Supplementary Material

Construction of Zeolite A Type Multivariate Metal-Organic Framework for Selective Sensing of Fe^{3+} and $Cr_2O_7^{2-}$

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#Khalid Talha and Alamgir contributed equally to this work.

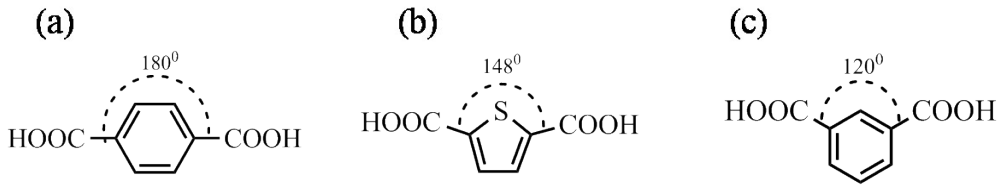


Figure S1. (a) linear linker; **(b)** the bent linker H_2TDC with 148° for BUT-26 synthesis; **(c)** bent linker H_2IPA with 120° angle for BUT-27 synthesis in this work.

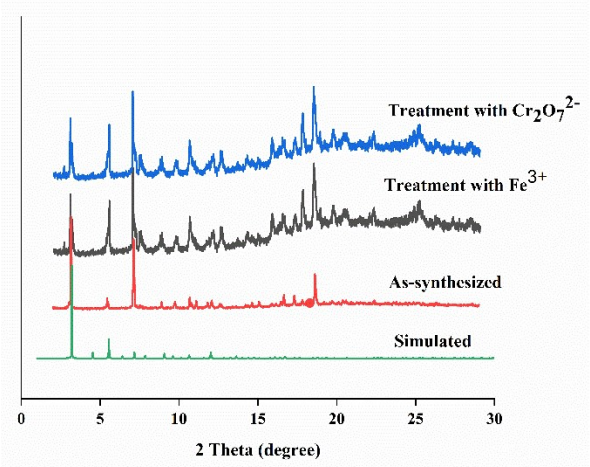


Figure S2. PXRD patterns BUT-27 with treatment of different ions.

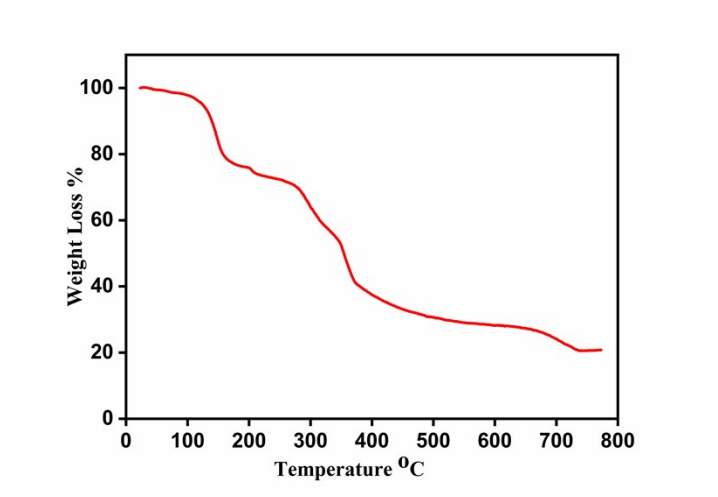
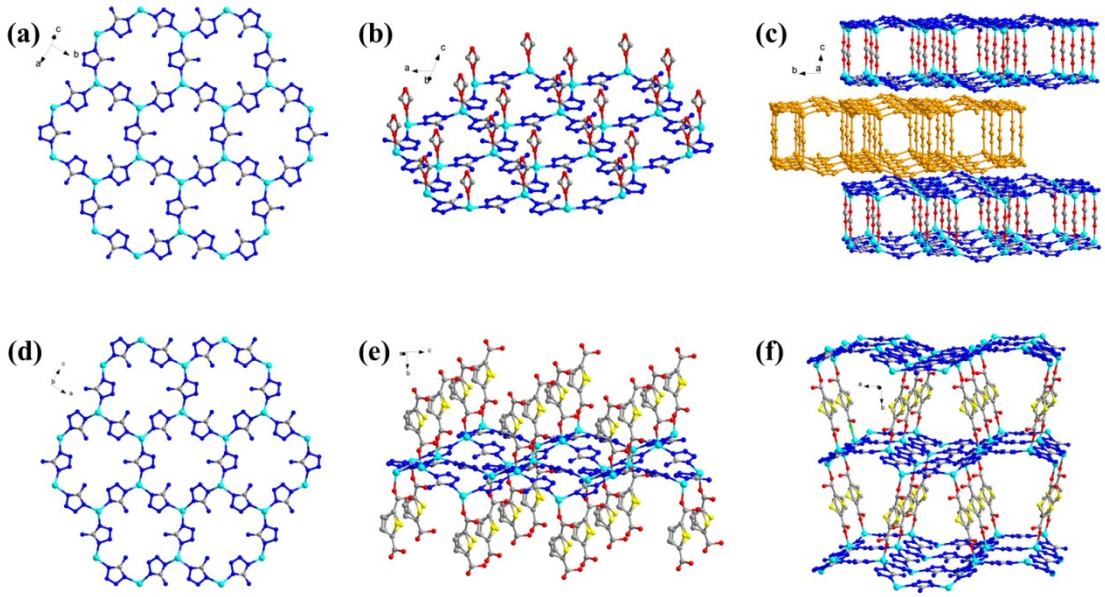


Figure S3. TGA curves of BUT-27.



FigureS4. Structure of the honeycomb-shaped layer of BUT-25 (a) and BUT-26 (d) formed by ATZ^- ligands and Zn^{2+} ions.(b) The formate ions distributed on the same side of the honeycomb-shaped layer. (c) Bilayers pillared by formate ions in BUT-25. (e) The TDC^{2-} ligands distributed on the two sides of the honeycomb-shaped layer. (f) The 3D layer-pillared structure of BUT-26 [1]

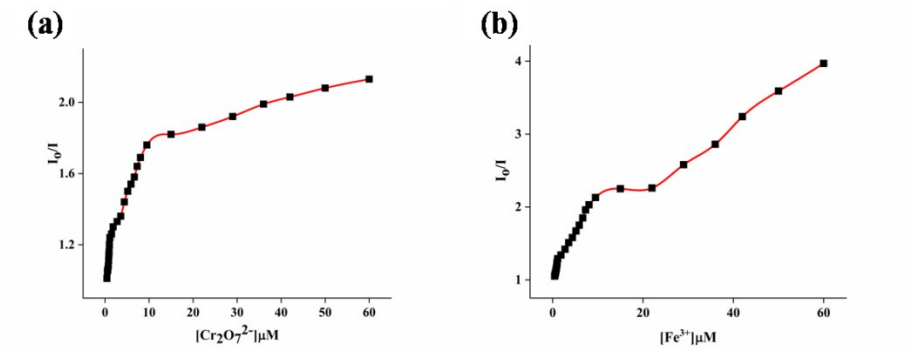


Figure S5. Stern-Volmer plot of BUT-27 suspension quenched by (a) $Cr_2O_7^{2-}$ (b) Fe^{3+} with different concentrations.

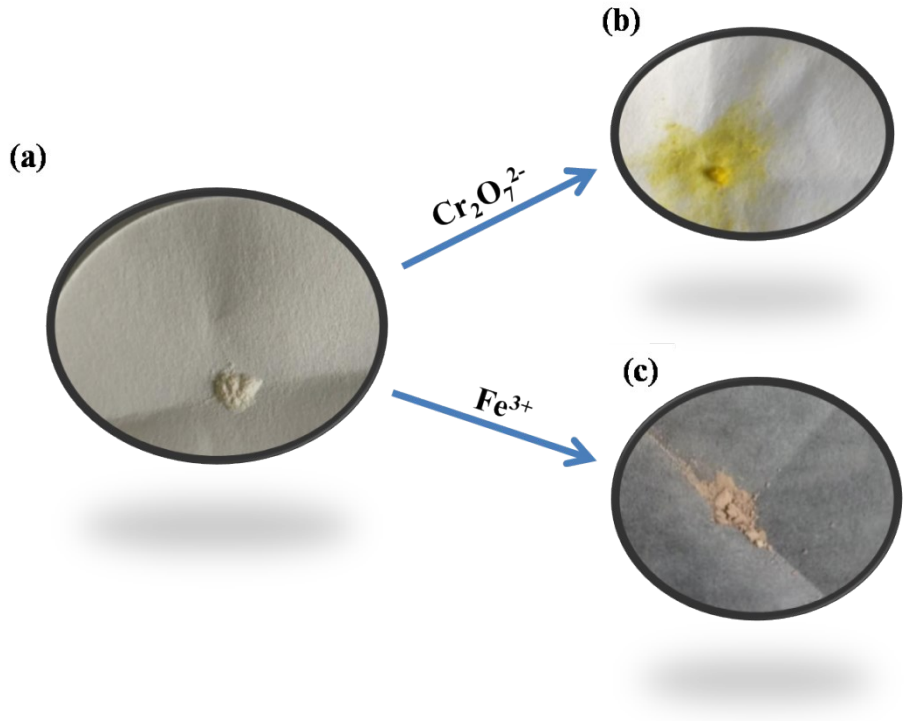


Figure S6. The photographs of BUT-27 samples. **(a)** as-synthesized sample; **(b)** after detection of $Cr_2O_7^{2-}$ ions. **(c)** after detection of Fe^{3+} ions.

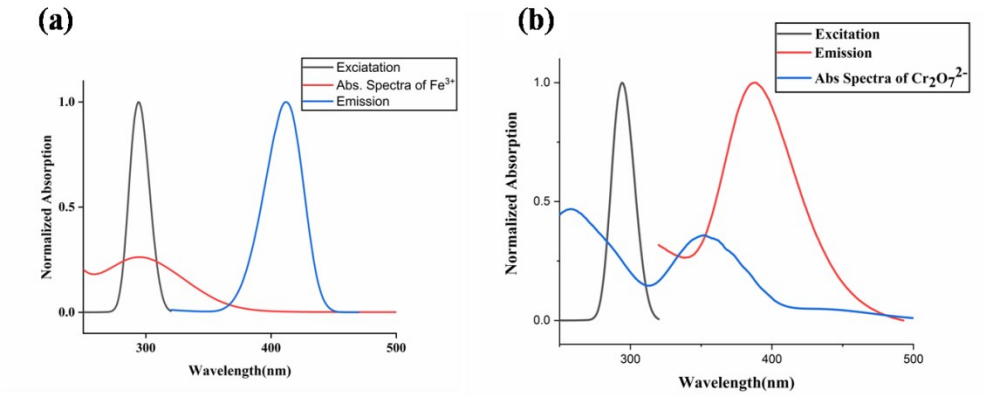


Figure S7. Spectral overlaps between UV-Vis absorption spectra of **(a)** Fe^{3+} **(b)** $Cr_2O_7^{2-}$ ions, exciatation and emission spectra of BUT-27**.**

Table S1. Crystal and Structure Refinement Data for BUT-27

Sample name	BUT-27
Formula	$C_{44}H_{38}N_{40}O_{25}Zn_8$
Formula Weight	2048.5g/mol
Space group	Pm-3m
a	27.5455(2)Å
b	27.5455(2) Å
c	27.5455(2) Å
α(deg)	90
β(deg)	90
γ (deg)	90
V	20900.3(5) $Å^3$
Z	3
D. calcd (g cm^{-3})	0.488
GOF on F^2	1.095
F(000)	3060.0
μ(mm-)	0.988
Rint	0.1051
R_1/wR_2 (all Data)	0.1234/3537

Table S2. Comparison of Performance of Reported MOFs for Detecting $Cr_2O_7^{2-}$

MOFs	K_{SV} (M^{-1})	Solvent	LOD μM	Ref
NMOF-2	$5.87x10^4$	Water	0.004	[2]
$[Cd_2(L1)(1,4\text{-}NDC)_2]_n$	$5.86x10^4$	H_2O		[3]
$[Zn_2(4,4'\text{-}nba)_2(1,4\text{-}bib)_2]_n$	$6.70x10^3$	H_2O	3.8	[4]
$\{[Zn_2(TPOM)(NH_2\text{-}BDC)_2]\cdot 4H_2O\}_n$	$7.79x10^3$	DMF	3.9	**[5]**
$[Zn(btz)]_n$	$4.23x10^3$	H_2O	2	**[6]**
$[Zn(IPA)(3\text{-}PN)]_n$	$1.37x10^3$	H_2O	12.02	**[7]**
$[Cd(IPA)(3\text{-}PN)]_n$	$2.91x10^3$	H_2O	2.26	**[7]**
BUT-28	$1.02x10^5$	H_2O	0.12	**[8]**
$\{[Cd(4BMPD)(BPDC)]\cdot 2H_2O\}_n$	$6.4x10^3$	H_2O	37.6	**[9]**
BUT-27	5.9×10^4	DMF/ H_2O	0.26	**This work**

Table S3. Comparison of Performance of Reported MOFs for Detecting Fe^{3+}

MOF	Solvent	K_{SV} (M^{-1})	LOD μM	Ref
ZSB-1	DMF		0.05	[10]
FJI-C8(Zn)	DMF	3.75×10^4	0.37	[11]
$\{[Zn(L)(bpp)]\cdot DMF\}_n$	DMF	2.56×10^4	7	[12]
HPU-1 (Zn)	H_2O	1.0×10^4	1000	[13]
$Cd_2(OBA)_2(BPTP)(H_2O)$	DMF		0.36	[14]
$[Zn(ATZ)_{1.5}(TDC)_{0.5}]_nNH_2(CH_3)_2$	DMF/H_2O	$1.7x10^5$	0.1	[1]
$[Zr_6O_4(OH)_4(2,7CDC)_6]\cdot 19H_2O\cdot 2DMF$	H_2O	5.5×10^3	0.018	[15]
Cu-MOFs	H_2O		0.5	[16]
BUT-27	DMF/ H_2O	1.1×10^3	0.19	This work

REFERENCES

(1) Talha, K.; He, T.; Xie, L.-H.; Wang, B.; Zhao, M.-J.; Zhang, Y.-Z.; Chen, Q.; Li, J.-R. A three-dimensional metal–organic framework with high performance of dual cation sensing synthesized via single-crystal transformation. *New J. Chem.,* **2020**, *44*, 11829-11834.

(2) Mukherjee, S.; Ganguly, S.; Samanta, D.; Das, D. Sustainable Green Route to Synthesize Functional Nano-MOFs as Selective Sensing Probes for CrVI Oxoanions and as Specific Sequestering Agents for $Cr_2O_7^{2-}$. *ACS Sustain. Chem. Eng.*, **2019**, *8*, 1195-1206.

(3) Yang, Y.-J.; Li, Y.-H.; Liu, D.; Cui, G.-H. A dual-responsive luminescent sensor based on a water-stable Cd (II)-MOF for the highly selective and sensitive detection of acetylacetone and $Cr_2O_7^{2-}$ in aqueous solutions. *CrystEngComm*., **2020**, *22*, 1166-1175.

(4) Xu, T.-Y.; Li, J.-M.; Han, Y.-H.; Wang, A.-R.; He, K.-H.; Shi, Z.-F. A new 3D four-fold interpenetrated dia-like luminescent Zn (ii)-based metal–organic framework: the sensitive detection of Fe^{3+}, $Cr_2O_7^{2-}$, and CrO_4^{2-} in water, and nitrobenzene in ethanol. *New J. Chem.,* **2020**, *44*, 4011-4022.

(5) Lv, R.; Wang, J.; Zhang, Y.; Li, H.; Yang, L.; Liao, S.; Gu, W.; Liu, X. An amino-decorated dual-functional metal–organic framework for highly selective sensing of Cr (III) and Cr (VI) ions and detection of nitroaromatic explosives. *J. Mater. Chem.,***2016**, *4*, 15494-15500.

(6) Cao, C.-S.; Hu, H.-C.; Xu, H.; Qiao, W.-Z.; Zhao, B. Two solvent-stable MOFs as a recyclable luminescent probe for detecting dichromate or chromate anions. *CrystEngComm.,* **2016**, *18*, 4445-4451.

(7) Parmar, B.; Rachuri, Y.; Bisht, K. K.; Laiya, R.; Suresh, E. Mechanochemical and conventional synthesis of Zn (II)/Cd (II) luminescent coordination polymers: dual sensing probe for selective detection of chromate anions and TNP in aqueous phase. *Inorg. Chem.,* **2017**, *56*, 2627-2638.

(8) Xu, M.-M.; Kong, X.-J.; He, T.; Wu, X.-Q.; Xie, L.-H.; Li, J.-R. A Stable Zr (IV)-Based Metal–Organic Framework Constructed from C═ C Bridged Di-isophthalate Ligand for Sensitive Detection of $Cr_2O_7^{2-}$in Water. *Inorg. Chem.,* **2018**, *57*, 14260-14268.

(9) Chen, S.; Shi, Z.; Qin, L.; Jia, H.; Zheng, H. Two new luminescent Cd (II)-metal–organic frameworks as bifunctional chemosensors for detection of cations Fe^{3+}, anions CrO_4^{2-}, and Cr2O72–in aqueous solution. *Cryst. Growth. Des.*, **2017**, *17*, 67-72.

(10) Han, L. J.; Zheng, D.; Chen, S. G.; Zheng, H. G.; Ma, J. A Highly Solvent-Stable Metal–Organic Framework Nanosheet: Morphology Control, Exfoliation, and Luminescent Property. *Small* **2018**, *14*, 1703873.

(11) Chen, C.-H.; Wang, X.-S.; Li, L.; Huang, Y.-B.; Cao, R. Highly selective sensing of Fe^{3+} by an anionic metal–organic framework containing uncoordinated nitrogen and carboxylate oxygen sites. *Dalton Trans.,* **2018**, *47*, 3452-3458.

(12) Chen, Z.; Mi, X.; Wang, S.; Lu, J.; Li, Y.; Li, D.; Dou, J. Two novel penetrating coordination polymers based on flexible S-containing dicarboxylate acid with sensing properties towards Fe3+ and Cr2O72-ions. *J. Solid State Chem.,* **2018**, *261*, 75-85.

(13) Li, H.; He, Y.; Li, Q.; Li, S.; Yi, Z.; Xu, Z.; Wang, Y. Highly sensitive and selective fluorescent probe for Fe 3+ and hazardous phenol compounds based on a water-stable Zn-based metal–organic framework in aqueous media. *RSC Adv.,* **2017**, *7*, 50035-50039.

(14) Han, L.-J.; Yan, W.; Chen, S.-G.; Shi, Z.-Z.; Zheng, H.-G. Exploring the detection of metal ions by tailoring the coordination mode of V-Shaped thienylpyridyl ligand in three MOFs. *Inorg. Chem.,***2017**, *56*, 2936-2940.

(15) Das, A.; Biswas, S. A multi-responsive carbazole-functionalized Zr (IV)-based metal-organic framework for selective sensing of Fe (III), cyanide and p-nitrophenol. *Sens. Actuators, B.*, **2017**, *250*, 121-131.

(16) Ming, F.; Hou, J.; Huo, D.; Zhou, J.; Yang, M.; Shen, C.; Zhang, S.; Hou, C. Copper-based metal–organic framework nanoparticles for sensitive fluorescence detection of ferric ions. *Anal.Methods,* **2019**, *11*, 4382-4389.