

## ESI

### Highly Selective Luminescent Sensor for CCl<sub>4</sub> Vapor and Pollutational Anions/Cations based on a Multi-responsive MOF

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Table S1. Selected bond lengths and bond angles for NBU-18.

|                      |            |                      |            |
|----------------------|------------|----------------------|------------|
| Cd(1)-O(5)#1         | 2.227(4)   | Cd(2)-O(6)#2         | 2.171(5)   |
| Cd(1)-O(5)#2         | 2.227(4)   | Cd(2)-N(1)           | 2.239(5)   |
| Cd(1)-O(8)#3         | 2.300(5)   | Cd(2)-O(10)#5        | 2.260(5)   |
| Cd(1)-O(8)           | 2.300(5)   | Cd(2)-O(8)           | 2.342(5)   |
| Cd(1)-O(9)#4         | 2.303(5)   | Cd(2)-O(7)           | 2.373(5)   |
| Cd(1)-O(9)#5         | 2.303(5)   | Cd(2)-O(9)#5         | 2.567(5)   |
| O(1)-C(2)#8          | 1.413(8)   | O(9)-Cd(1)#4         | 2.303(5)   |
| O(5)-Cd(1)#9         | 2.227(4)   | O(9)-Cd(2)#6         | 2.567(5)   |
| O(6)-Cd(2)#9         | 2.171(5)   | O(10)-Cd(2)#6        | 2.260(5)   |
| O(5)#1-Cd(1)-O(5)#2  | 180.000(1) | O(8)-Cd(2)-O(9)#5    | 75.37(17)  |
| O(5)#1-Cd(1)-O(8)#3  | 88.53(19)  | O(8)-Cd(2)-O(7)      | 54.26(17)  |
| O(5)#1-Cd(1)-O(8)    | 91.47(19)  | O(8)-Cd(1)-O(9)#4    | 98.5(2)    |
| O(5)#1-Cd(1)-O(9)#4  | 89.59(17)  | O(8)-Cd(1)-O(9)#5    | 81.5(2)    |
| O(5)#1-Cd(1)-O(9)#5  | 90.41(17)  | O(8)#3-Cd(1)-O(8)    | 180.000(1) |
| O(5)#2-Cd(1)-O(8)#3  | 91.47(19)  | O(8)#3-Cd(1)-O(9)#4  | 81.5(2)    |
| O(5)#2-Cd(1)-O(8)    | 88.53(19)  | O(8)#3-Cd(1)-O(9)#5  | 98.5(2)    |
| O(5)#2-Cd(1)-O(9)#4  | 90.41(17)  | O(9)#4-Cd(1)-O(9)#5  | 180.000(1) |
| O(5)#2-Cd(1)-O(9)#5  | 89.59(17)  | O(10)#5-Cd(2)-O(8)   | 98.0(2)    |
| O(6)#2-Cd(2)-N(1)    | 94.3(2)    | O(10)#5-Cd(2)-O(7)   | 102.6(2)   |
| O(6)#2-Cd(2)-O(10)#5 | 132.0(2)   | O(10)#5-Cd(2)-O(9)#5 | 53.76(18)  |
| O(6)#2-Cd(2)-O(8)    | 94.3(2)    | N(1)-Cd(2)-O(10)#5   | 103.9(2)   |
| O(6)#2-Cd(2)-O(7)    | 121.8(2)   | N(1)-Cd(2)-O(8)      | 141.3(2)   |
| O(6)#2-Cd(2)-O(9)#5  | 85.57(19)  | N(1)-Cd(2)-O(7)      | 89.7(2)    |
| O(7)-Cd(2)-O(9)#5    | 121.73(17) | N(1)-Cd(2)-O(9)#5    | 142.9(2)   |

Symmetry transformations used to generate equivalent atoms:

#1 -x+3/2, -y+3/2, -z+2; #2 x, y, z-1; #3 -x+3/2, -y+3/2, -z+1; #4 -x+2, y, -z+3/2; #5 x-1/2, -y+3/2, z-1/2; #6 x+1/2, -y+3/2, z+1/2; #7 -x+3/2, -y+1/2, -z+1; #8 -x+2, y, -z+5/2; #9 x, y, z+1.

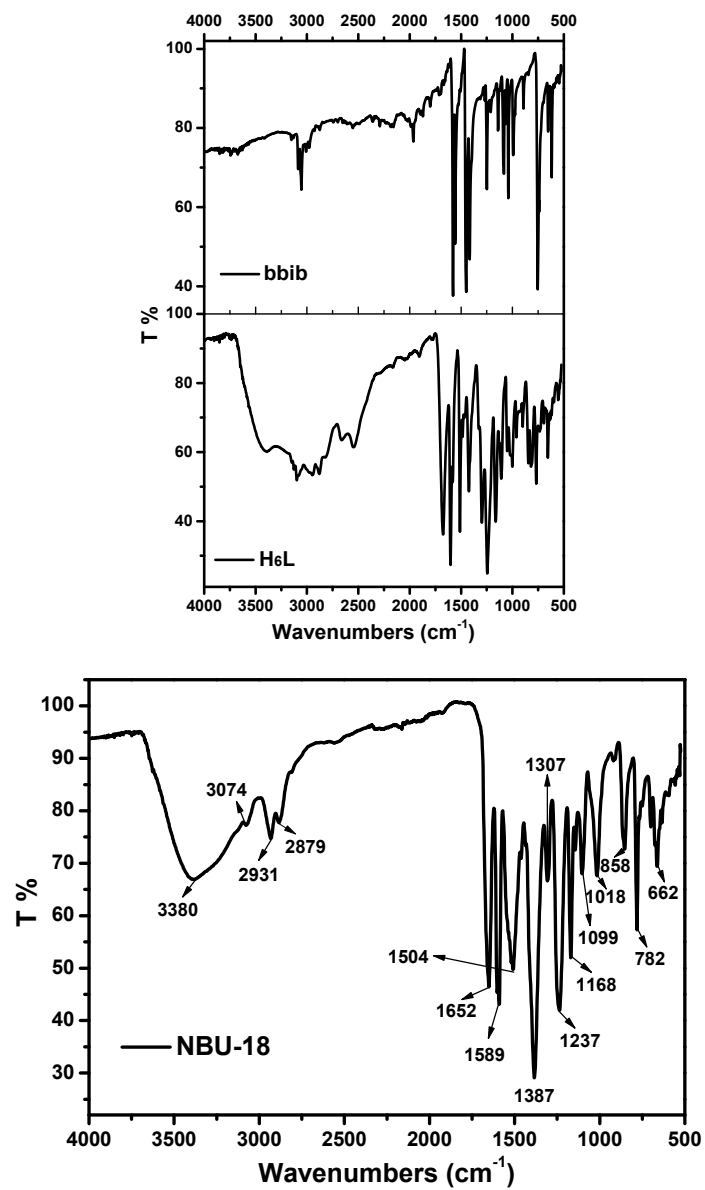
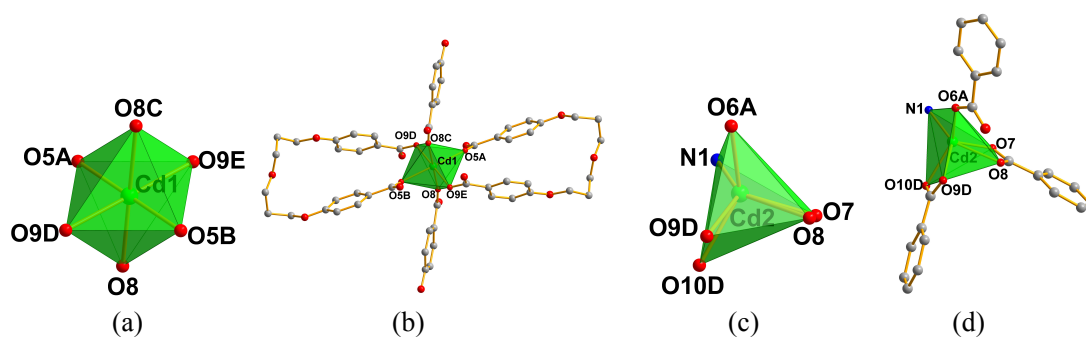
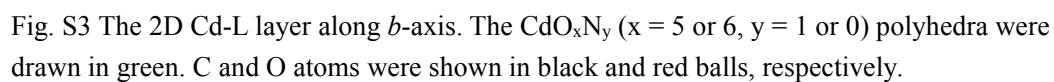
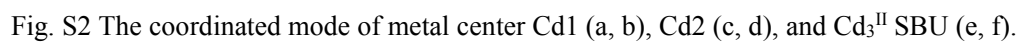


Fig. S1 FT-IR spectra of free H<sub>6</sub>L, bbib, and MOF NBU-18.





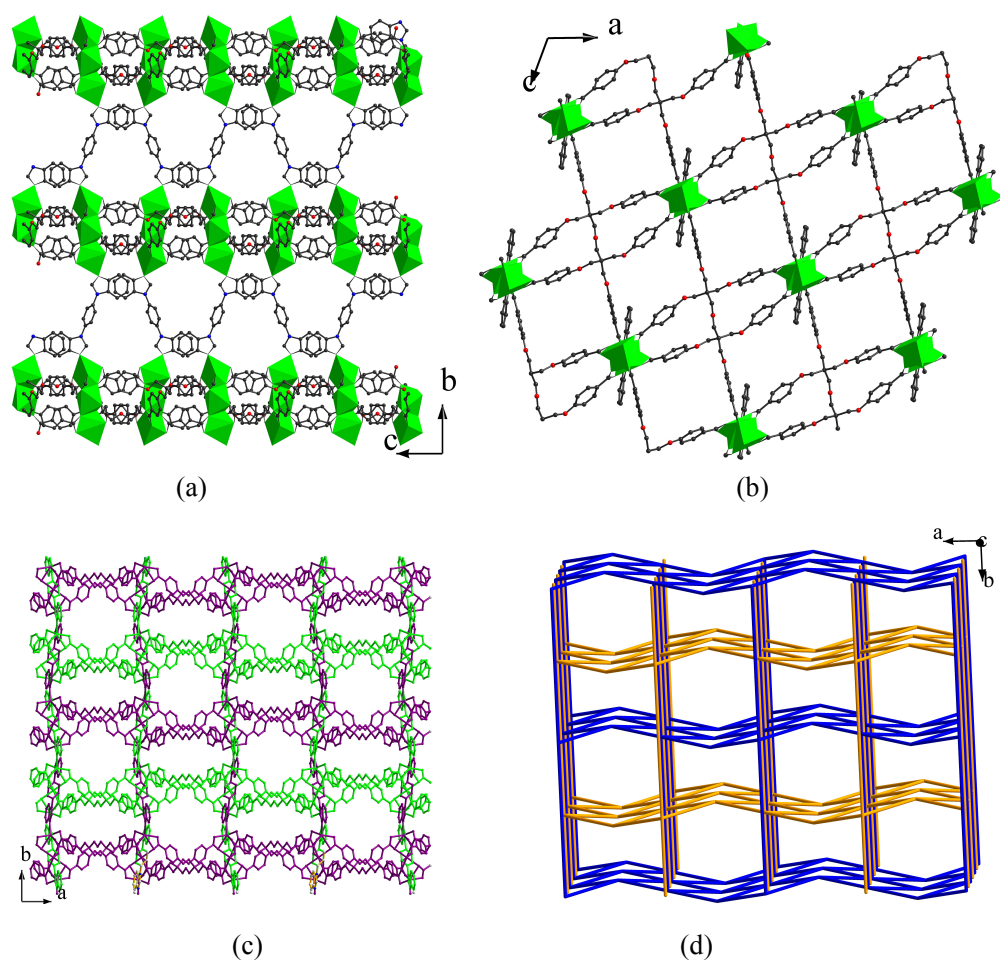
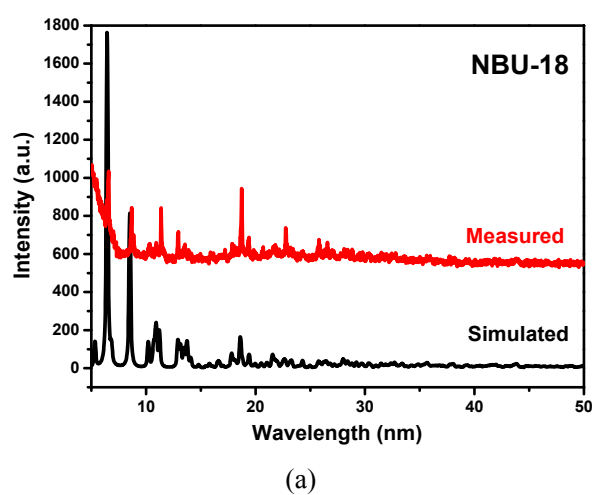
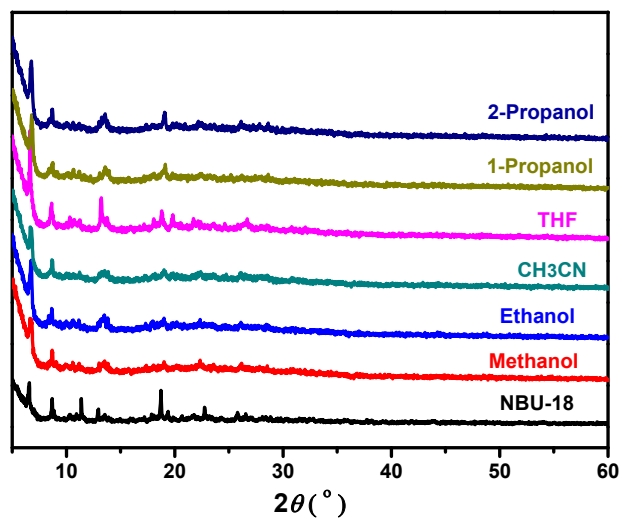


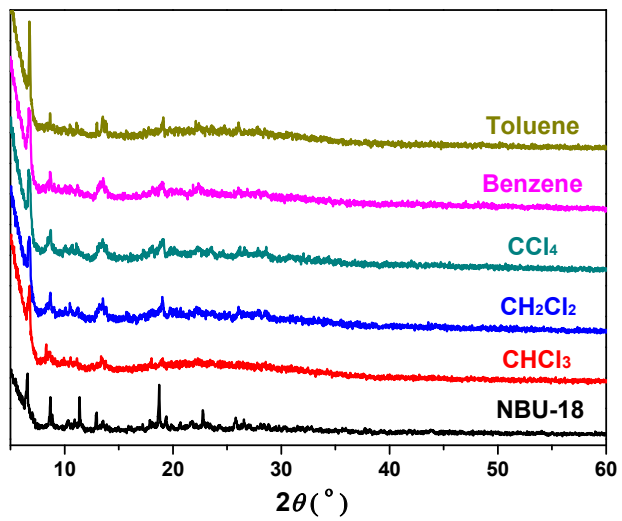
Fig. S5 View the 3D one-fold net along  $a$ -axis (a), and  $b$ -axis (b). The 2-fold interpenetrated 3D net (c) and the corresponding simplified 2-nodal  $fsc$  net (d) along  $c$ -axis.



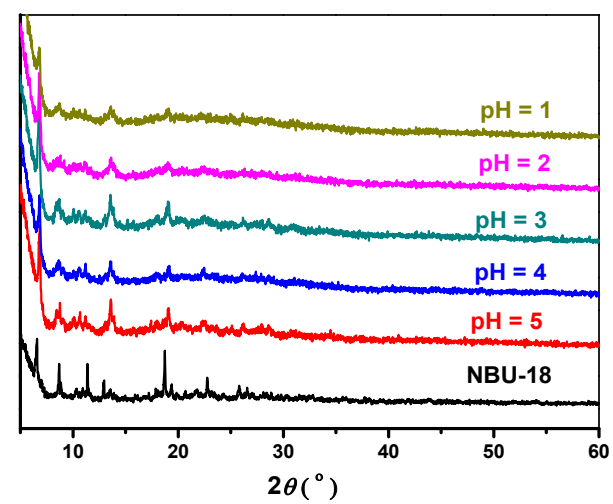




(b)



(c)



(d)

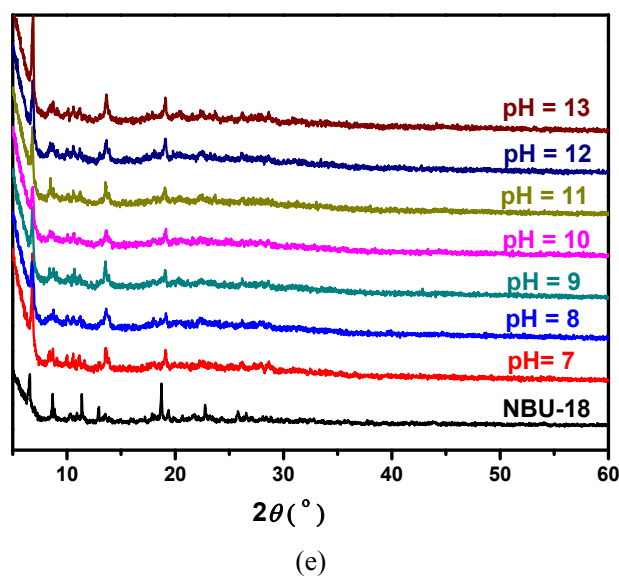


Fig. S6 (a) The PXRD patterns of as-synthesized sample NBU-18 (red, measured) and the calculated pattern (black, simulated) from its crystal structure. (b and c) The PXRD patterns of NBU-18 samples after immersed into various solvents for 24 h. (d and e) The PXRD patterns of NBU-18 samples after immersed into different pH aqueous solutions for 12 h.

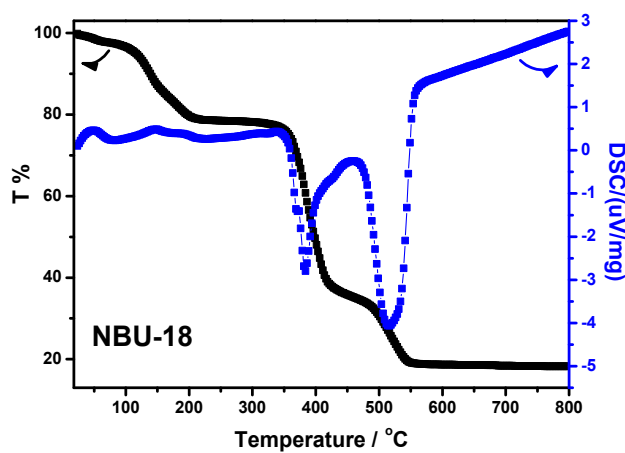


Fig. S7 TG-DSC curves of **NBU-18** under N<sub>2</sub> atmosphere at a heating rate of 10 °C/min.

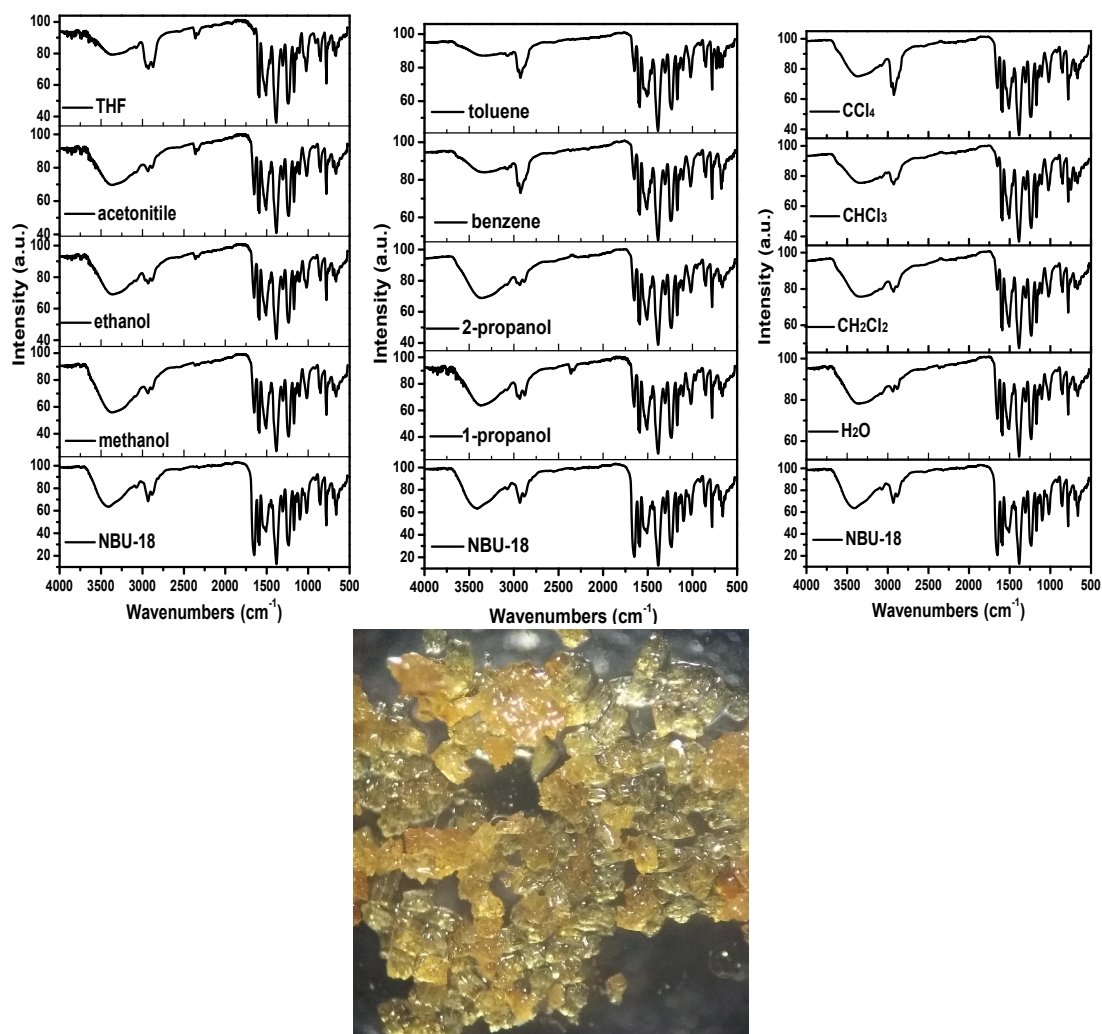


Fig. S8. FTIR spectra of MOF NBU-18 samples after treatment in various solvents for 24 hours and image of NBU-18 crystals after treatment in various solvents.

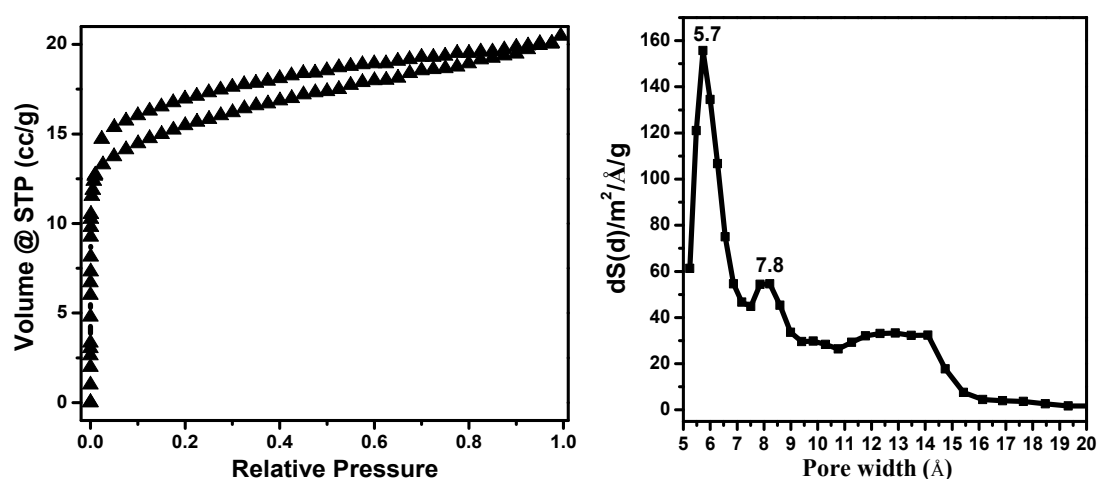


Fig. S9 Gas adsorption-desorption isotherm and pore size distribution of NBU-18 for  $\text{N}_2$  at 77 K. Considering the structure features of NBU-18 compound with a high-solvent-accessible volume of  $4085.8 \text{ \AA}^3$  (42.3%) of the crystal unit cell volume ( $9665.2 \text{ \AA}^3$ ) based on PLATON calculation and three sets of channels with  $20.8 \times 14.7 \text{ \AA}^2$  along  $c$ -axis,  $10.4 \times 8.5 \text{ \AA}^2$  along  $a$ -axis, and  $9.0 \times 8.8$

$\text{\AA}^2$  along  $b$ -axis (including van der Waals radius), its gas adsorption isotherm for  $\text{N}_2$  at 77 K was performed on ASAP 2050 V1.01 E and Autosorb MP-1 apparatuses at 1 atm. Prior to the measurement, the as-synthesized sample of NBU-18 was immersed in methanol for three days, the methanol was refreshed three times during the exchange. The resulting methanol-exchanged sample of NBU-18 was transferred into dichloromethane solvent for 12 h. Similarly, fresh dichloromethane was also exchanged for three times. The resulting exchanged sample was then evacuated ( $10^{-3}$  Torr) successively at room temperature and 80 °C. As shown in Fig. S9, the NBU-18 exhibits a single step type I sorption behavior with a relatively small  $\text{N}_2$  gas sorption amount ( $54.3 \text{ cm}^3 \text{ g}^{-1}$ ). Its pore size distribution ( $5.7 \text{ \AA}$  and  $7.8 \text{ \AA}$ ) matches well with the crystal structure model.

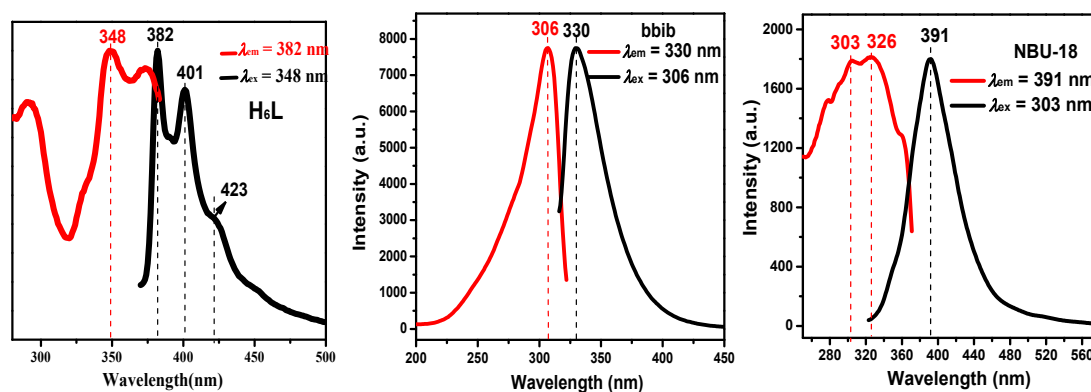


Fig. S10. The solid-state emission and excitation spectra of NBU-18 as well as the emission spectra of free H<sub>6</sub>L and bbib ligands.

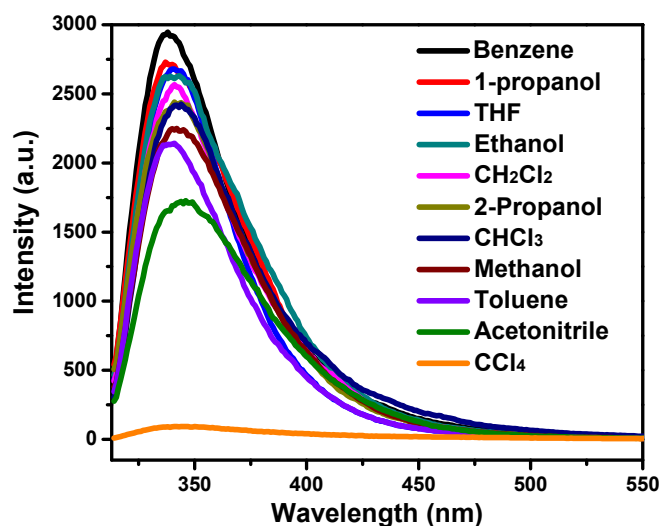


Fig. S11 Emission spectra of NBU-18 in various organic solvents at room temperature ( $\lambda_{ex} = 291 \text{ nm}$ )

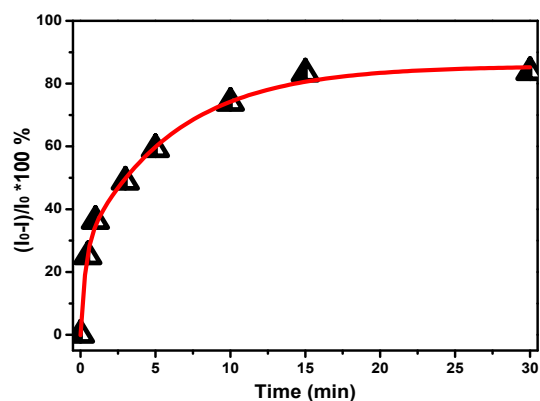


Fig. S12. The relationship between fluorescence quench percentage of PL intensity for NBU-18 and exposing time for CCl<sub>4</sub> vapor, in which  $I_0$  and  $I$  = the fluorescence intensity of the emulsion in the absence and presence of CCl<sub>4</sub> vapor, respectively.

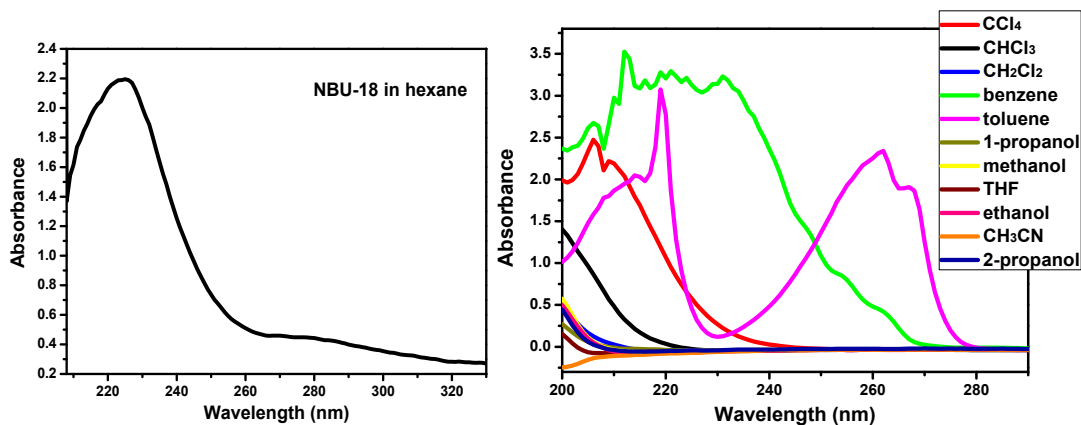


Fig. S13. The UV-vis spectra of various organic solvents and NBU-18 in hexane at room temperature.

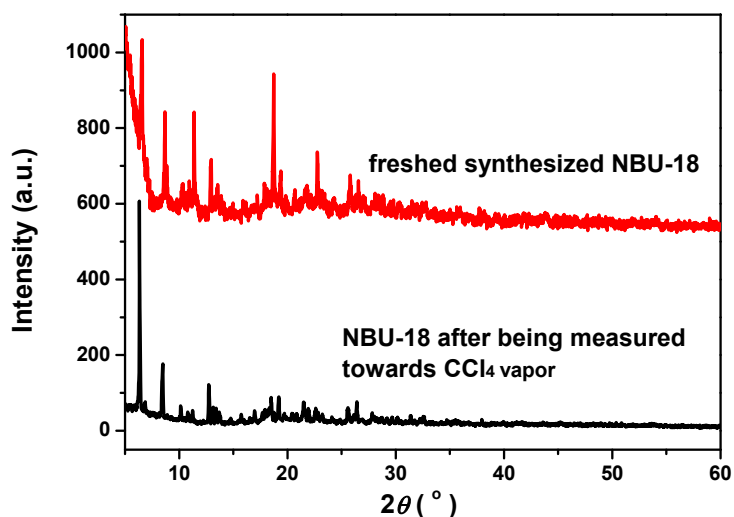


Fig. S14 The PXRD pattern of NBU-18 after being measured toward CCl<sub>4</sub> vapor for 12 h.

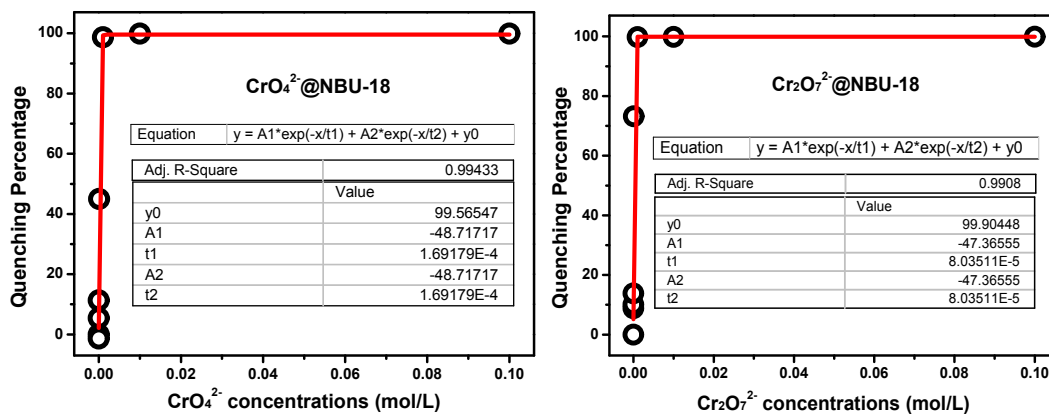


Fig. S15. The relationship between fluorescence quench percentage of PL intensities from NBU-18 and the concentration of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and CrO<sub>4</sub><sup>2-</sup>, respectively.

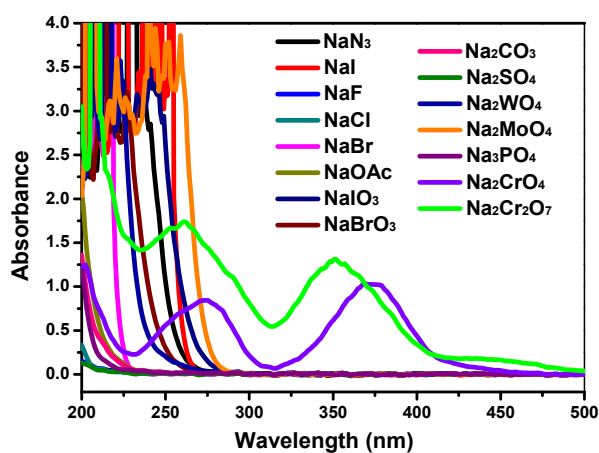


Fig. S16. The UV-vis spectra of the aqueous solutions with different anions at room temperature.

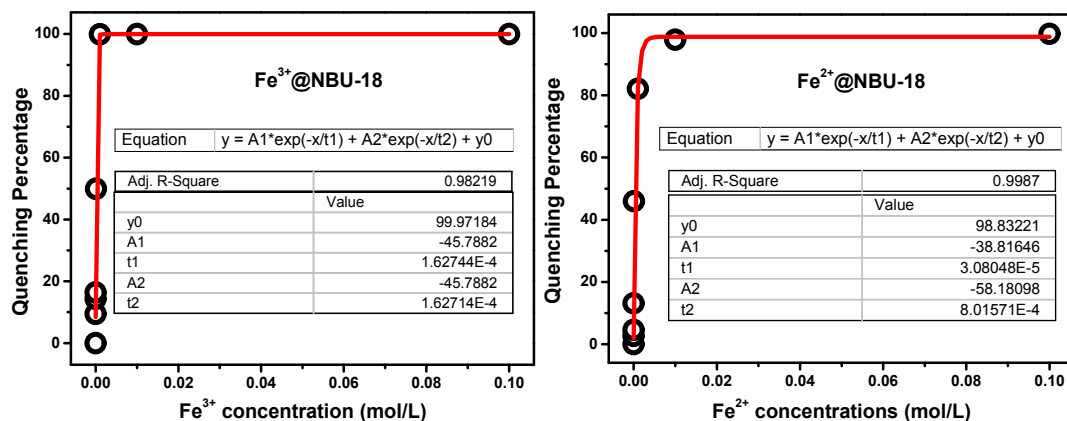


Fig. S17 The relationship between fluorescence quench percentage of PL intensities from NBU-18 and the concentration of Fe<sup>2+</sup> and Fe<sup>3+</sup>, respectively.

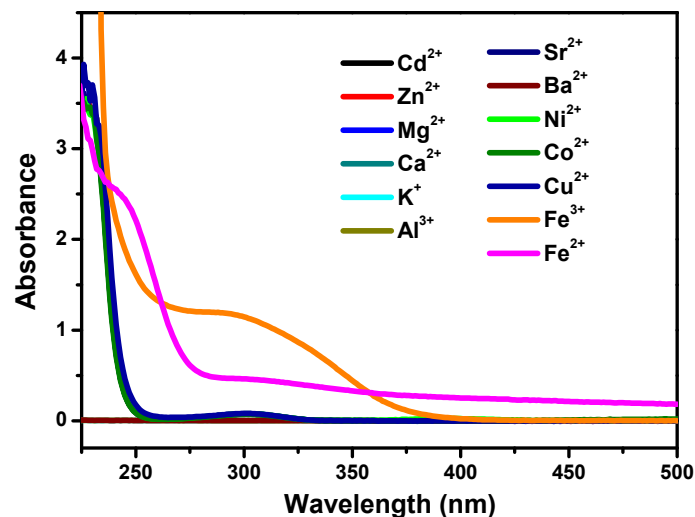
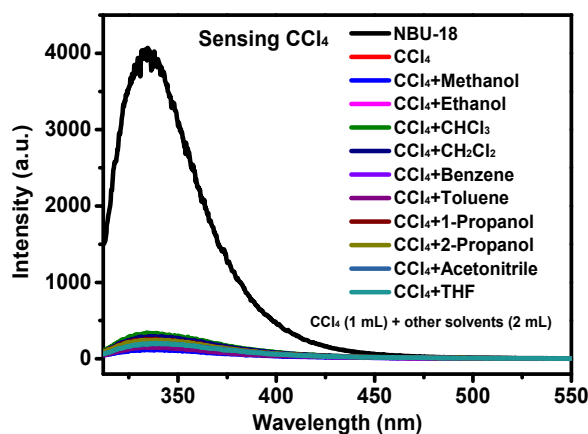
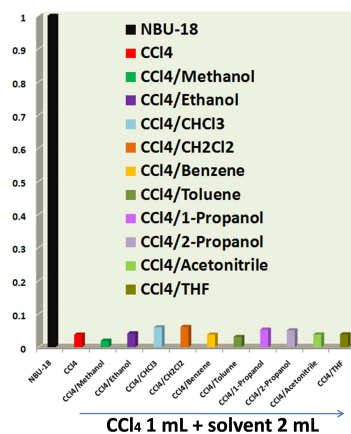


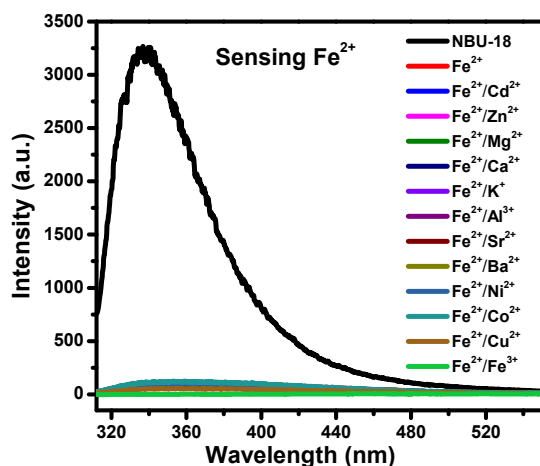
Fig. S18 The UV-vis spectra of the aqueous solutions with different cations at room temperature.



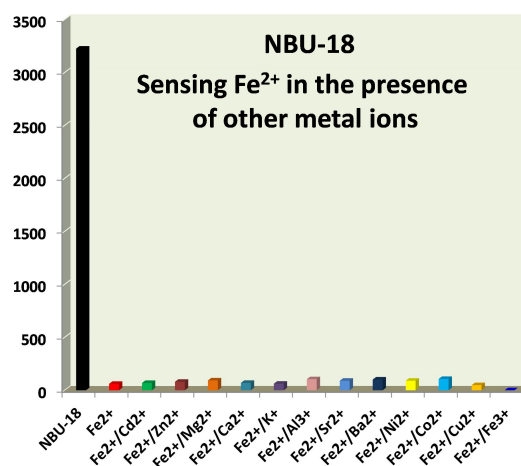
(a)



(b)



(c)



(d)

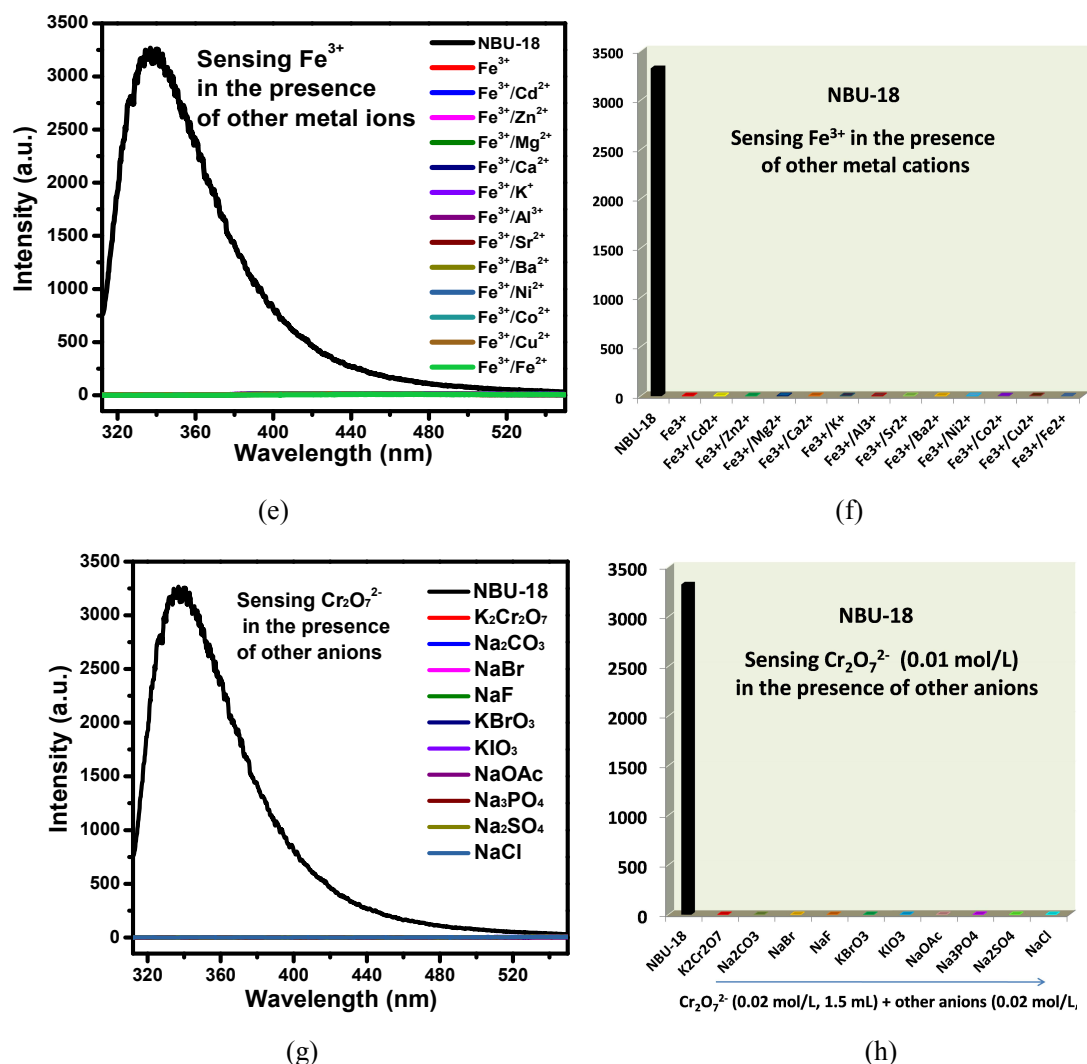


Fig. S19 (a and b) Luminescence spectra and intensities of NBU-18 in mixed solvents of  $\text{CCl}_4$  (1 mL) and other organic solvents (2 mL) under the excitation of 291 nm. (c and d) The luminescence spectra and its intensity of the aqueous solutions of NBU-18 in the presence of  $\text{Fe}^{2+}$  (0.01 mol/L) and other cations (0.01 mol/L). (e and f) The luminescence spectra and its intensity of the aqueous solutions of NBU-18 in the presence of  $\text{Fe}^{3+}$  (0.01 mol/L) and other cations (0.01 mol/L). (g and h) The luminescence spectra and its intensity of the aqueous solutions of  $\text{Cr}_2\text{O}_7^{2-}$ @NBU-18 (0.01 mol/L) in the presence of various anions (0.01 mol/L).

The anti-interference sensing experiments were prepared as follows and were carried out.

(a) NBU-18 sample of 5 mg was added into the  $\text{CCl}_4$  solvent (1 mL), further introducing various other solvents of 2 mL, containing methanol ( $\text{CH}_3\text{OH}$ ), ethanol ( $\text{EtOH}$ ), trichloromethane ( $\text{CHCl}_3$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ), tetrachloromethane ( $\text{CCl}_4$ ), benzene, toluene, 1-propanol, 2-propanol, acetonitrile ( $\text{CH}_3\text{CN}$ ) and tetrahydrofuran (THF), respectively.

(b) NBU-18 sample of 5 mg was added into the aqueous solution of  $\text{Fe}^{2+}$  (0.02 mol/L, 1.5 mL), then adding various aqueous solutions with other metal cations (0.02 mol/L, 1.5 mL) containing  $\text{K}^{+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ , to keep the concentration of  $\text{Fe}^{2+}$  at 0.01 mol/L in aqueous solution when other metal ions were introduced into the NBU-18 system. For  $\text{Fe}^{3+}$ , similar preparation was carried out except for  $\text{Fe}^{3+}$  (0.02 mol/L, 1.5 mL) instead of  $\text{Fe}^{2+}$  aqueous solution.



(c) NBU-18 sample of 5 mg was added into the aqueous solution of  $\text{Cr}_2\text{O}_7^{2-}$  (0.02 mol/L, 1.5 mL), then adding various aqueous solutions with other anions (0.02 mol/L, 1.5 mL) containing  $\text{CO}_3^{2-}$ ,  $\text{Br}^-$ ,  $\text{F}^-$ ,  $\text{BrO}_3^-$ ,  $\text{IO}_3^-$ ,  $\text{CH}_3\text{COO}^-$  ( $\text{OAc}^-$ ),  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Cr}_2\text{O}_7^{2-}$ , to keep the concentration of  $\text{Cr}_2\text{O}_7^{2-}$  at 0.01 mol/L in aqueous solution when other anions were introduced into the NBU-18 system.

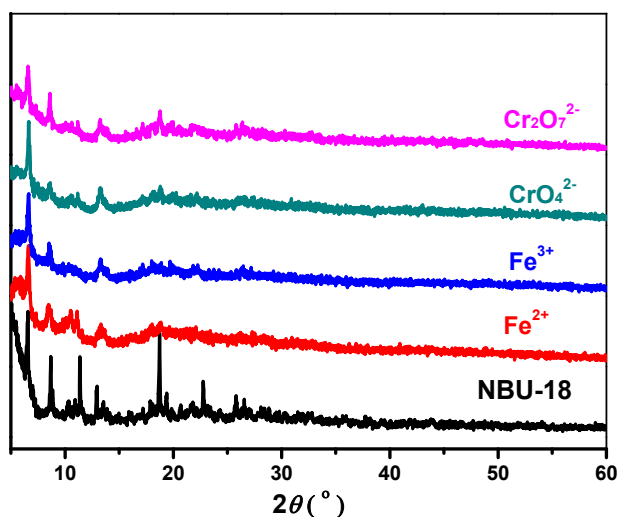


Fig. S20 The PXRD pattern of freshly synthesized NBU-18 and the ones after being measured toward  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$  ions.

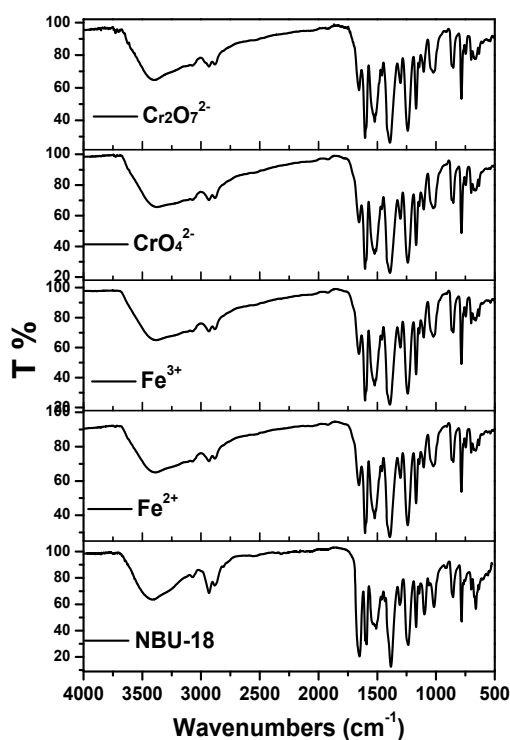


Fig. S21 The FT-IR spectra of freshly synthesized NBU-18 and the ones after being measured toward  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{CrO}_4^{2-}/\text{Cr}_2\text{O}_7^{2-}$  ions.