Electronic Supplementary Information

A metal-organic framework featuring highly sensitive fluorescence sensing for Al^{3+} ions

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Experimental section

Crystal Structure Determination.

Single crystal X-ray diffraction data of **NKM-102** was measured on a Rigaku XtaLAB MM007 CCD diffractometer at 100 K with Cu Kα radiation (λ= 1.5418 Å) by ω scan mode. The structure of **NKM-102** was solved by direct methods using the *SHELXTL* program and refined by full-matrix least-squares methods with *SHELXL*.[S1] All non-hydrogen atoms were refined with anisotropic thermal parameters. The highly disordered solvents molecules were removed through the *SUQEEZE* program in *PLATON*.[S2] The crystallographic data of **NKM-102** were summarized in Table S1, and the selected bond lengths and angles were given in Tables S2 and S3. Full crystallographic data for **NKM-102** have been deposited with the CCDC (2090957).

These data can be obtained free of charge from the Cambridge Crystallographic www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data and structure refinement of **NKM-102**.

Compound reference	**NKM-102**
Chemical formula	$C_{116}H_{96}N_6O_{30}Cd_5$
Formula Mass	2616.08
Crystal system	Triclinic
a/Å	8.9895(3)
b/Å	11.5404(3)
c/Å	33.0283(7)
α/°	95.255(2)
β/°	96.857(2)
γ/°	102.441(2)
Unit cell volume/Å^3	3297.64(16)
Temperature/K	99.99(10)
Space group	*P*
No. of formula units per unit cell, *Z*	1
Radiation type	Cu K*α*
Absorption coefficient, *μ*/mm^{-1}	6.897
No. of reflections measured	26545
No. of independent reflections	12920
R_{int}	0.0440
Final R_1 values ($I > 2\sigma(I)$)	0.0668
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1712
Final R_1 values (all data)	0.0721
Final $wR(F^2)$ values (all data)	0.1748
Goodness of fit on F^2	1.049

Table S2. Selected bond lengths (Å) for **NKM-102**.

Cd(1)-O(5)#6	2.349(4)	Cd(2)-O(2)	2.363(3)
Cd(1)-O(7)	2.218(4)	Cd(2)-O(15)	2.289(5)
Cd(1)-O(2)#6	2.372(5)	Cd(2)-C(1)	2.749(6)
Cd(1)-O(14)	2.301(5)	Cd(2)-C(31)	2.736(6)
Cd(1)-O(3)	2.213(6)	Cd(3)-O(11)#1	2.221(4)
Cd(1)-O(13)	2.270(8)	Cd(3)-O(11)	2.221(4)
Cd(2)-O(5)	2.479(4)	Cd(3)-O(10)#2	2.337(4)

Cd(2)-O(1)	2.441(4)	Cd(3)-O(10)#3	2.337(4)
Cd(2)-O(6)	2.316(4)	Cd(3)-N(2)#4	2.314(5)
Cd(2)-N(1)	2.278(4)	Cd(3)-N(2)#5	2.314(5)
Cd(2)-O(8)#2	2.316(4)		

#1 3-X,3-Y,2-Z #2 +X,1+Y,+Z #3 3-X,2-Y,2-Z
#4 2+X,+Y,+Z #5 1-X,3-Y,2-Z #6 +X,-1+Y,+Z

Table S3. Selected bond angles (°) for **NKM-102**.

O(8)#6-Cd(1)-O(10)#6	82.00(18)	O(7)-Cd(2)-O(10)	132.7(2)
O(1)-Cd(1)-O(8)#6	88.0(2)	O(7)-Cd(2)-C(28)	27.1(2)
O(1)-Cd(1)-O(10)#6	91.9(2)	O(7)-Cd(2)-C(43)	160.5(2)
O(1)-Cd(1)-O(15)	90.6(2)	N(1)-Cd(2)-O(8)	141.42(18)
O(1)-Cd(1)-O(14)	90.9(4)	N(1)-Cd(2)-O(9)	86.33(19)
O(15)-Cd(1)-O(8)#6	96.9(2)	N(1)-Cd(2)-O(7)	87.1(2)
O(15)-Cd(1)-O(10)#6	177.2(2)	N(1)-Cd(2)-O(23)	86.0(2)
O(11)-Cd(1)-O(8)#6	88.3(3)	O(10)-Cd(2)-C(28)	106.0(2)
O(11)-Cd(1)-O(1)	176.1(3)	O(10)-Cd(2)-C(43)	27.8(2)
O(11)-Cd(1)-O(10)#6	86.3(3)	O(13)-Cd(2)-O(8)	84.8(2)
O(11)-Cd(1)-O(15)	91.2(3)	O(13)-Cd(2)-O(9)	84.6(2)
O(11)-Cd(1)-O(14)	92.6(5)	O(13)-Cd(2)-O(7)	91.6(2)
O(8)-Cd(2)-C(43)	106.67(19)	C(43)-Cd(2)-C(28)	133.6(2)
O(9)-Cd(2)-O(8)	132.19(17)	O(10)-Cd(2)-O(9)	55.05(18)
O(9)-Cd(2)-C(28)	159.4(2)	O(5)-Cd(3)-O(5)#1	180.0
O(9)-Cd(2)-C(43)	27.3(2)	O(5)-Cd(3)-O(3)#2	98.1(2)
O(7)-Cd(2)-O(8)	54.33(18)	O(5)#1-Cd(3)-O(3)#3	98.1(2)
O(7)-Cd(2)-O(9)	171.8(2)	O(5)-Cd(3)-O(3)#3	81.9(2)
N(1)-Cd(2)-O(10)	137.7(2)	O(5)#1-Cd(3)-O(3)#2	81.9(2)
N(1)-Cd(2)-O(13)	99.2(2)	O(5)-Cd(3)-N(2)#4	92.4(2)
N(1)-Cd(2)-C(28)	114.1(2)	O(5)-Cd(3)-N(2)#5	87.6(2)
N(1)-Cd(2)-C(43)	111.6(2)	O(5)#1-Cd(3)-N(2)#5	92.4(2)
O(23)-Cd(2)-O(8)	89.5(2)	O(5)#1-Cd(3)-N(2)#4	87.6(2)
O(23)-Cd(2)-O(9)	98.5(2)	O(3)#3-Cd(3)-O(3)#2	180.0(2)
O(23)-Cd(2)-O(7)	85.9(2)	N(2)#5-Cd(3)-O(3)#3	96.07(19)
O(23)-Cd(2)-O(10)	83.8(2)	N(2)#4-Cd(3)-O(3)#2	96.07(19)
O(23)-Cd(2)-C(28)	86.0(2)	N(2)#5-Cd(3)-O(3)#2	83.93(19)
O(23)-Cd(2)-C(43)	89.8(2)	N(2)#4-Cd(3)-O(3)#3	83.93(19)
O(10)-Cd(2)-O(8)	79.46(18)	N(2)#4-Cd(3)-N(2)#5	180.0

#1 3-X,3-Y,2-Z #2 +X,1+Y,+Z #3 3-X,2-Y,2-Z
#4 2+X,+Y,+Z #5 1-X,3-Y,2-Z #6 +X,-1+Y,+Z

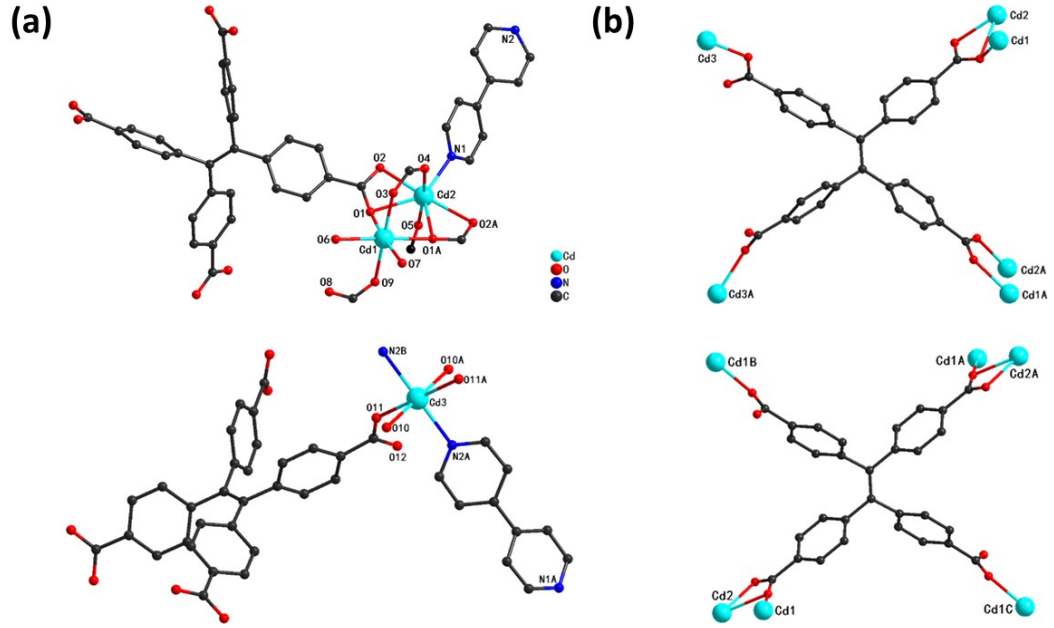

Fig. S1. (a) The coordination environment of Cd(II) ion in **NKM-102**; (b) The coordination modes of the deprotonated $TCPE^{4-}$ ligand.

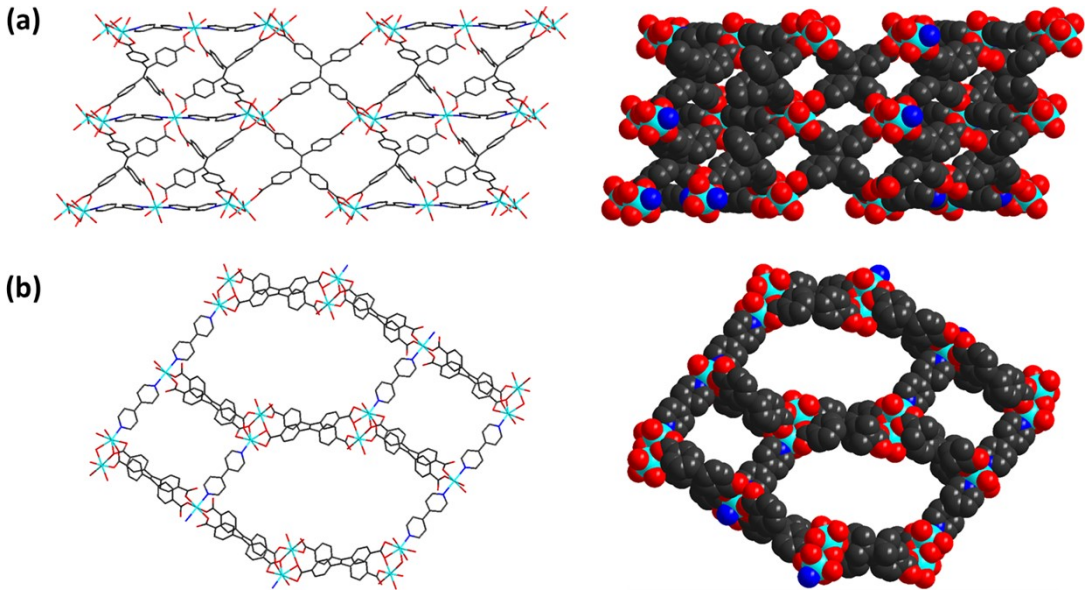

Fig. S2. (a) The structure of **NKM-102** viewed along *a* axis; (b) The structure of **NKM-102** viewed along *b* axis.

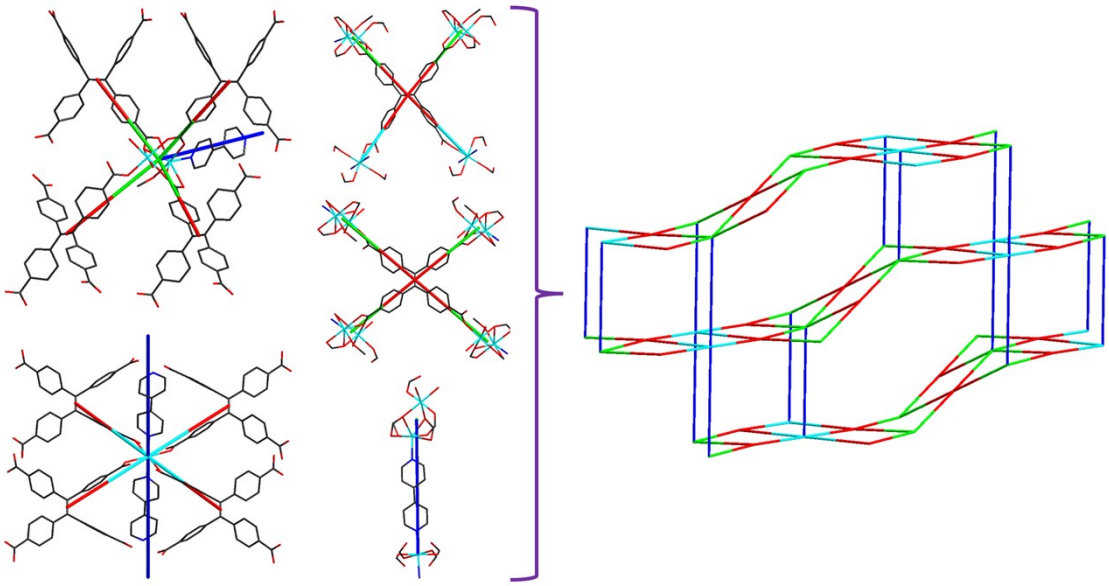

Fig. S3. The framework topology of (4, 4, 5, 6)-connected network with point (Schläfli) symbol of $\{4^4\cdot6^{10}\cdot8\}\{4^4\cdot6^2\}_3\{4^4\cdot6^6\}_2$.

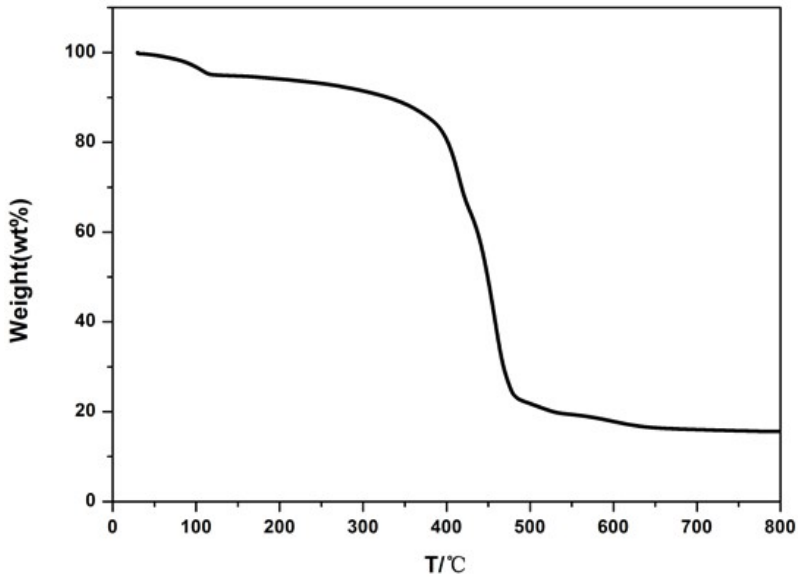

Fig. S4. TGA curve of **NKM-102**.

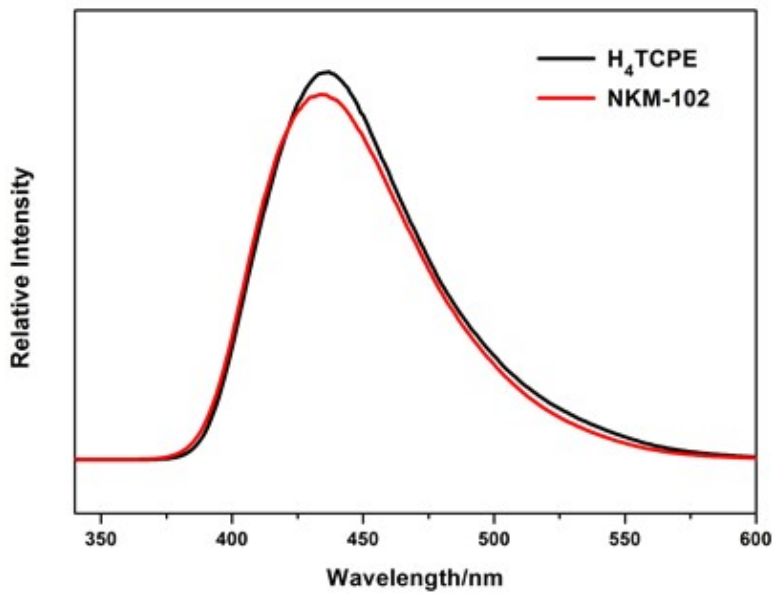

Fig. S5. The solid-state fluorescence spectra of H_4TCPE ligand and **NKM-102**.

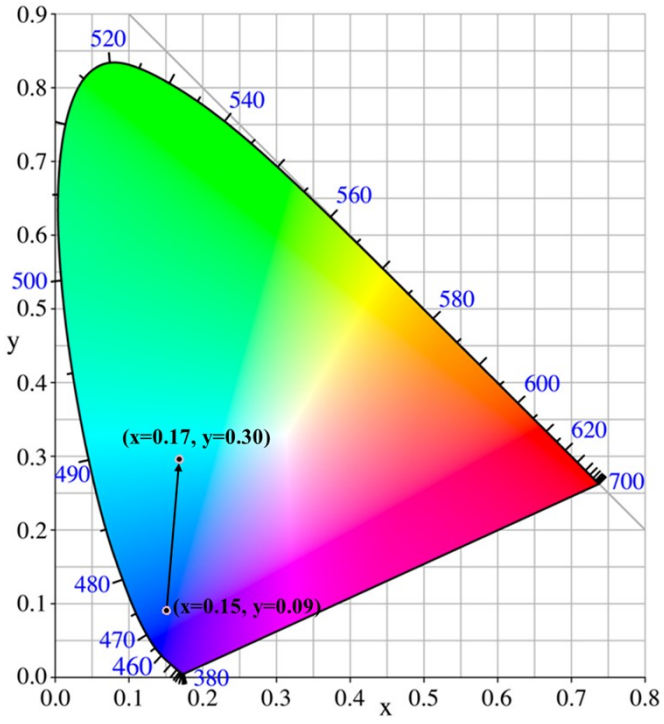

Fig. S6. The CIE chromaticity diagram showing the color coordinates of **NKM-102** and **NKM-102** upon the addition of Al^{3+} ions in C_2H_5OH.

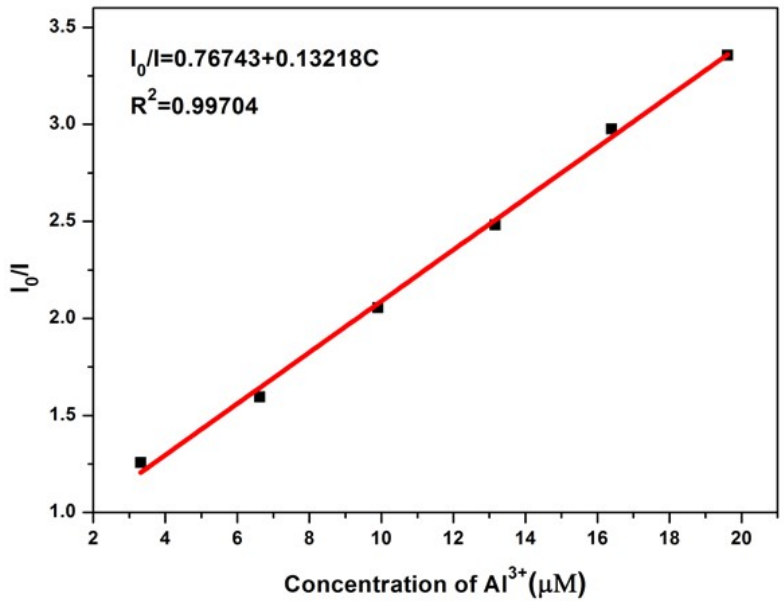

Fig. S7. Fitting plot of the detection limit Al^{3+} ions in C_2H_5OH solution for **NKM-102**.

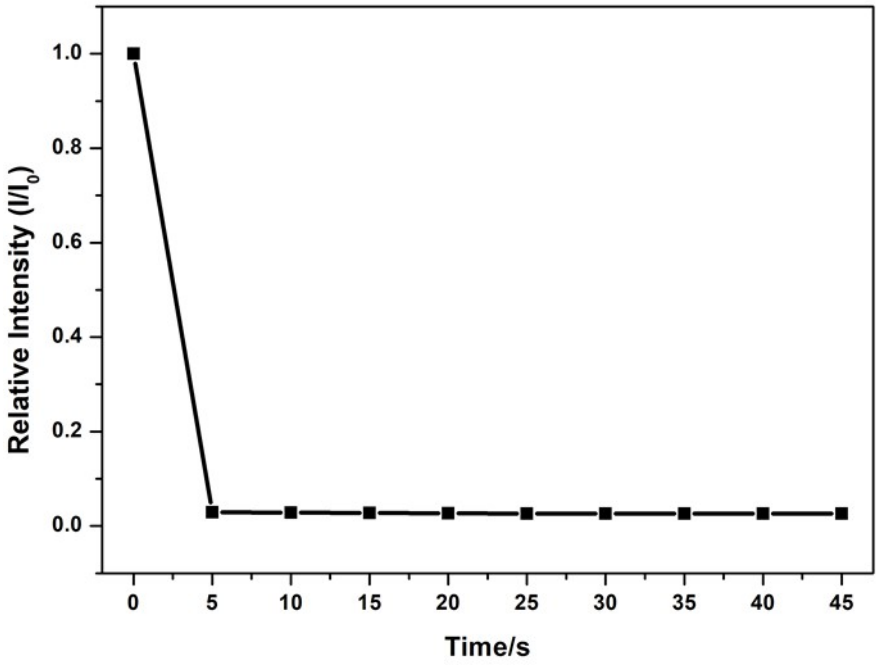

Fig. S8. Time-dependent response of the emission of **NKM-102** toward Al^{3+} ions in C_2H_5OH solution.

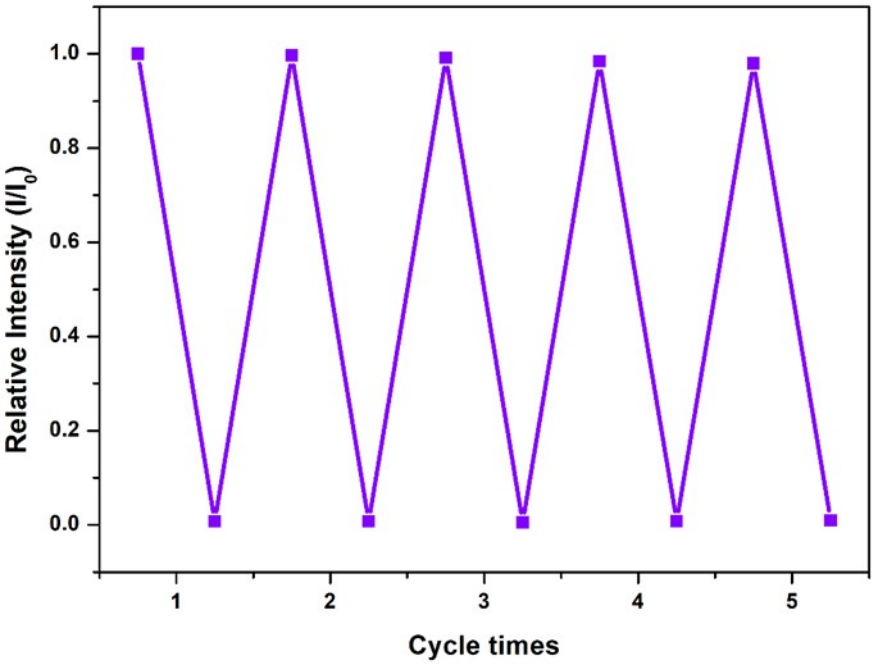

Fig. S9. Recycle sensing performances of **NKM-102** toward Al^{3+} ions in C_2H_5OH solution.

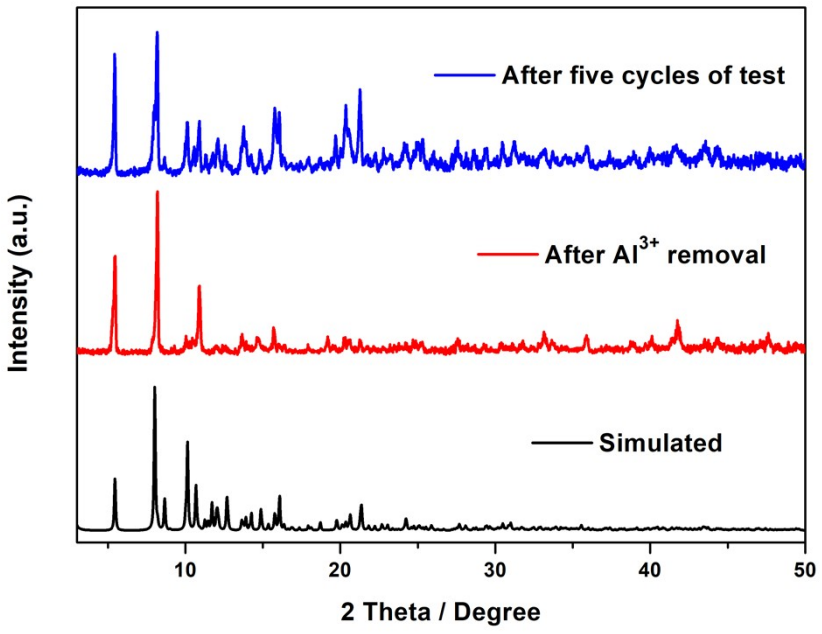

Fig. S10. The PXRD patterns of **NKM-102** after Al^{3+} ions removal and after five consecutive cycles of fluorescence sensing experiments.

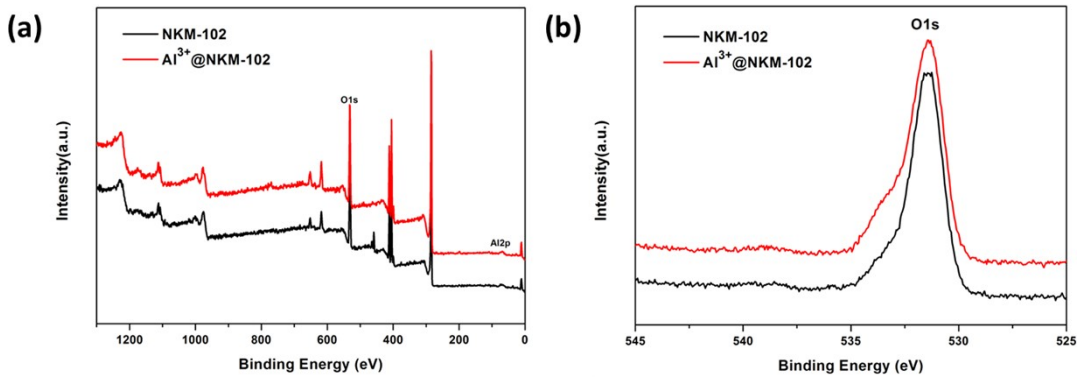

Fig. S11. XPS spectra (a) and O 1s XPS spectra (b) for **NKM-102** (black line) and Al^{3+}@**NKM-102** (derived from immersing **NKM-102** into Al^{3+} ions solution; red line).

Table S4. Comparison of literature reports for MOFs as sensors of Al^{3+} ions.

MOF	Detection Limit	Ref.
NKM-102	**5.86 μM (158 ppb)**	**this work**
Cd_2(syn-dftpmcp)(1,3-BDC)$_2$	183 ppb	S3
UiO-66-NH_2-SA	6.98 μM (188 ppb)	S4
{[Zn_2(μ_3-HCIP)$_2$(μ-bpt)]·2H_2O}$_n$	760 ppb	S5
{[Co_3(phen)$_2$HL)$_2$]·(H_2O)$_2$}$_n$	960 ppb	S6
[H_3O]$_2$[$Eu_{2.5}$(BTB)$_3$(OAc)$_{0.5}$(H_2O)$_3$]	100 μM (2.70*10^3 ppb)	S7
[Co_2(dmimpym)(nda)$_2$]$_n$	1.89*10^4 ppb	S8
Tb-TCPP	7.79 nM (0.21 ppb)	S9
GUPT-2	0.269 μM (7.26 ppb)	S10
[CuI(BPDPE)]$_n$	2.1 μM (56.66 ppb)	S11
UiO-(OH)$_2$@RhB	10 nM (0.27 ppb)	S12

References

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