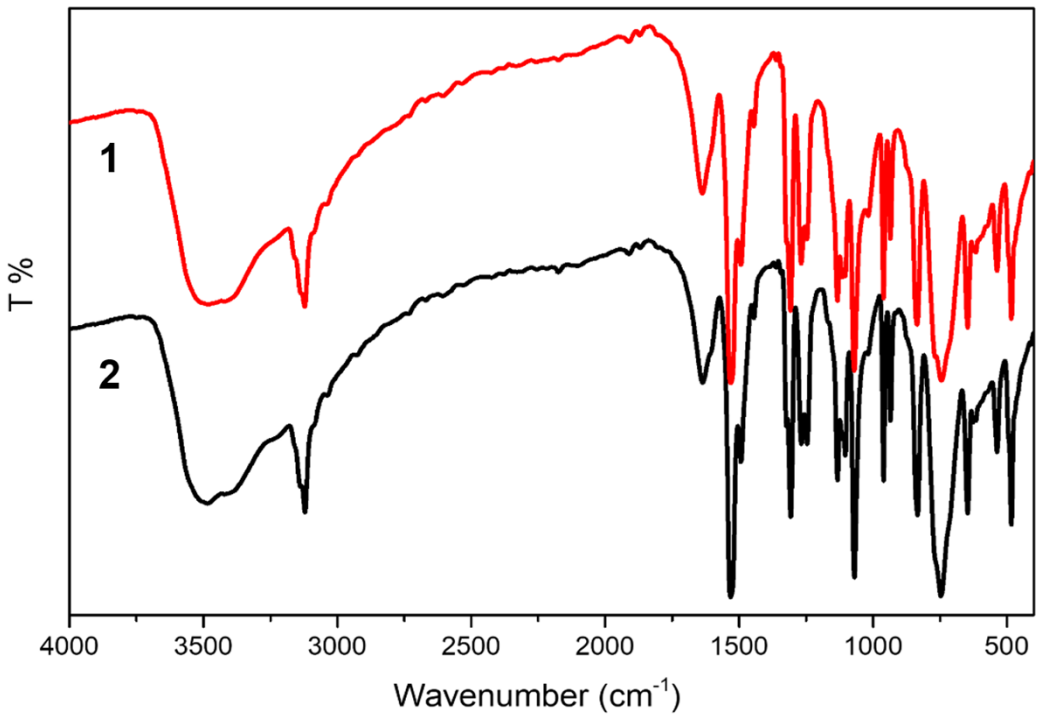
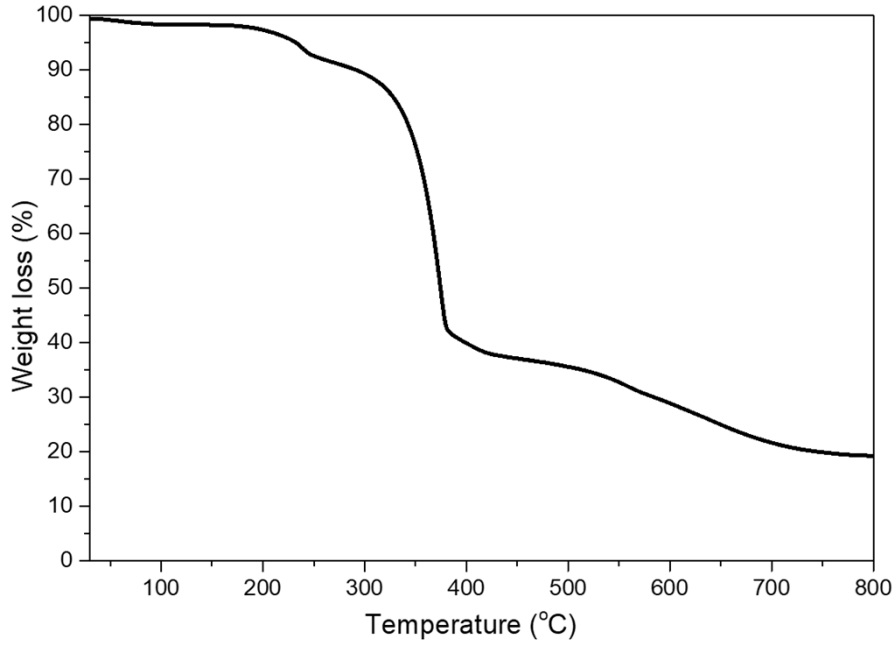
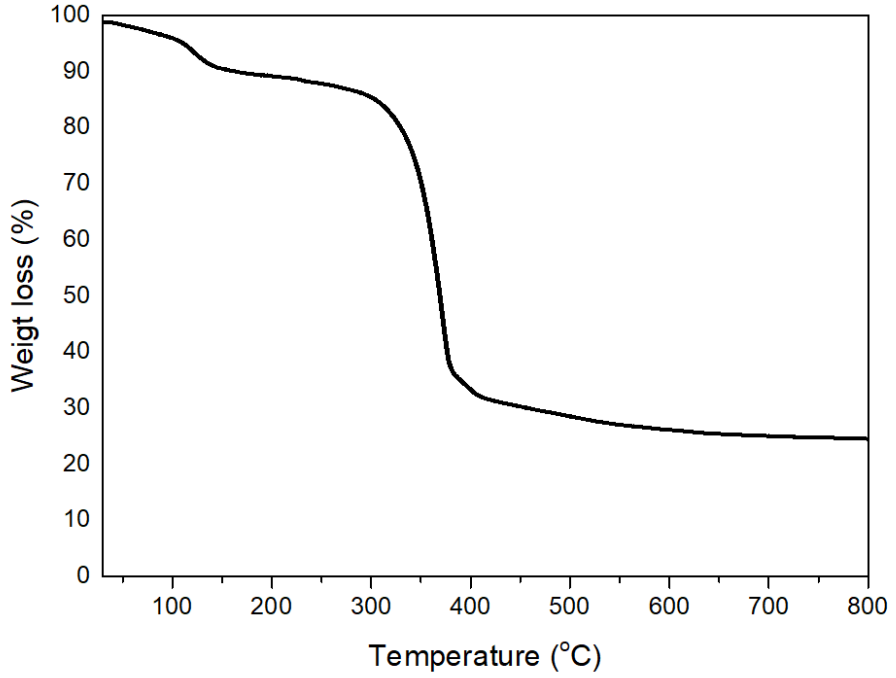


Fig. S4. FT-IR spectra of complexes **1** and **2**.



(a)



(b)

Fig. S5. TG curves of complexes **1** (a) and **2** (b).

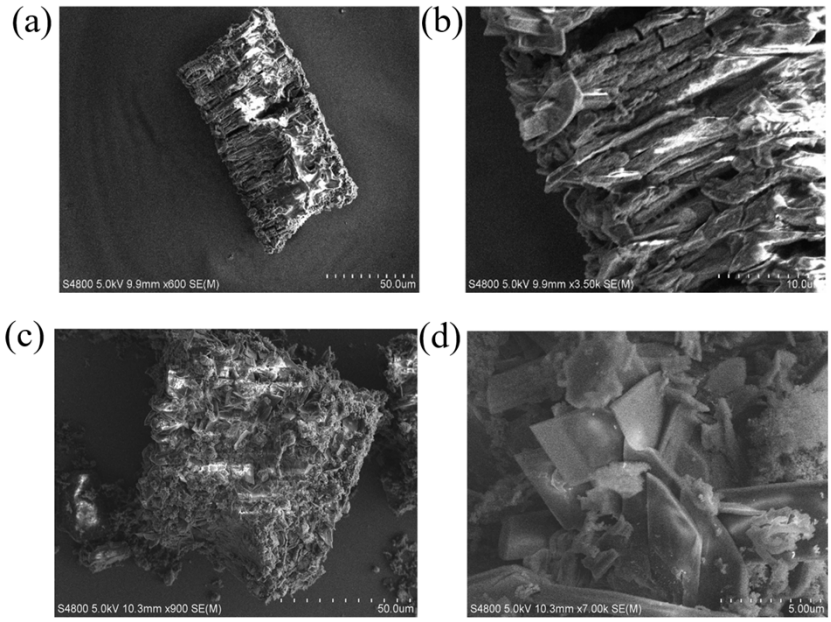


Fig. S6. SEM images of complex **1** (a, b) and **2** (c, d).

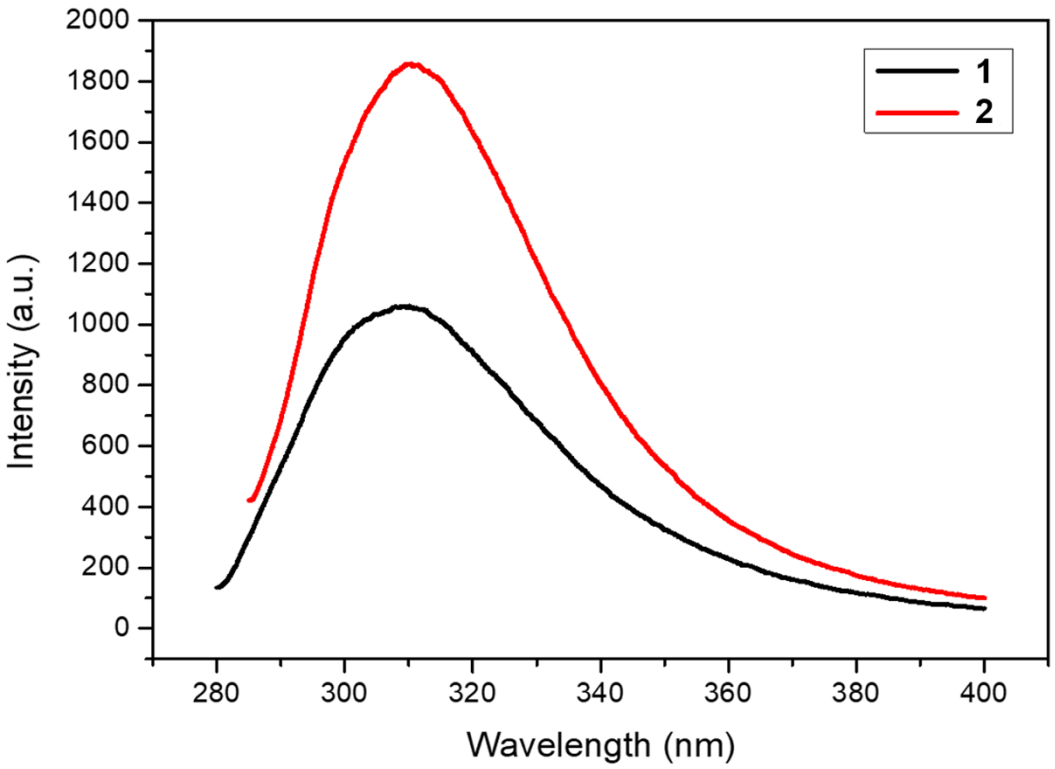


Fig. S7. The fluorescence emission bands of complexes **1** and **2**.

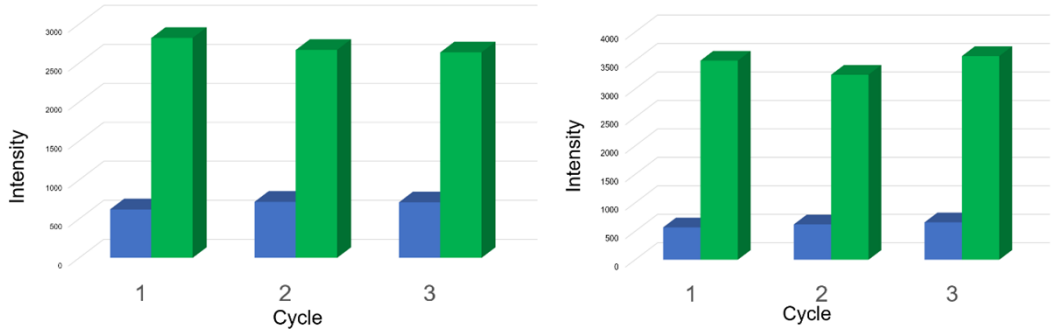


Fig. S8. Recyclability of complexes **1** (a) and **2** (b) for the detection of Arg.

Table S3 Standard deviation and Detection limit calculation.

	1	**2**
1	1054.768	817.312
2	1054.344	816.936
3	1053.986	816.806
4	1054.212	817.483
5	1054.258	817.245
Standard deviation (σ)	0.286	0.278
Slope (m)	1.39×10^{4} M^{-1}	1.50×10^{4} M^{-1}
Detection limit (3σ/m)	6.17×10^{-5} M	5.56×10^{-5} M

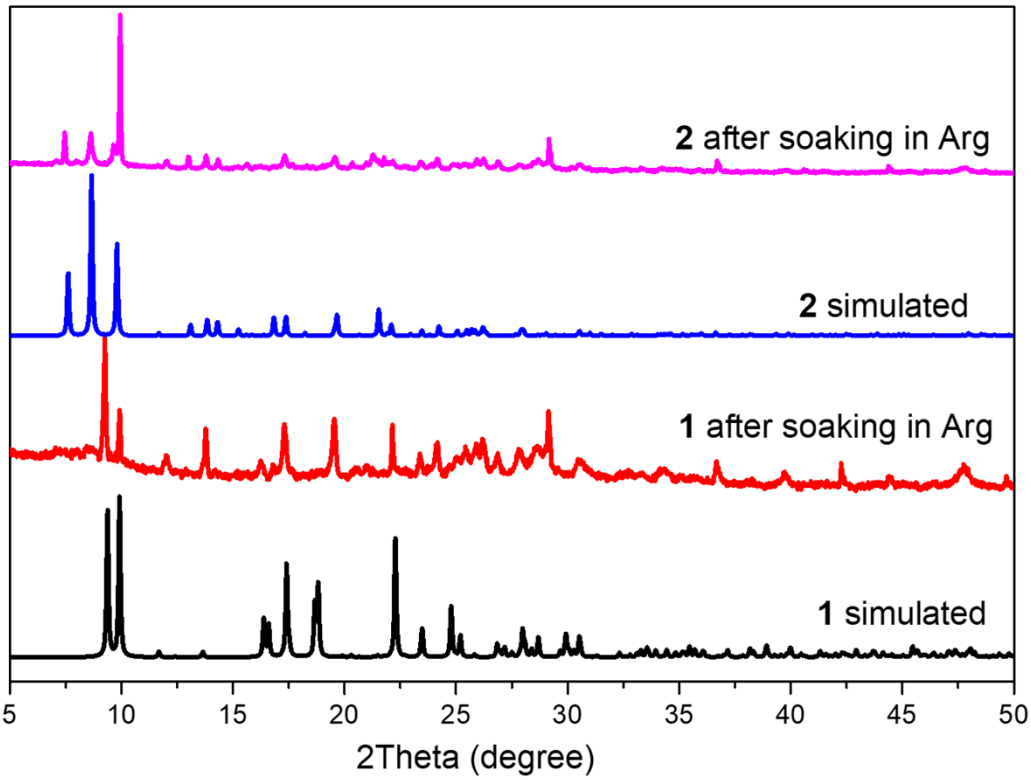
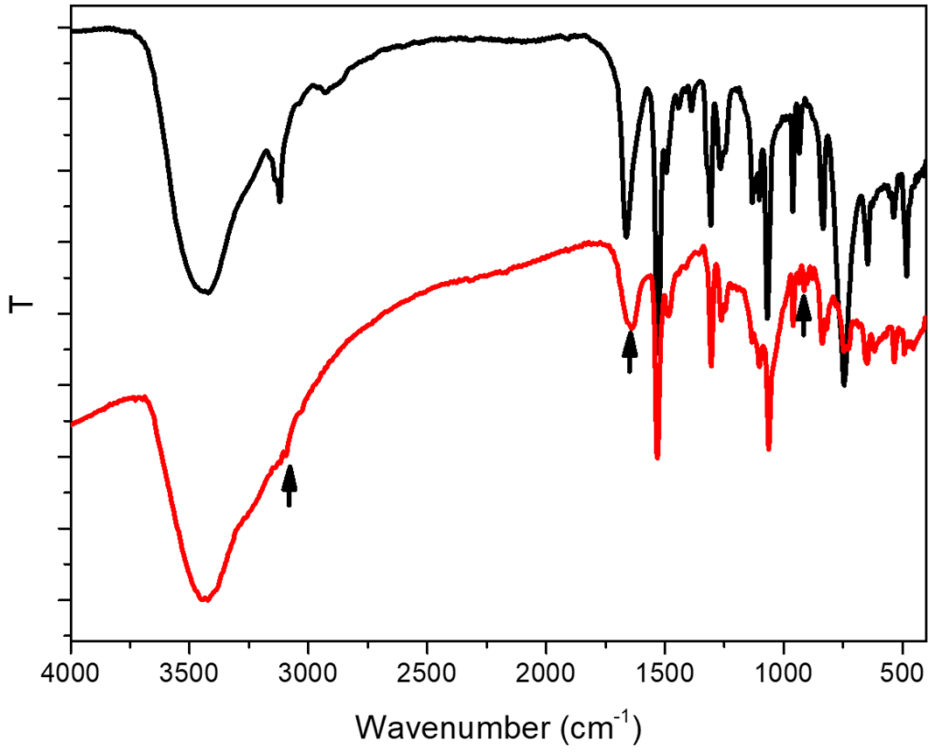
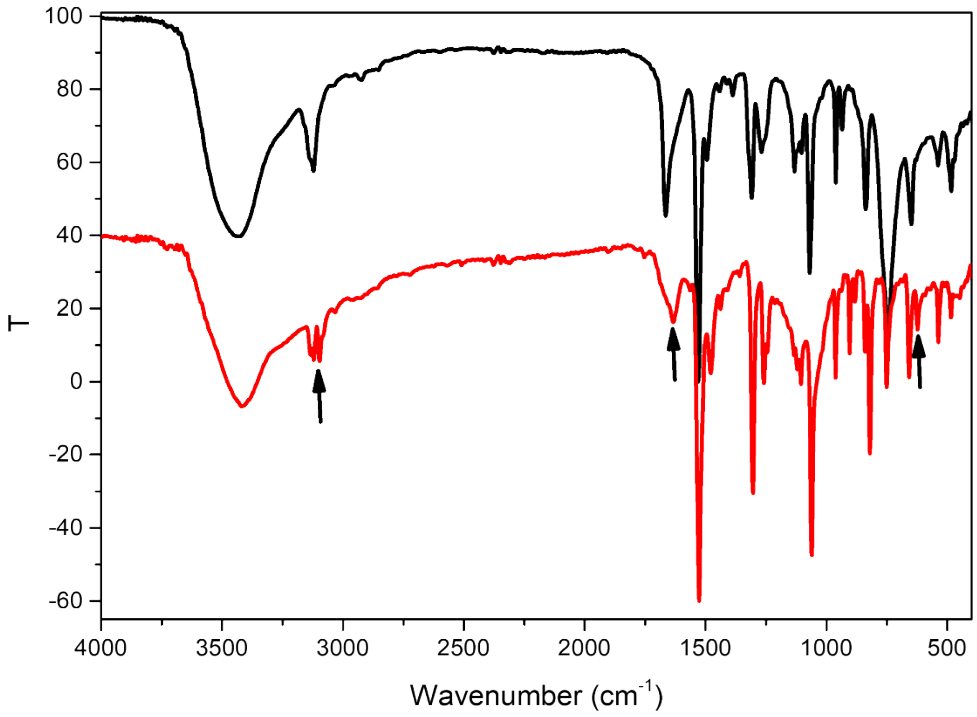


Fig. S9. PXRD patterns of complexes **1** and **2** after soaking in the solution of Arg.

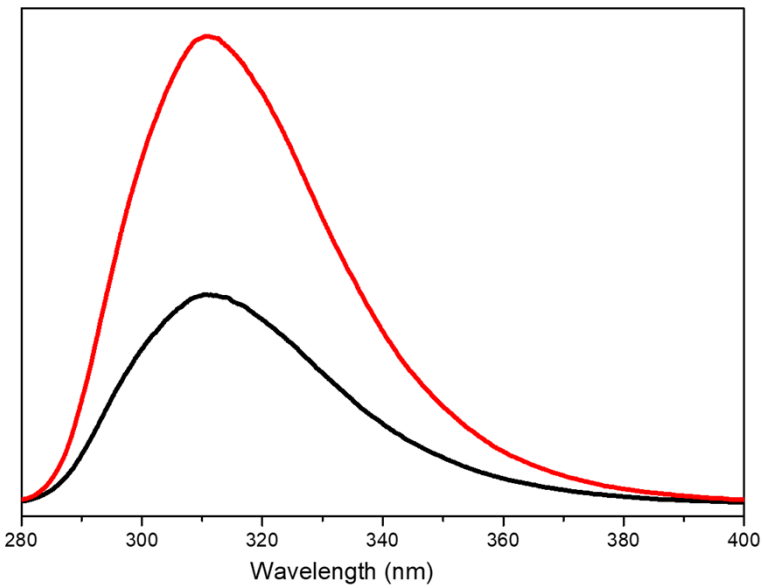


(a)

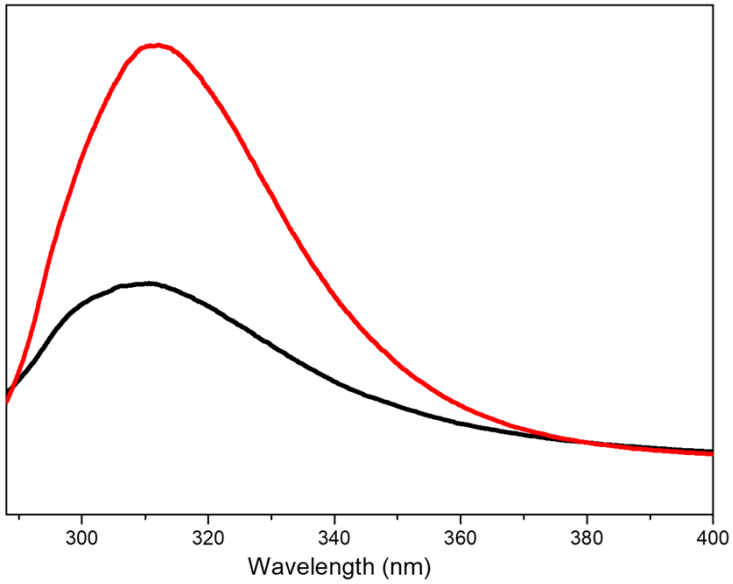


(b)

Fig. S10. FT-IR spectra of complexes **1** (a) and **2** (b) before (black line) and after (red line) soaking in the solution of Arg.



(a)



(b)

Fig. S11. Fluorescence emission bands of complexes **1** (a) and **2** (b) before and after the addition of guanidine carbonate.

Reference:

1. G. M. Sheldrick, *SADABS*, Program for Empirical Absorption Correction of Area Detector Data, 1996.
2. G. M. Sheldrick, Crystal structure refinement with SHELXL. *Acta Crystallogr. C*, 2015, **71**, 3-8.
3. P. van der Sluis and A. L. Spek, BYPASS: an effective method for the refinement of crystal structures containing disordered solvent regions. *Acta Crystallogr. A*, 1990, **46**, 194-201.
4. A. Spek,, Single-crystal structure validation with the program PLATON. *J. Appl. Crystallogr.*, 2003, **36**, 7-13.