Supplementary Information

A multifunctional microporous anionic metal–organic framework for column-chromatographic dye separation and selective detection and adsorption of Cr^{3+}

Shu-Ran Zhang,[a] Jing Li,[a] Dong-Ying Du,*[a] Jun-Sheng Qin,[a] Shun-Li Li,[b] Wen-Wen He,[a] Zhong-Min Su*[a] and Ya-Qian Lan*[a,b]

[a] Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, Jilin, People's Republic of China. E-mail: zmsu@nenu.edu.cn

[b] Jiangsu Key Laboratory of Biofunctional Materials, School of Chemistry and Materials Science, Nanjing Normal University, Nanjing 210023, Jiangsu, People's Republic of China. E-mail: yqlan@njnu.edu.cn

Table S1 Crystal data and structure refinements for **NENU-505**.

Identification code	**NENU-505**
Formula	$C_{14}H_{26}N_{3.5}O_{9.5}Zn$
Formula weight	460.18
Crystal system	Monoclinic
Space group	*C*2/*c*
a (Å)	27.7680(11)
b (Å)	7.9000(6)
c (Å)	18.2980(14)
α (°)	90.00
β (°)	108.3290(15)
γ (°)	90.00
V (Å^3)	3810.3(4)
Z	4
D_{calcd}.[g cm^{-3}]	1.114
F(000)	1300
Reflections collected	13597
R(int)	0.0330
Goodness-of-fit on F^2	0.834
R_1^{a} [$I>2\sigma(I)$]	0.0479
wR_2^{b}	0.1464

$^aR_1 = \sum\left\|F_o\right| - \left|F_c\right\| / \sum\left|F_o\right|$. $^bwR_2 = \left|\sum w(\left|F_o\right|^2 - \left|F_c\right|^2)\right| / \sum\left|w(F_o^{\,2})^2\right|^{1/2}$.

Table S2 The selected bond lengths [Å] and angles [deg] for **NENU-505**.

Bond length [Å]		Bond angle [deg]	
Zn(1)-O(3)	1.910(2)	O(3)-Zn(1)-O(5)	113.55(11)
Zn(1)-O(5)	1.930(2)	O(3)-Zn(1)-O(2)#1	114.98(10)
Zn(1)-O(2)#1	1.9476(19)	O(5)-Zn(1)-O(2)#1	112.06(12)
Zn(1)-O(1)#2	1.9615(18)	O(3)-Zn(1)-O(1)#2	94.48(9)
		O(5)-Zn(1)-O(1)#2	109.41(12)
		O(2)#1-Zn(1)-O(1)#2	110.97(10)

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

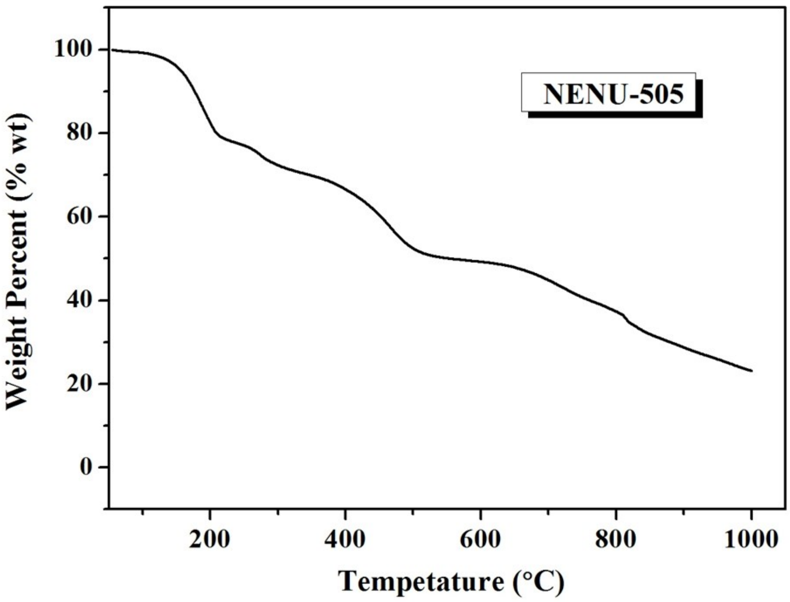

Fig. S1 The TGA curve of **NENU-505** was measured under N_2 atmosphere from 50 °C to 1000 °C at the heating rate of 10 $°C \cdot min^{-1}$.

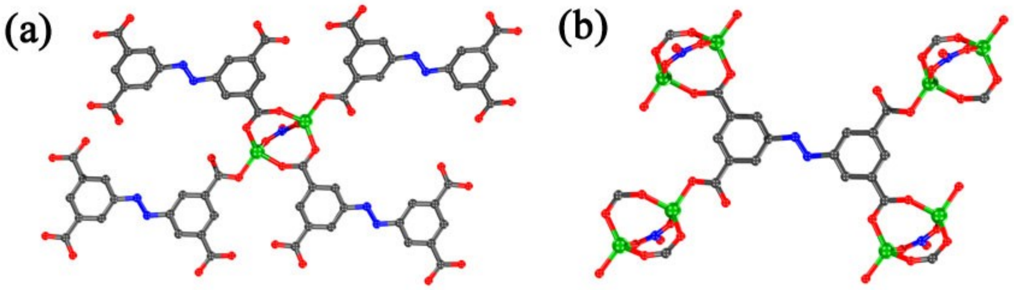

Fig. S2 Coordination environments of (a) binuclear $[Zn_2(CO_2)_4(NO_3)]$ cluster and (b) the H_4ABTC ligand in **NENU-505**, respectively.

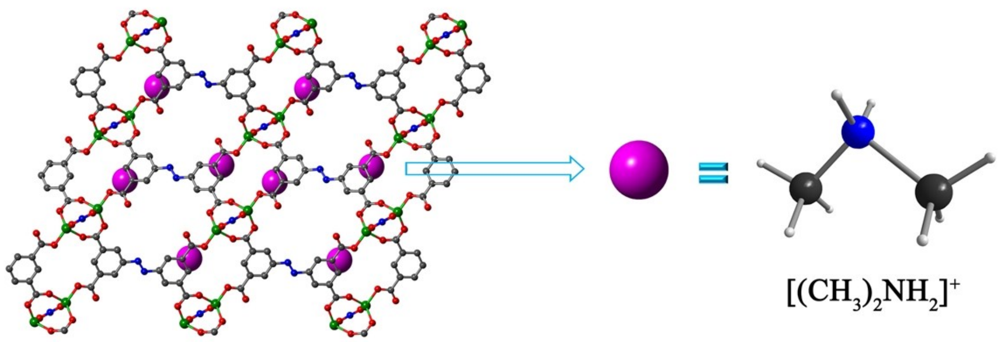

Fig. S3 The schematic representation of $[(CH_3)_2NH_2]^+$ ions located in the 3D framework of **NENU-505** along the *b* axis.

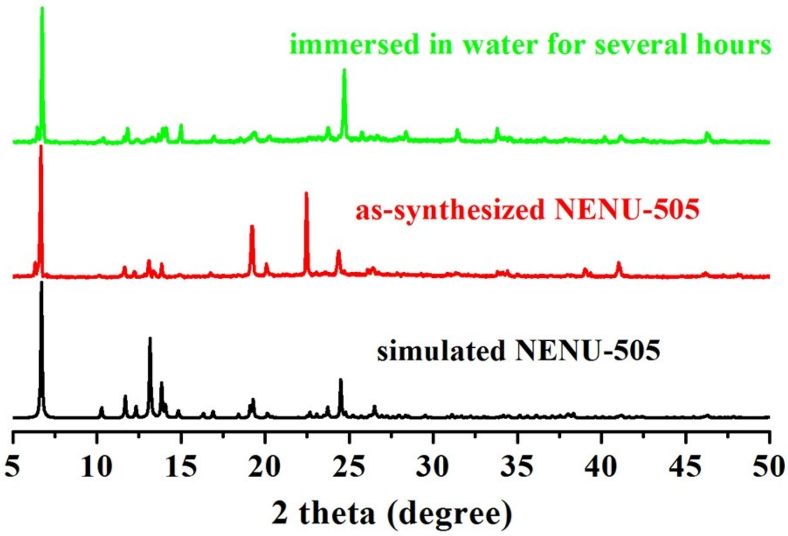

Fig. S4 XRPD patterns of simulated **NENU-505** (black), as-synthesized **NENU-505** (red) and immersed in water for a few hours (green).

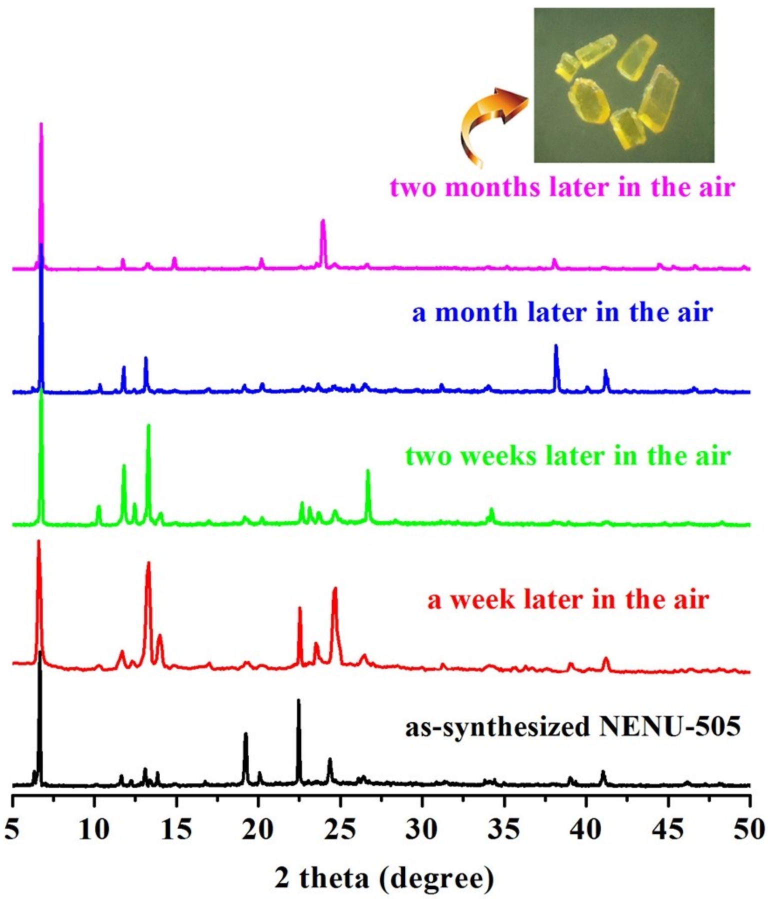

Fig. S5 XRPD patterns of as-synthesized **NENU-505** (black) and **NENU-505** samples exposed in the air after a week (red), two weeks (green), a month (blue) and two months (pink), respectively. Inset: the optical image of **NENU-505** exposed after two months in the air.

Table S3 Comparison of MB adsorption capacity in various adsorbents.

Materials	Adsorption capacity (mg g^{-1})	Ref.
Graphene oxide	397	1
ErCu–POM (**Er-3**)	391.3	2
$PW_{11}V$@MIL-101	371	3
Cd-MOF (**2**)	317.9	4
Activated carbon	135	5
Zn-DDQ	135	6
Cd-MOF (**1**)	105	4
Cu-DDQ	90	6
Pb-DDQ	86	6
NENU-505	33.5	This work
Cd-MOF (**3**)	30	4
MOF@graphite oxide	18	7
446-MOF	17	8
Zn-MOF	0.75	9

Table S4 The adsorption capacity of **NENU-505** at room temperature for every dye.

Dye composition	Adsorption capacity for MB (mg g^{-1})	Adsorption capacity for BR 2 (mg g^{-1})	Adsorption capacity for BG 1 (mg g^{-1})
Single component dye (MB)	33.5	_UD[a]	_UD[a]
Single component dye (BR 2)	_UD[a]	4.5	_UD[a]
Single component dye (BG 1)	_UD[a]	_UD[a]	17.6
Mixture dye (MB and BR 1)	33.3	_UD[a]	_UD[a]
Mixture dye (MB and MO)	33.4	_UD[a]	_UD[a]
Mixture dye (BG 1 and BR 1)	_UD[a]	_UD[a]	17.3

[a] UD: undetected

Table S5 The ICP percentage of Cr^{3+} encapsulated by **NENU-505** in multi-element solutions.

Multi-element solution	The ICP percentage of Cr^{3+} (%)
1: Fe^{2+}, Cu^{2+} and Cr^{3+}	4.056
2: Cu^{2+}, Ni^{2+} and Cr^{3+}	4.009
3: Cu^{2+}, Co^{2+} and Cr^{3+}	3.858
4: Ni^{2+}, Co^{2+} and Cr^{3+}	4.069

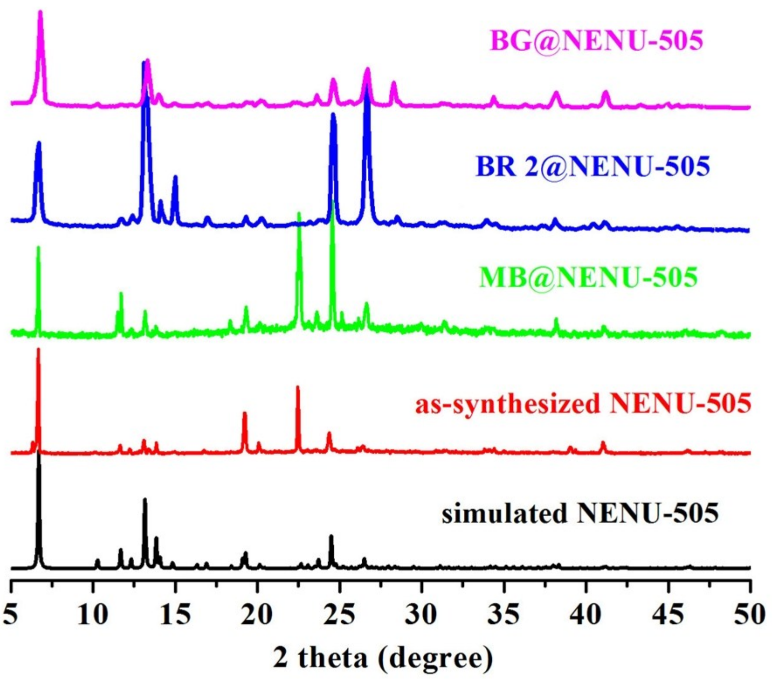

Fig. S6 XRPD patterns of simulated **NENU-505** (black), as-synthesized **NENU-505** (red) and after the absorption of MB (green), BR 2 (blue) and BG (pink), respectively.

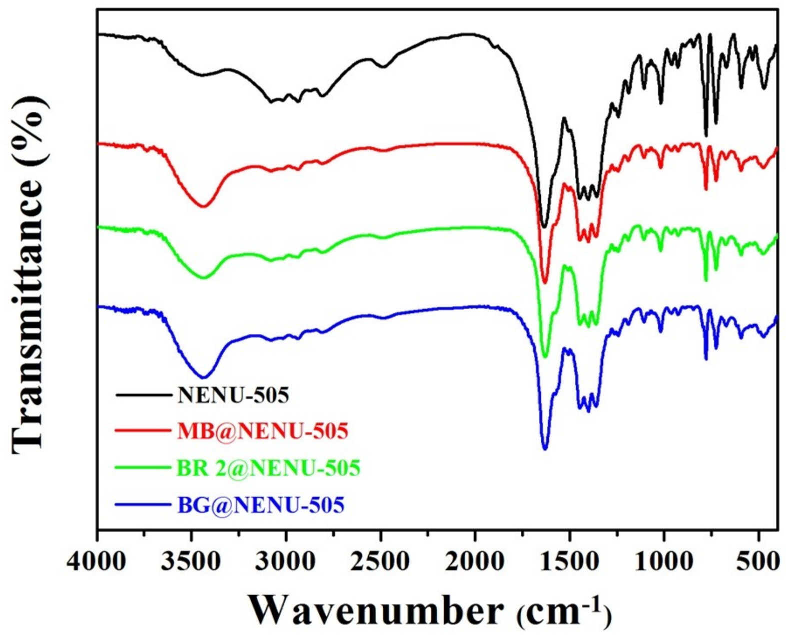

Fig. S7 IR spectra of **NENU-505**, **MB@NENU-505**, **BR 2@NENU-505**, and **BG@NENU-505**.

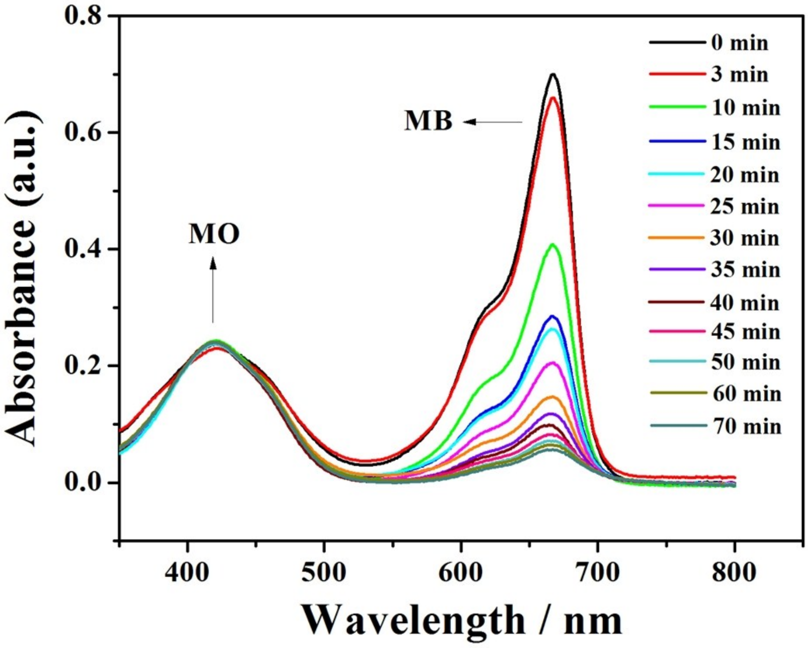

Fig. S8 UV/Vis spectra of DMA solution of mixed MB and MO with **NENU-505**.

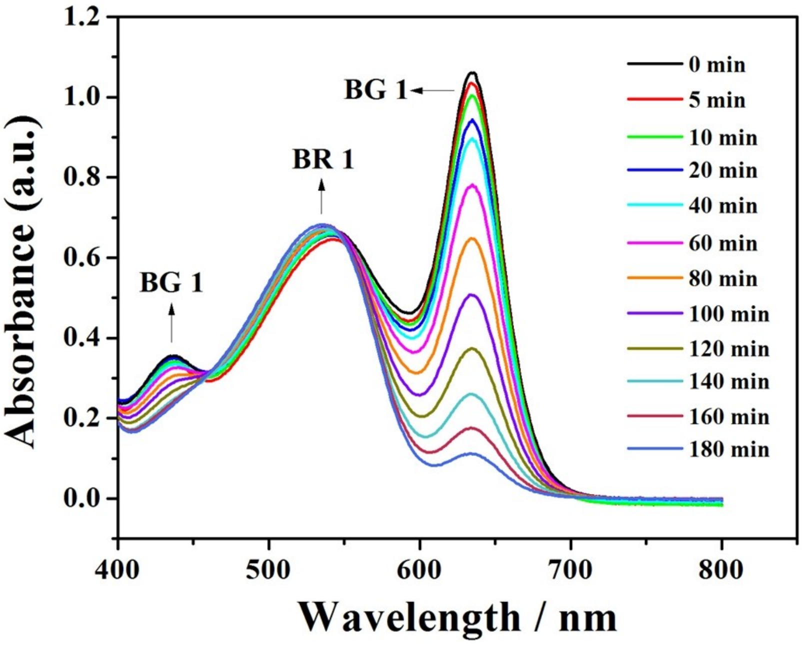

Fig. S9 UV/Vis spectra of DMA solution of mixed BG 1 and BR 1 with **NENU-505**.

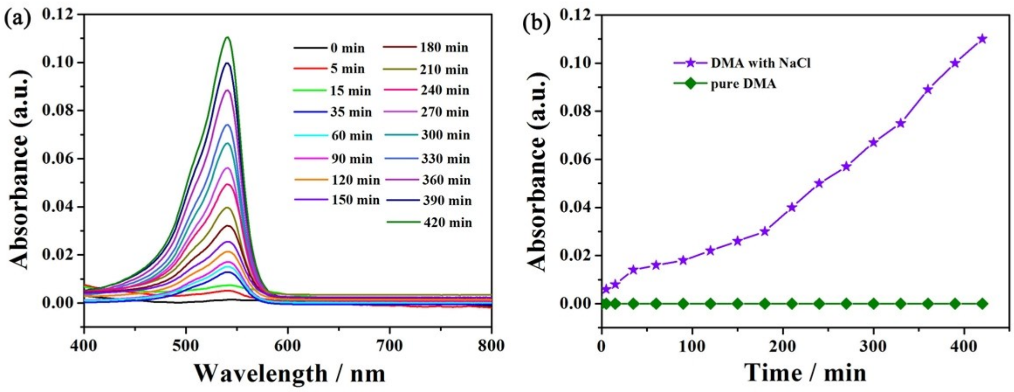

Fig. S10 (a) The BR 2 released from **BR 2@NENU-505** in a saturated solution of NaCl in DMA monitored by UV absorption. (b) The release-rate comparison of BR 2 from **BR 2@NENU-505** in a saturated solution of NaCl in DMA (purple) and pure DMA (dark green).

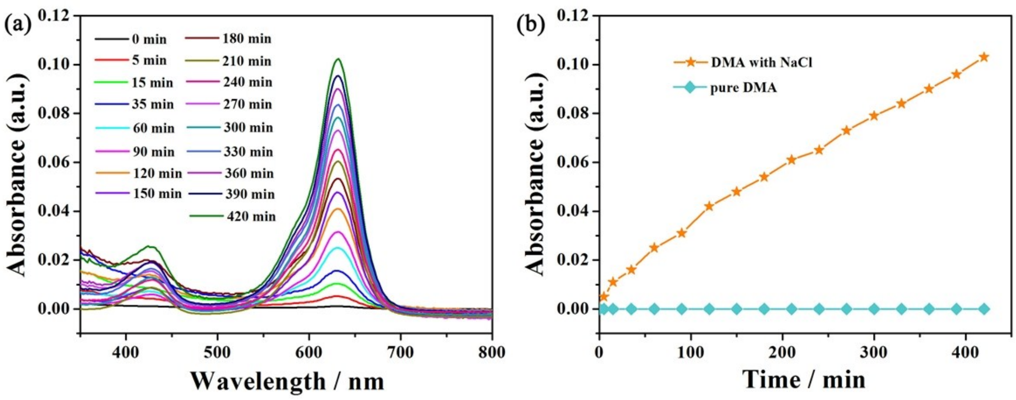

Fig. S11 (a) The BG 1 released from **BG 1@NENU-505** in a saturated solution of NaCl in DMA monitored by UV absorption. (b) The release-rate comparison of BG 1 from **BG 1@NENU-505** in a saturated solution of NaCl in DMA (orange) and pure DMA (pale green).

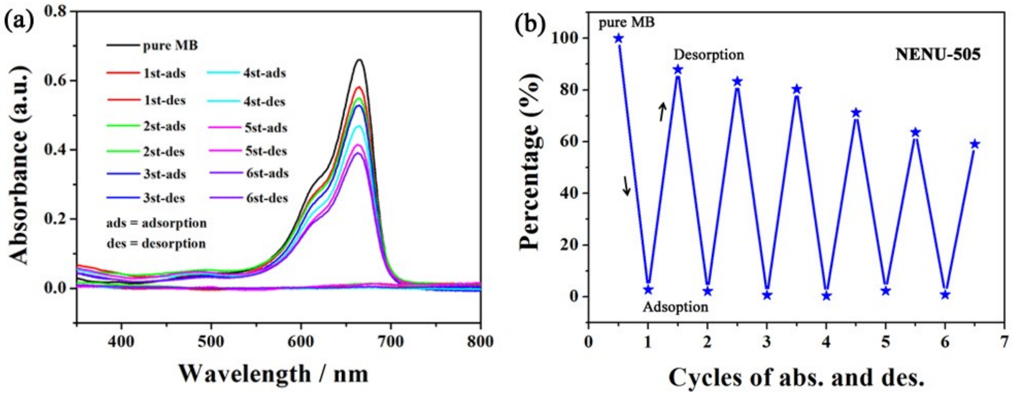

Fig. S12 (a) UV-vis spectra of MB solution in DMA after adsorption experiments with **NENU-505**, as well as the MB released (desorption) from **MB@NENU-505** using a saturated solution of NaCl in DMA. (b) The adsorption and desorption efficiency of **NENU-505** toward MB after six cycles.

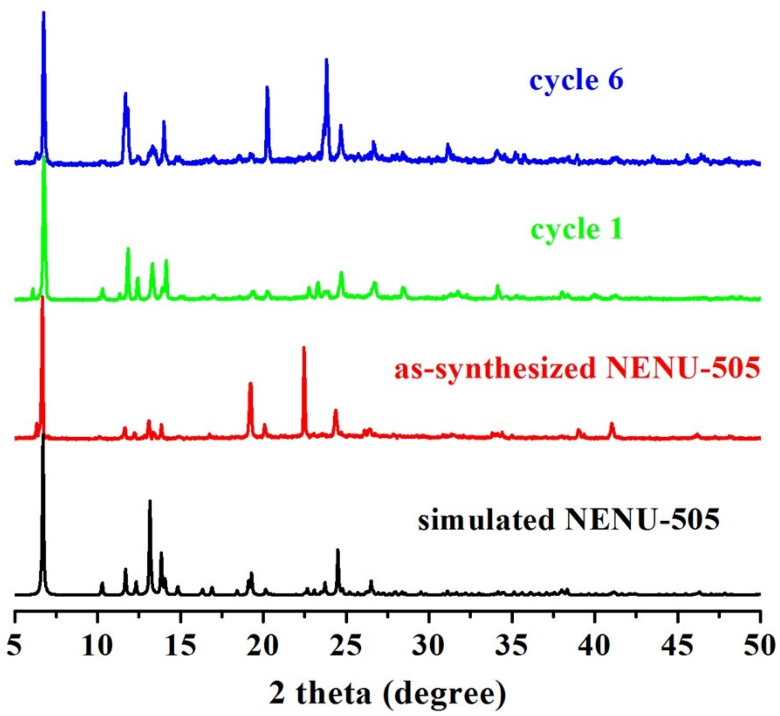

Fig. S13 XRPD patterns of **NENU-505** toward MB after adsorption–desorption cycle 1 and cycle 6.

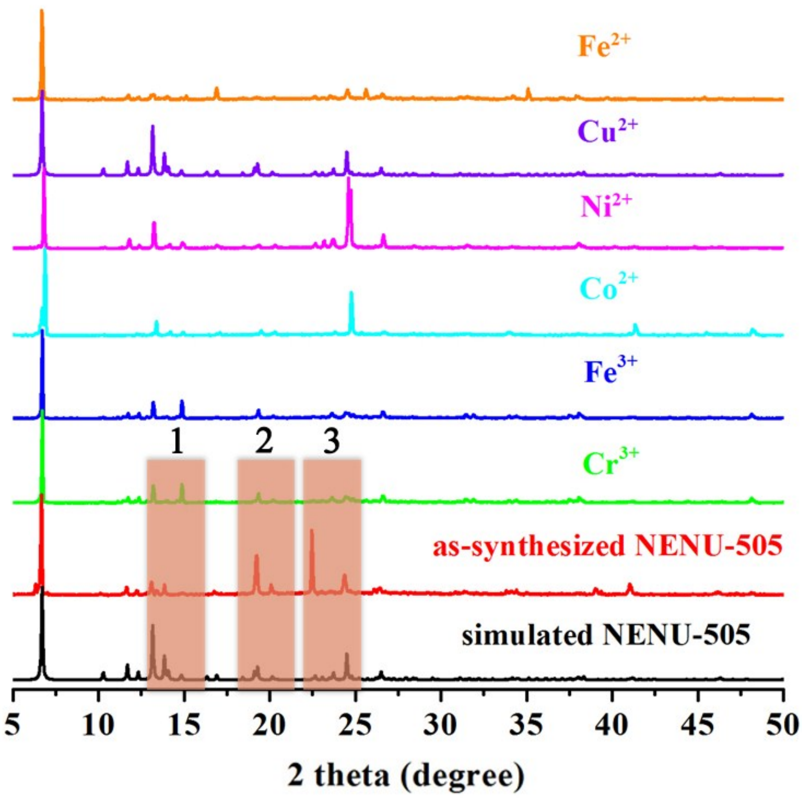

Fig. S14 XRPD patterns of **NENU-505** immersed in different metal ions.

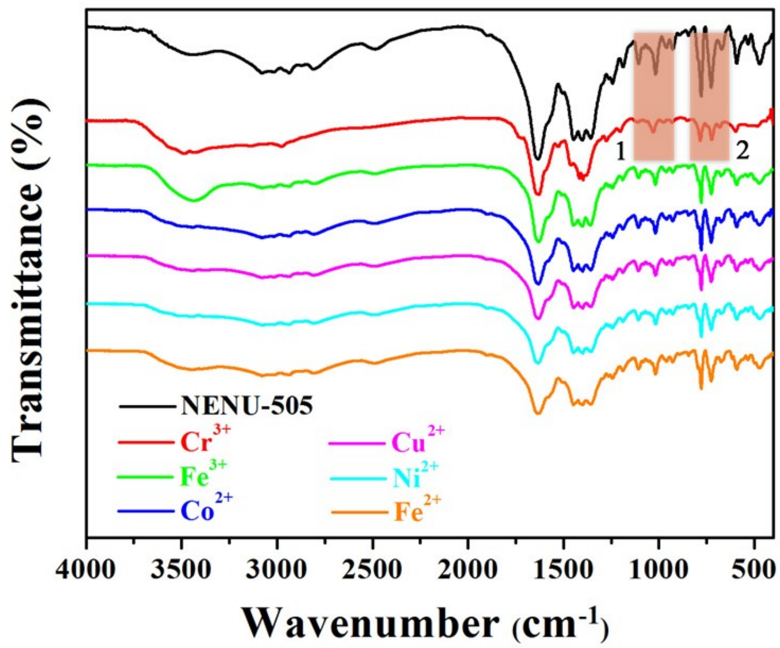

Fig. S15 IR spectra of **NENU-505** immersed in different metal ions.

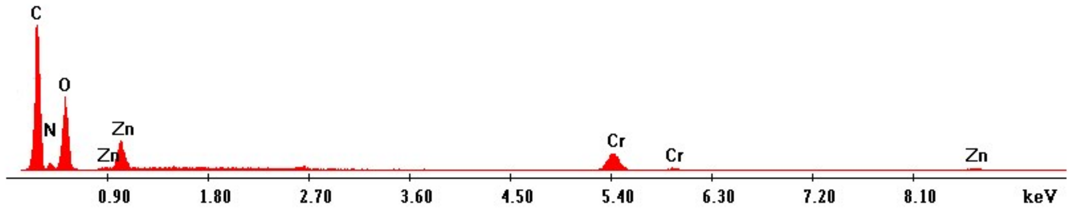

Fig. S16 EDS analysis of **Cr^{3+}@NENU-505**.

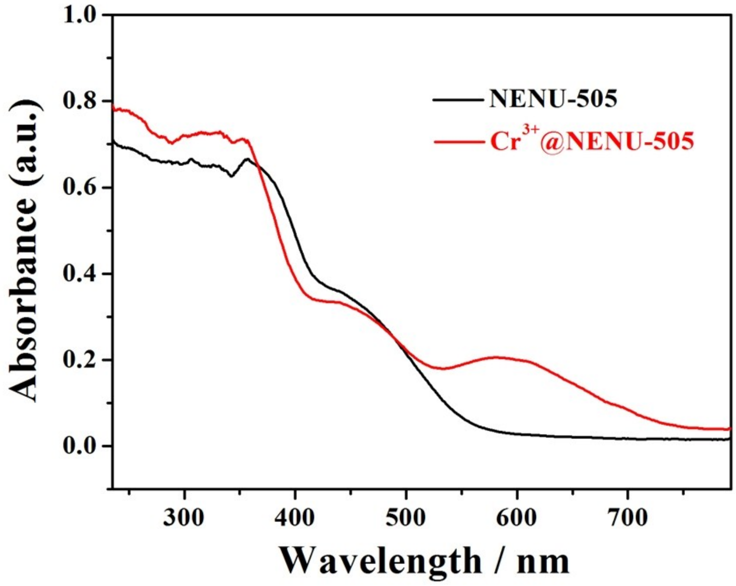

Fig. S17 UV/Vis spectra of solid **NENU-505** and **Cr^{3+}@NENU-505**.

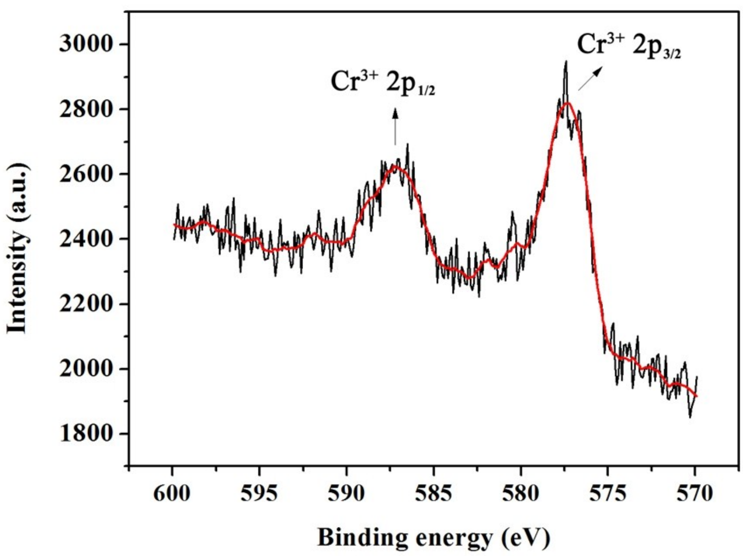

Fig. S18 XPS spectrum of Cr^{3+} for **Cr^{3+}@NENU-505**.

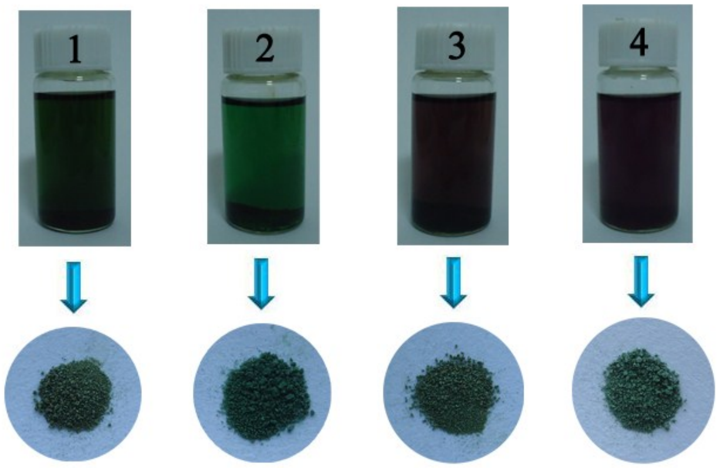

Fig. S19 The photographs of **NENU-505** in 10 mL DMA solutions containing three equal concentration of each metal ion (1: Fe^{2+}, Cu^{2+} and Cr^{3+}; 2: Cu^{2+}, Ni^{2+} and Cr^{3+}; 3: Cu^{2+}, Co^{2+} and Cr^{3+}; 4: Ni^{2+}, Co^{2+} and Cr^{3+}, 0.01 M).

Notes and References

1 J.-D. Xiao, L.-G. Qiu, X. Jiang, Y.-J. Zhu, S. Ye and X. Jiang, *Carbon*, 2013, **59**, 372.

2 F.-Y. Yi, W. Zhu, S. Dang, J.-P. Li, D. Wu, Y.-h. Li and Z.-M. Sun, *Chem. Commun.*, 2015, **51**, 3336.

3 A.-X. Yan, S. Yao, Y.-G. Li, Z.-M. Zhang, Y. Lu, W.-L. Chen and E.-B. Wang, *Chem. Eur. J.*, 2014, **20**, 6927.

4 F.-Y. Yi, J.-P. Li, D. Wu and Z.-M. Sun, *Chem. Eur. J.*, 2015, **21**, 11475.

5 The national standard of the People's Republic of China: wooden granular activated carbon for water purification. GB/T13803.2-1999.

6 Y. Zhu, Y.-M. Wang, S.-Y. Zhao, P. Liu, C. Wei, Y.-L. Wu, C.-K. Xia and J.-M. Xie, *Inorg. Chem.*, 2014, **53**, 7692.

7 L. Li, X. L. Liu, H. Y. Geng, B. Hu, G. W. Song and Z. S. Xu, *J. Mater. Chem. A*, 2013, **1**, 10292.

8 M. Du, X. Wang, M. Chen, C.-P. Li, J.-Y. Tian, Z.-W. Wang and C.-S. Liu, *Chem. Eur. J.*, 2015, **21**, 9713.

9 C.-Y. Sun, X.-L. Wang, C. Qin, J.-L. Jin, Z.-M. Su, P. Huang and K.-Z. Shao, *Chem. Eur. J.*, 2013, **19**, 3639.