Electronic Supplementary Information (ESI):

Structural tuning of Zn(II)-MOFs based on pyrazole functionalized carboxylic acid ligands for organic dye adsorption

Xiao-Ting Liu,[†a,b] Si-Si Chen,[†a] Si-Miao Li,[a] Hong-Xiang Nie,[a,b] Yao-Qing Feng,[a] Yi-Ning Fan,[a] Mei-Hui Yu,[*a,b] Ze Chang[*a,b,c] and Xian-He Bu[a,b,d]

[a.] *School of Materials Science and Engineering, National Institute for Advanced Materials, Tianjin Key Laboratory of Metal and Molecule-Based Material Chemistry, Nankai University, Tianjin 300350, China.*

[b.] *Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China.*

[c.] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China.*

[d.] *State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China.*

[†] *These authors contribute equally to this work.*

Corresponding Author

E-mail: *changze@nankai.edu.cn; mh@nankai.edu.cn*

Experimental Section

Chemicals and Materials

All the reagents and solvents were purchased commercially and were not further purified when used. 4-(1H-pyrazol-4-yl)benzoic acid (H_2PBA) was purchased from Shanghai Boyners Pharmaceutical. $Zn(NO_3)_2 \cdot 6H_2O$ and DMF solvent were purchased from Concord Technology (Tianjin). 5-(1H-pyrazole-4-carboxamido)isophthalic acid (H_3Pycia) was synthesized according to the reference[S1]. The structures of H_3Pycia H_2PBA ligands were shown in Fig. S1.

Materials and Instrumentation

Thermogravimetric analysis (TGA) was performed on a Rigaku Thermo Plus EVO2 8121 analyzer in N_2 environment with a heating rate of 10°C min^{-1} from 20°C to 800°C, using an empty Al_2O_3 crucible as reference. Powder X-ray diffraction (PXRD) data analysis were collected on a Rigaku Mini Flex600 diffractometer using Cu Kα radiation (λ =1.54184 Å) in the 2θ range of 3–50° with a scanning rate of 3° min^{-1}. Simulation of the PXRD patterns were carried out based on the single-crystal data by diffraction crystal module of the Mercury version 2.4 software. UV-Visible absorption spectral measurements were carried out on a Persee TU-1950 UV-Vis spectrophotometer.

General Methods for X-ray Crystallography

The structure determination of MOF-**1** was performed on a Rigaku 007 Saturn70 diffractometer at 113 K with Mo-Kα radiation (λ = 0.71073 Å). The structure determination of MOF-**2** was performed on a Rigaku XtalAB Pro MM007 DW diffractometer at 273 K with Cu-Ka radiation (λ = 1.54178 Å). The structures were solved with direct methods using SHELXS package of the SHELXTL software and refined with SHELXL package. The disordered guest molecules in MOF-**1** and MOF-**2** are removed by SQUEEZE program as implemented in PLATON and the results were appended in the CIF files. Crystal data and selected bond lengths and angles were listed in Table S1-S3.

Synthesis of MOF-1: $Zn(NO_3)_2 \cdot 6H_2O$ (0.15 mmol, 44.5 mg) and H_3Pycia (0.075 mmol, 20.6 mg) were dissolved in DMF/H_2O/HNO_3 (4.05 mL, 3:1:0.05, v/v/v). The mixture is transferred into an autoclave to react at 140 °C for 72 h and subsequently cooled to room temperature. Block-shaped colorless crystals were obtained with 80% yield (based on Zn). IR data: 3426s, 2792w, 1637s, 1535s, 1325m, 1245w, 1175w, 1112w, 1048m, 1004m, 863s, 769s, 720s, 663s, 443w (Fig. S2).

Synthesis of MOF-2: $Zn(NO_3)_2 \cdot 6H_2O$ (0.20 mmol, 59.4 mg), H_3Pycia (0.05 mmol, 13.8 mg) and H_2PBA (0.05 mmol, 9.4 mg) were dissolved in DMF/H_2O (4 mL, 3:1, v/v). The mixture is transferred into a glass bottle to react at 92 °C for 72 h and subsequently cooled to room temperature. Bud-shaped colorless crystals were obtained with 80% yield (based on Zn). IR data: 3566s, 3114w, 2802w, 2360m, 1558s, 1387s, 1237m, 1181m, 1052m, 954w, 861m, 780s, 721s, 607w, 505w, 457w (Fig. S3).

Dye adsorption

An exact amount of the adsorbents (10 mg) is added into the 20 mg/L DMF solution (4 mL) of MB^+, TO^+, SD^0, CM^0, MO^-, LB^-, $R6G^+$, VB^+, and 20 mg/L DMF solution (4 mL, 1:1 by volume ratio) of MB^+/SD^0, MB^+/CM^0, MB^+/MO^-, MB^+/LB^- and TO^+/SD^0, TO^+/CM^0, TO^+/MO^-, TO^+/LB^-, respectively. UV-vis absorption spectra are recorded simultaneously.

The adsorption capacity of MOF-**1** and MOF-**2** toward MB^+ and TO^+ can be deduced from the dependence of the saturated adsorption amount (q_e) on the initial concentration of the adsorbent (c_0) according to the eq:

$$q_e = (C_0 - C_t) \times V \div m$$

where V (l) is the volume of dye solution, m (g) is the mass of adsorbent, C_0 and C_t (mg/l) are the initial and residual concentration of dye solutions, respectively.

In this experiment, 10 mg MOF adsorbent was added into 4 ml MB^+ and 4 ml TO^+ DMF solutions with a series of known initial concentrations, respectively. After 48 h,

the residues of MB^+ and TO^+ in solutions was determined UV-Vis spectrophotometer and the concentration was determined based on absorbance-concentration calibration curve (Fig. S17).

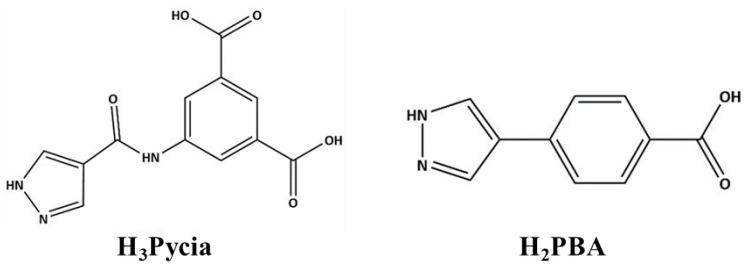

Fig. S1. The structures of H_3Pycia and H_2PBA ligands.

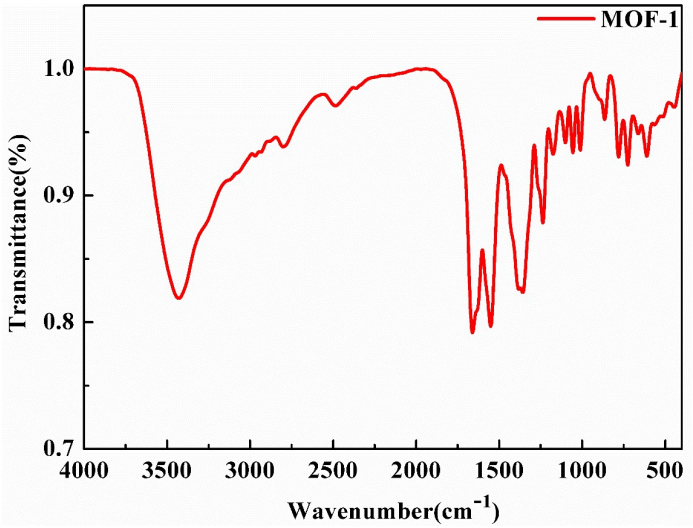

Fig. S2. The IR spectrum of MOF-**1**.

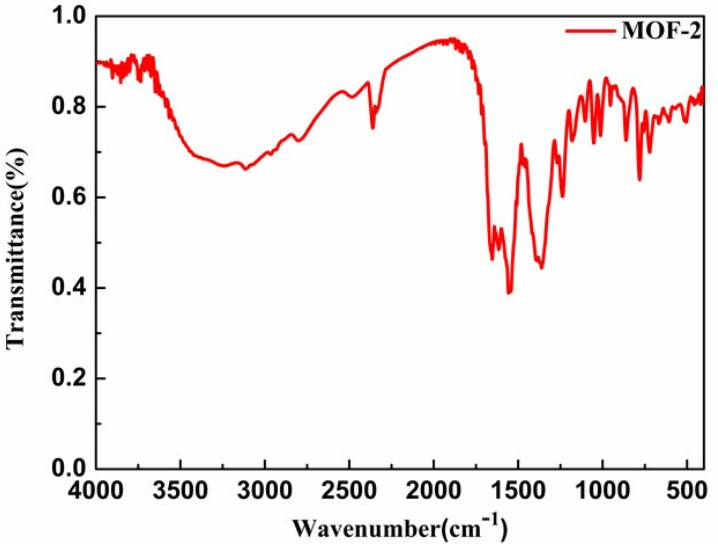

Fig. S3. The IR spectrum of MOF-**2**.

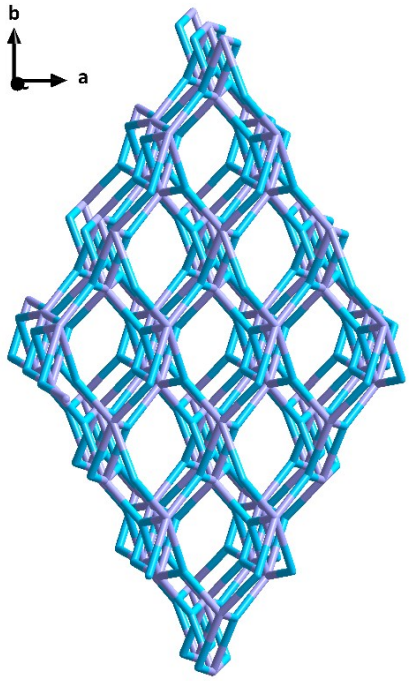

Fig. S4. Topology of MOF-**1**.

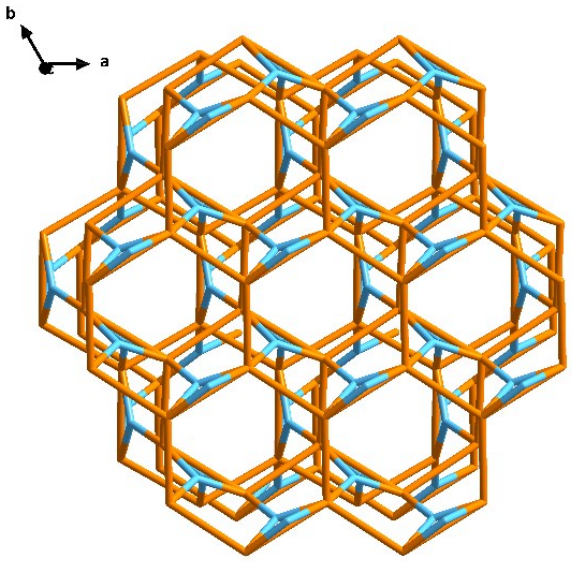

Fig. S5. Topology of MOF-**2**.

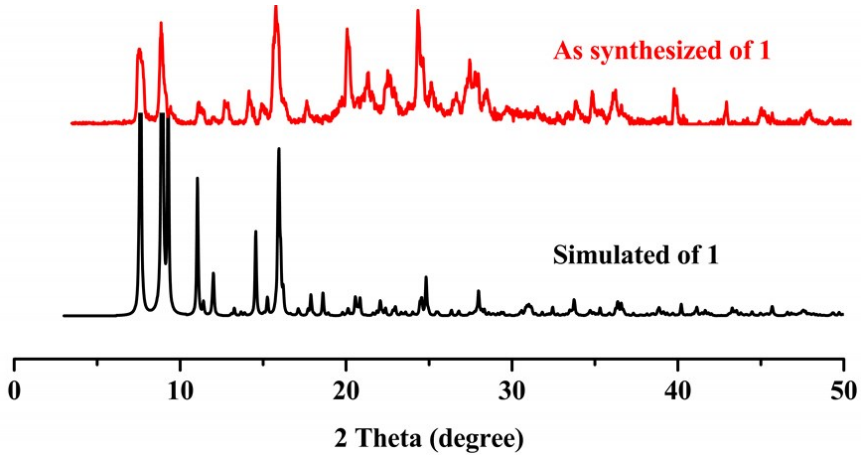

Fig. S6. Experimental and simulated powder X-Ray diffraction patterns for MOF-**1**.

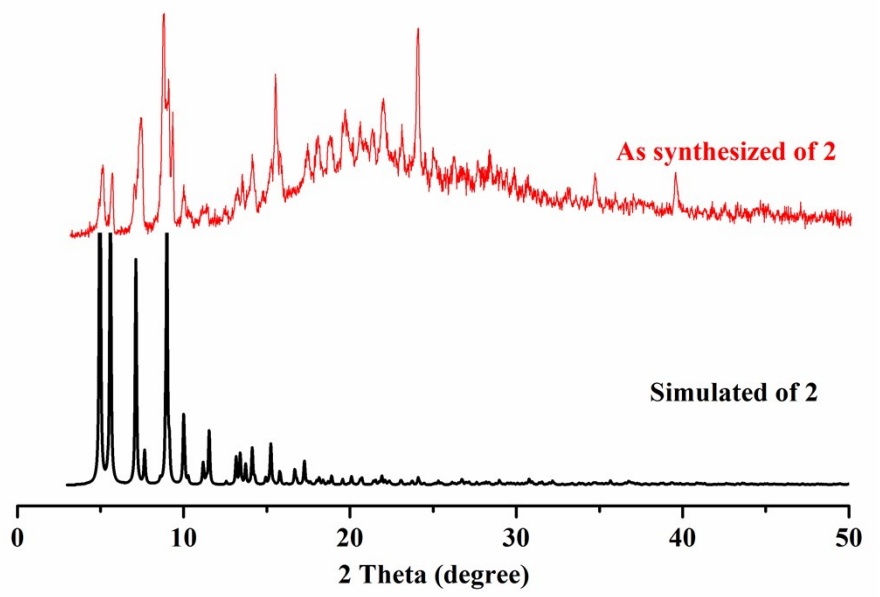

Fig. S7. Experimental and simulated powder X-Ray diffraction patterns for MOF-**2**.

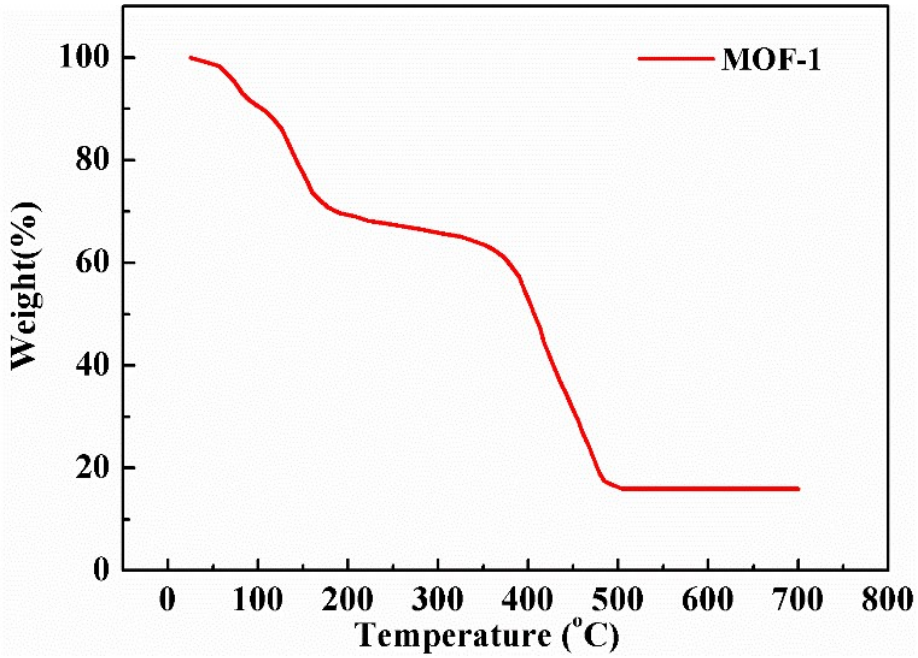

Fig. S8. The TGA curve of MOF-**1**.

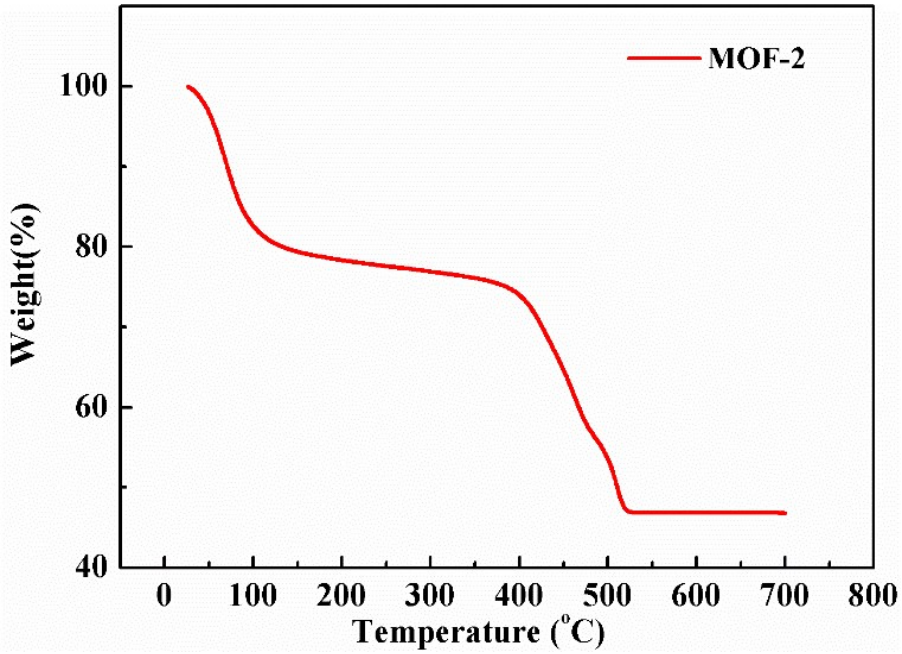

Fig. S9. The TGA curve of MOF-**2**.

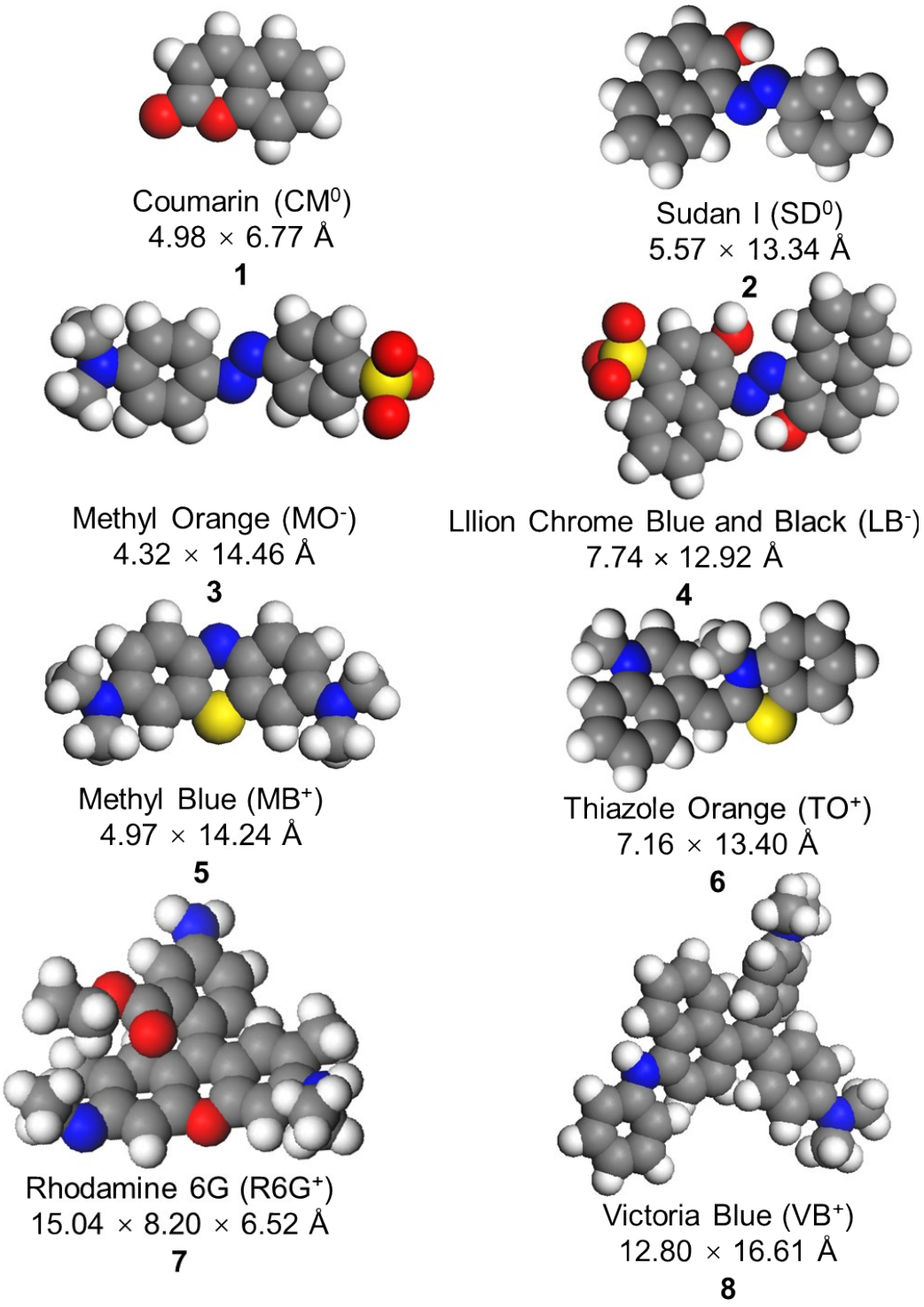

Fig. S10. The structures of eight dyes optimized by DFT calculation with Gaussian 09 program package[S2]. Grey, red, blue, yellow and white balls represent for C, O, N, S, H atoms.

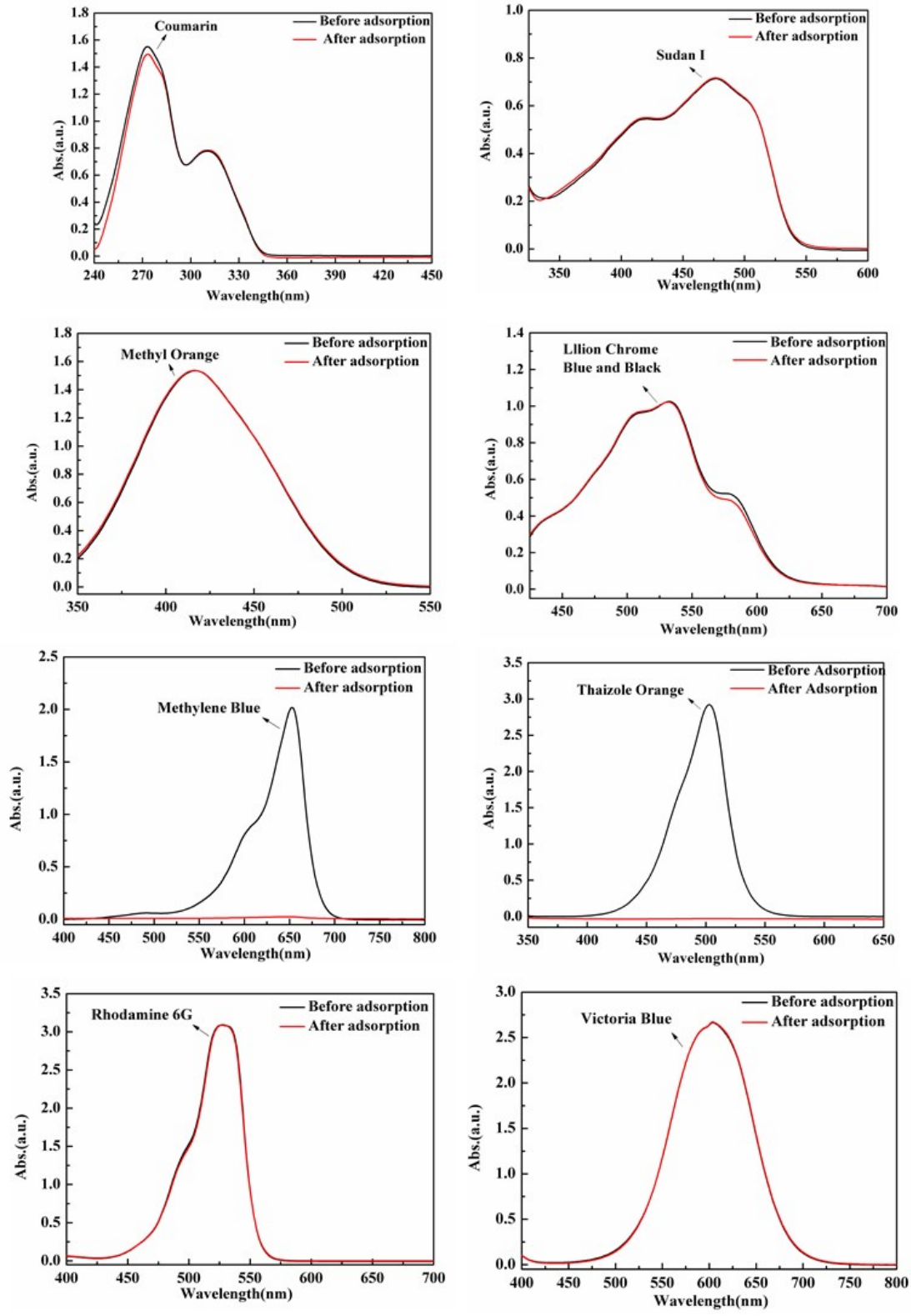

Fig. S11. UV/Vis absorption spectra of the DMF solutions of dyes before (black) and after 24 h adsorption with MOF-**1**.

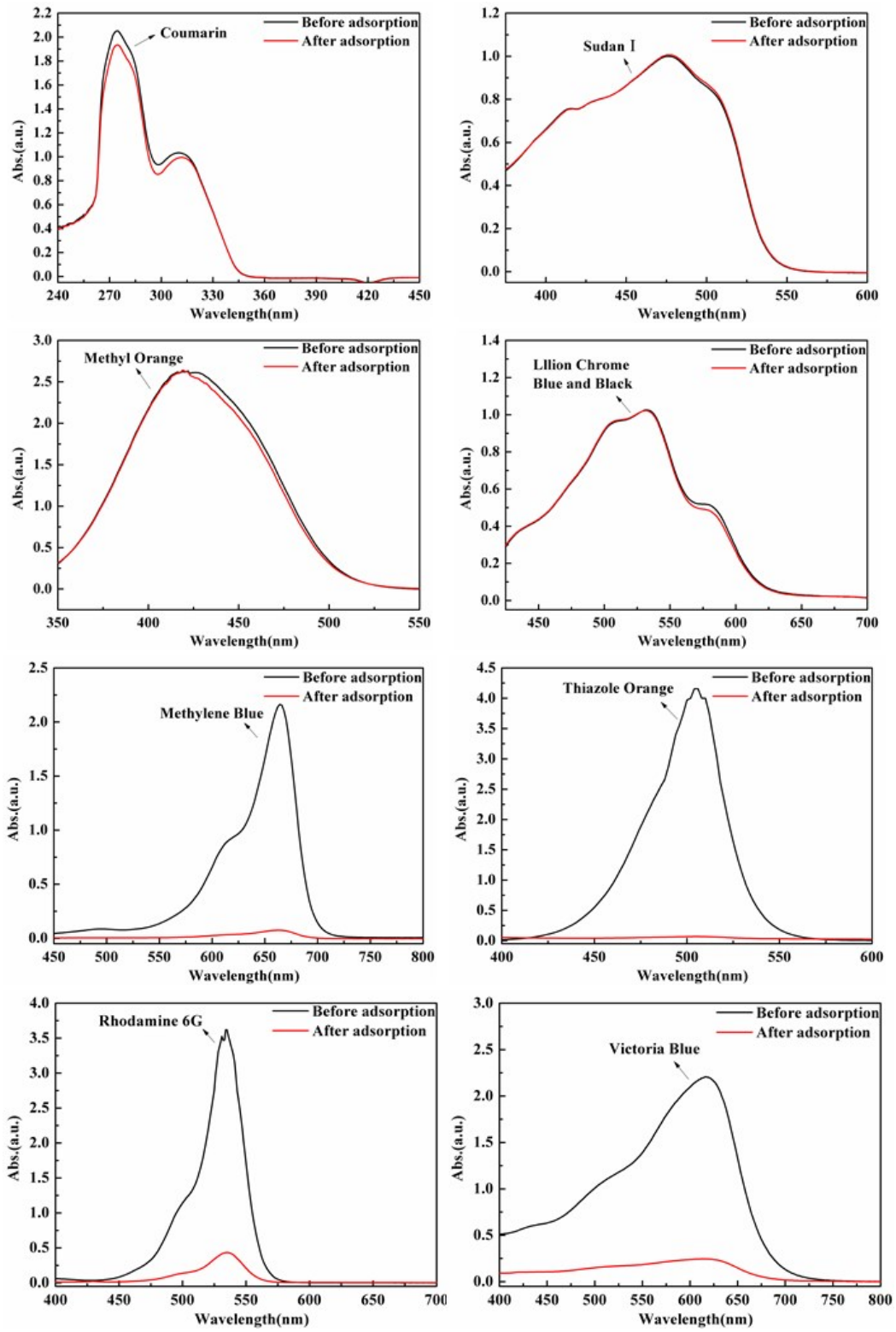

Fig. S12. UV/Vis absorption spectra of the DMF solutions of dyes before (black) and after 24 h adsorption with MOF-**2**.

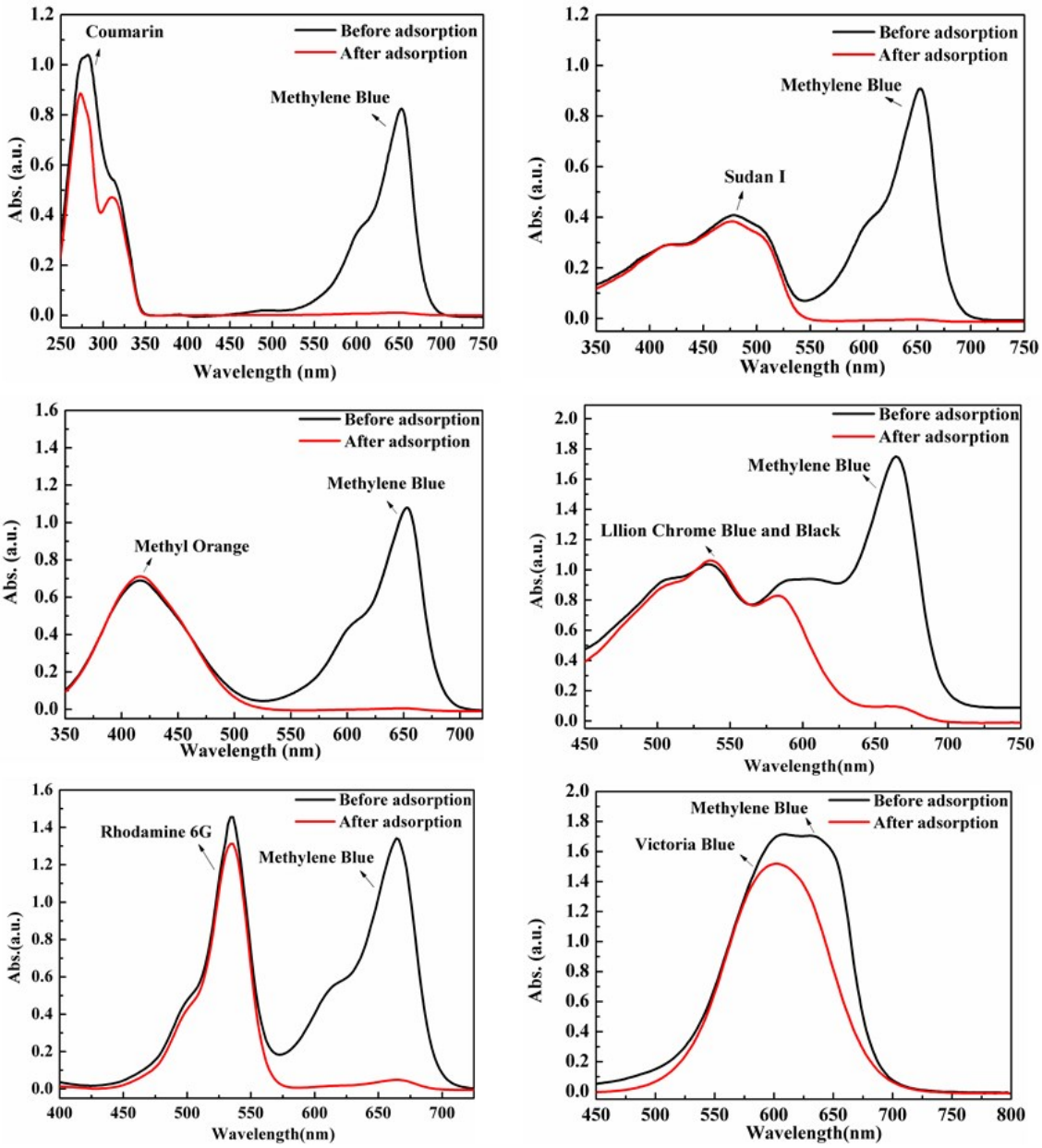

Fig. S13. UV/Vis absorption spectra of the DMF solutions of mixed dyes (MB^+ and other dyes) before (black) and after (red) 24 h adsorption with MOF-**1**.

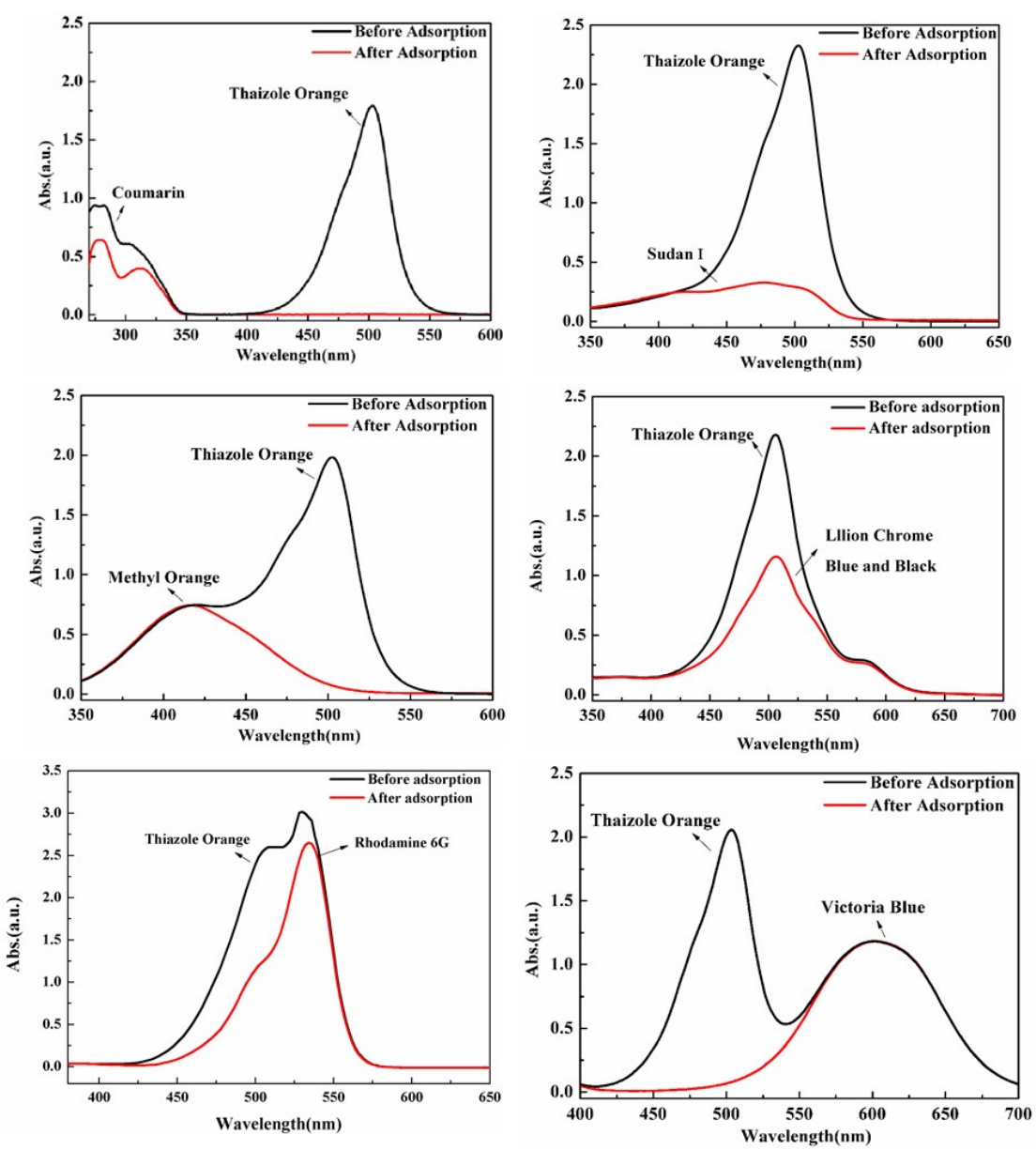

Fig. S14. UV/Vis absorption spectra of the DMF solutions of mixed dyes (TO^+ and other dyes) before (black) and after (red) 24 h adsorption with MOF-**1**.

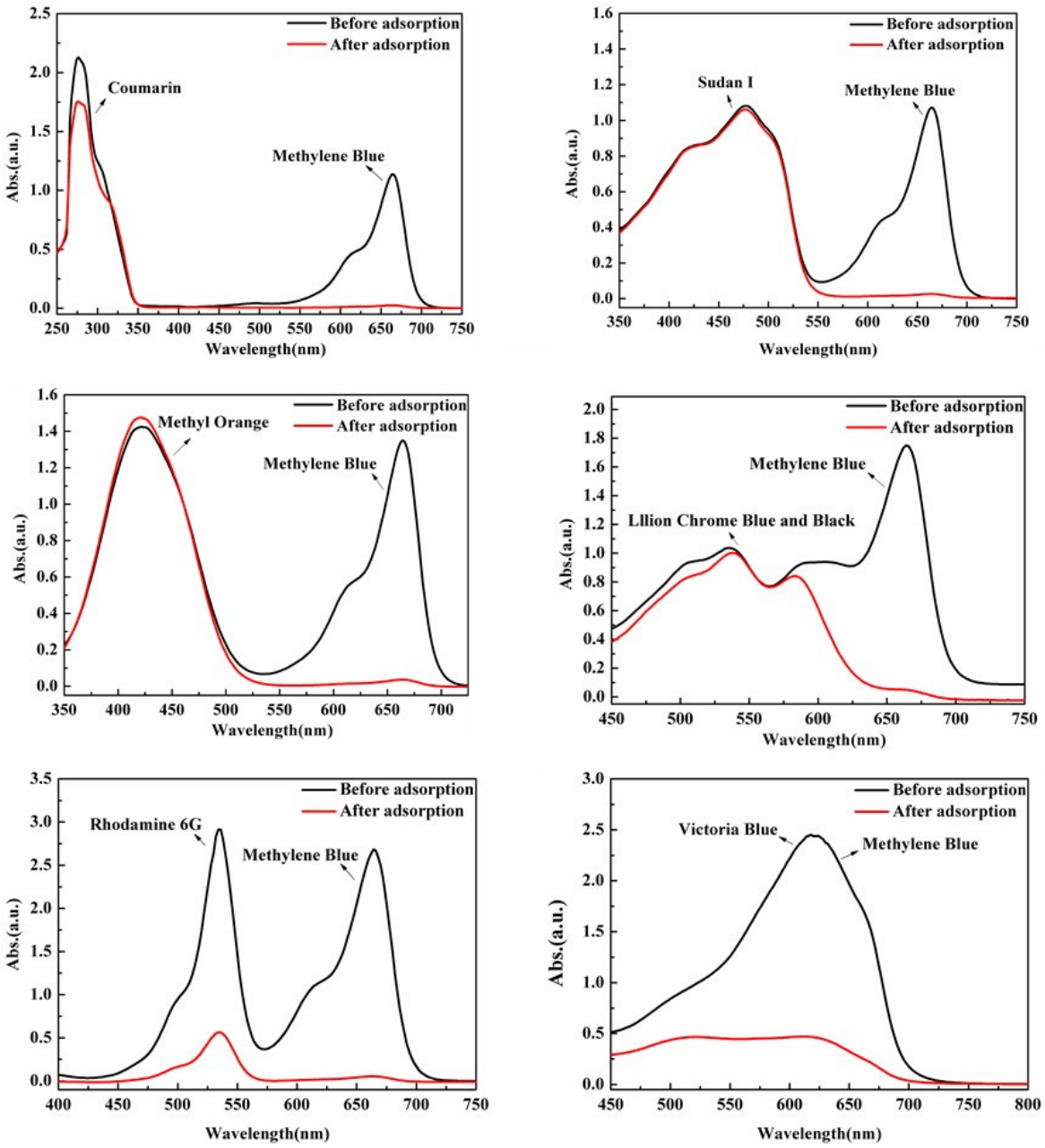

Fig. S15. UV/Vis absorption spectra of the DMF solutions of mixed dyes (MB^+ and other dyes) before (black) and after (red) 24 h adsorption with MOF-**2**.

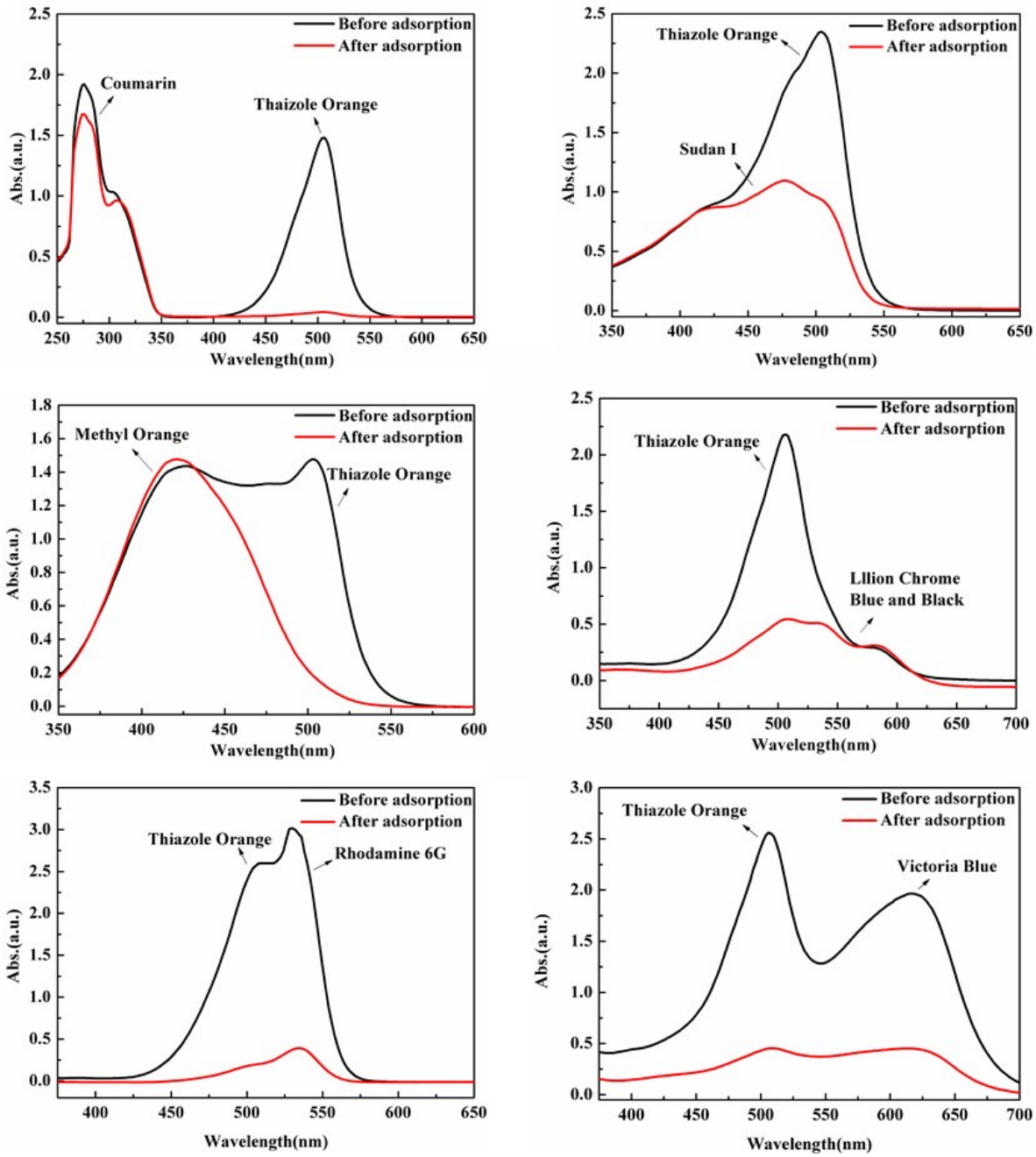

Fig. S16. UV/Vis absorption spectra of the DMF solutions of mixed dyes (TO^+ and other dyes) before (black) and after (red) 24 h adsorption with MOF-**2**.

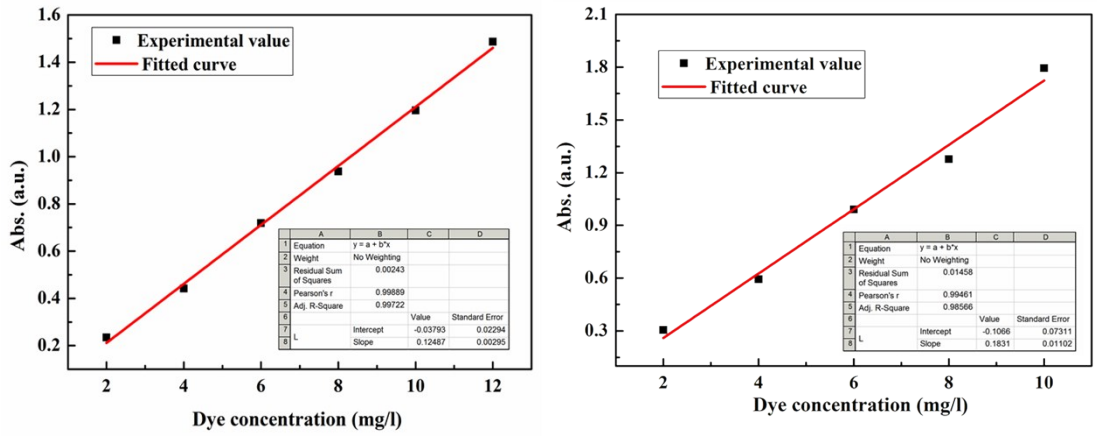

Fig. S17. The calibration curves of MB^+ solution and TO^+ solution.

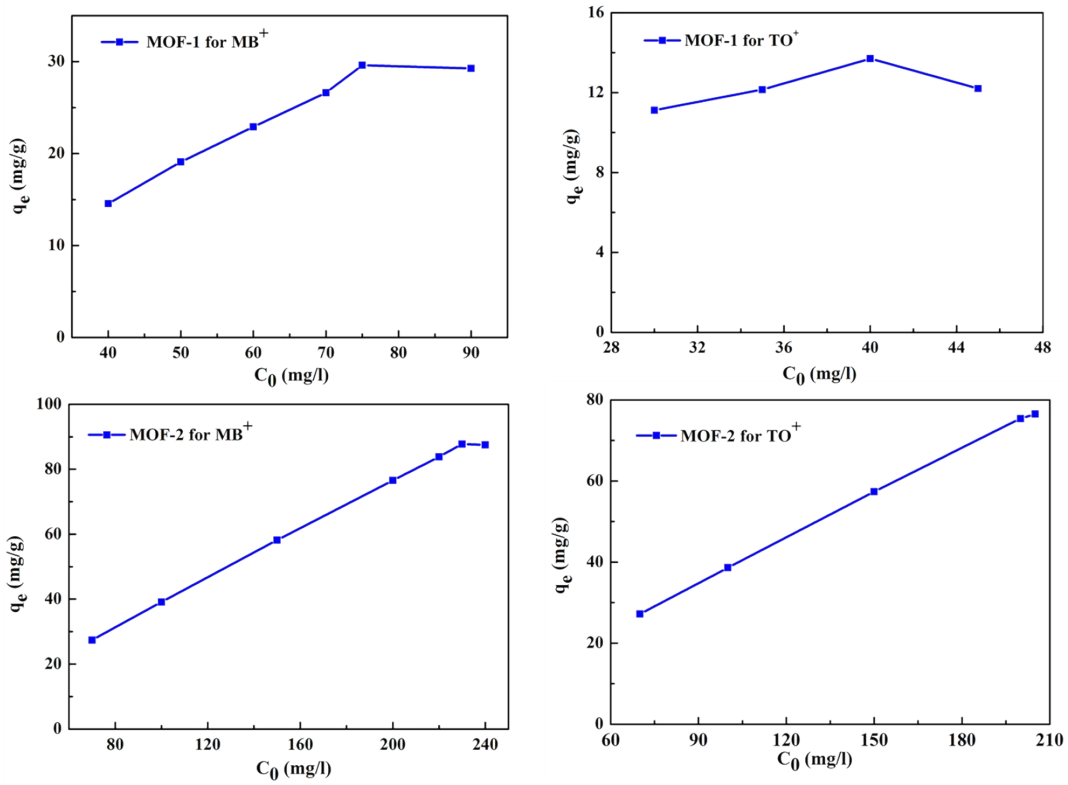

Fig. S18. The q_e-c_0 profile involving adsorption capacity of MB^+ and TO^+ by MOF-**1** and MOF-**2**.

Table S1. Crystal data and refinement details for MOF-**1** and MOF-**2**.

Compound reference	MOF-**1**	MOF-**2**
Chemical formula	$C_{12}H_6N_3O_5Zn$	$C_{22}H_{11}N_5O_7Zn_2$
Formula Mass	337.57	588.10
Crystal system	orthorhombic	trigonal
Space group	*Pbcn*	$P3_221$
Temperature/K	113	273
a/Å	13.338(3)	20.5369(12)
b/Å	23.519(5)	20.5369(12)
c/Å	19.056(4)	34.603(2)
α/°	90	90
β/°	90	90
γ/°	90	120
Unit cell volume/Å^3	5978(2)	12638.9(17)
No. of formula units per unit cell, *Z*	8	6
μ/mm^{-1}	0.833	0.834
F(000)	1352.0	1764.0
Radiation type	Mo Kα	Cu Kα
No. of reflections measured	60840	43126
No. of independent reflections	5874	16091
R_{int}	0.0471	0.0679
Final R_1 values ($I > 2\sigma(I)$)	0.0724	0.0616
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.2159	0.1523
Final R_1 values (all data)	0.0831	0.1171
Final $wR(F^2)$ values (all data)	0.2290	0.1832
Goodness of fit on F^2	1.100	0.860

Table S2. Selected bond lengths [Å] and angles [°] for (MOF-**1**).

Zn1-N1	2.003(3)	Zn1-O1^{i}	1.950(3)
Zn1-O1^{iii}	1.950(3)	Zn1-N1^{iv}	2.003(3)
Zn2-N2	1.987(3)	Zn2-N2^{iv}	1.987(3)
Zn2-O4^{v}	1.969(4)	Zn2-O4^{vi}	1.969(4)
O1-C12	1.272(5)	O2-C12	1.229(5)
O3-C11	1.250(7)	O4-C11	1.243(7)
O5-C4	1.217(6)	N1-N2	1.366(4)
N1-C1	1.340(5)	N2-C3	1.333(5)
N3-C4	1.346(5)	N3-C5	1.422(6)
C1-C2	1.384(5)	C2-C3	1.406(5)
C2-C4	1.466(6)	C5-C6	1.384(7)
C5-C10	1.366(7)	C6-C7	1.397(6)
C7-C8	1.388(6)	C7-C12	1.505(7)
C8-C9	1.399(8)	C9-C10	1.381(7)
N3-H3A	0.86	C1-H1	0.93
C3-H3	0.93	C6-H6	0.93
C8-H8	0.93	C10-H10	0.93
C9-C11	1.483(7)		
N1-Zn1-O1^{i}	111.22(11)	O1^{i}-Zn1-O1^{iii}	118.66(11)
O1^{i}-Zn1-N1^{iv}	103.28(11)	N2-Zn2-O4^{v}	102.72(13)
N2-Zn2-O4^{vi}	119.00(15)	O4^{v}-Zn2-O4^{vi}	104.06(17)
C12-O1-Zn1^{ii}	114.7(3)	Zn1-N1-C1	127.0(2)
N2-N1-C1	107.6(3)	N1-N2-C3	109.1(3)
C4-N3-C5	128.3(4)	C1-C2-C4	126.1(3)
C3-C2-C4	129.3(3)	O5-C4-C2	121.2(4)
N3-C4-C2	116.5(4)	C6-C5-C10	120.4(4)
C5-C6-C7	119.3(4)	C8-C7-C12	120.3(4)
C7-C8-C9	119.6(4)	C10-C9-C11	119.8(5)
C5-C10-C9	121.3(5)	O4-C11-C9	117.3(5)
O1-C12-O2	124.0(4)	C4-N3-H3A	116
C5-N3-H3A	116	N2-C3-H3	126
C2-C3-H3	126	C7-C8-H8	120
C9-C8-H8	120		

Symmetry codes: (i) 1/2-x, 1/2-y, -1/2+z; (ii) -1/2-x, 1/2-y, 1/2+z; (iii) 1/2+x, 1/2-y, -z; (iv) 1-x, y, -1/2-z; (v) 1-x, 1-y, -z; (vi) x, 1-y, -1/2+z.

Table S3. Selected bond lengths [Å] and angles [°] for (MOF-**2**).

Zn1-O2	1.923(5)	Zn1-N5^{i}	1.937(8)
Zn1-N2^{viii}	2.004(5)	Zn1-O6^{v}	1.906(7)
Zn2-O5	2.640(6)	Zn2-O4	1.924(5)
Zn2-O7^{iv}	1.999(5)	Zn2-N4	1.999(7)
O1-C4	1.265(12)	Zn2-N1^{vi}	1.876(10)
O3-C11	1.231(10)	O2-C11	1.288(10)
O5-C12	1.225(13)	O4-C12	1.359(11)
O7-C22	1.210(9)	O6-C22	1.297(13)
N1-C1	1.382(9)	N1-N2	1.423(8)
N3-C4	1.322(13)	N2-C3	1.343(11)
N4-N5	1.441(9)	N3-C5	1.316(10)
N5-C13	1.353(13)	N4-C15	1.307(14)
C2-C3	1.422(10)	C1-C2	1.483(10)
C5-C6	1.516(11)	C2-C4	1.402(13)
C6-C7	1.270(13)	C5-C10	1.423(13)
C7-C11	1.503(12)	C7-C8	1.433(13)
C9-C10	1.398(13)	C8-C9	1.395(12)
C13-C14	1.266(16)	C9-C12	1.463(12)
C14-C16	1.455(16)	C14-C15	1.357(11)
C16-C21	1.405(15)	C16-C17	1.419(13)
C18-C19	1.298(14)	C17-C18	1.347(17)
C19-C22	1.507(17)	C19-C20	1.425(12)
C1-H1	0.93	C20-C21	1.373(18)
C6-H6	0.93	C3-H3	0.93
C10-H10	0.93	C8-H8	0.93
C15-H15	0.93	C13-H13	0.93
C18-H18	0.93	C17-H17	0.93
C21-H21	0.93	C20-H20	0.93
O2-Zn1-N5^{i}	124.3(3)	O2-Zn1-O6^{v}	111.2(3)
O2-Zn1-N2^{viii}	102.1(2)	N5^{i}-Zn1-O6^{v}	107.3(3)
N5^{i}-Zn1-N2^{viii}	104.6(3)	O6^{v}-Zn1-N2^{viii}	105.5(4)
O4-Zn2-O5	56.2(2)	O4-Zn2-N4	112.2(3)
O4-Zn2-O7^{iv}	102.9(2)	O4-Zn2-N1^{vi}	127.0(2)
O5-Zn2-N4	89.7(3)	O5-Zn2-O7^{iv}	158.7(2)
O5-Zn2-N1^{vi}	88.6(3)	N4-Zn2-O7^{iv}	103.9(2)

N4-Zn2-N1^{vi}	105.0(4)	O7^{iv}-Zn2-N1^{vi}	103.3(4)
Zn1-O2-C11	113.1(5)	Zn2-O4-C12	106.0(5)
Zn2-O5-C12	76.8(5)	C22-O6-Zn1^{v}	128.5(6)
C22-O7-Zn2^{iii}	137.1(8)	N2-N1-C1	101.2(6)
N2-N1-Zn2^{vii}	118.7(4)	C1-N1-Zn2^{vii}	140.1(5)
N1-N2-C3	112.5(5)	N1-N2-Zn1^{viii}	117.4(5)
C3-N2-Zn1^{viii}	129.6(4)	C4-N3-C5	127.7(8)
Zn2-N4-N5	115.9(6)	Zn2-N4-C15	135.9(6)
N5-N4-C15	108.2(6)	N4-N5-C13	100.1(7)
N4-N5-Zn1^{ii}	118.8(5)	C13-N5-Zn1^{ii}	140.9(6)
N1-C1-C2	115.1(6)	C1-C2-C3	99.0(6)
C1-C2-C4	126.9(7)	C3-C2-C4	134.2(8)
N2-C3-C2	111.9(6)	O1-C4-N3	121.8(9)
O1-C4-C2	122.5(9)	N3-C4-C2	115.5(8)
N3-C5-C6	119.9(7)	N3-C5-C10	127.1(8)
C6-C5-C10	112.5(7)	C5-C6-C7	124.0(8)
C6-C7-C8	120.9(8)	C6-C7-C11	121.0(8)
C8-C7-C11	117.9(8)	C7-C8-C9	120.3(8)
C8-C9-C10	118.4(8)	C8-C9-C12	118.7(8)
C10-C9-C12	122.9(8)	C5-C10-C9	123.9(8)
O2-C11-O3	124.6(8)	O2-C11-C7	114.1(7)
O3-C11-C7	121.3(7)	O4-C12-O5	120.3(8)
O4-C12-C9	112.2(8)	O5-C12-C9	126.5(8)
N5-C13-C14	116.2(7)	C13-C14-C15	105.5(9)
C13-C14-C16	130.0(8)	C15-C14-C16	124.5(9)
N4-C15-C14	110.0(8)	C14-C16-C17	124.1(10)
C14-C16-C21	123.2(8)	C17-C16-C21	112.6(10)
C16-C17-C18	125.6(11)	C17-C18-C19	121.6(9)
C18-C19-C20	116.9(10)	C18-C19-C22	123.3(8)
C20-C19-C22	119.8(9)	C19-C20-C21	122.6(11)
C16-C21-C20	120.6(9)	O6-C22-O7	124.7(11)
O6-C22-C19	118.6(7)	O7-C22-C19	116.7(10)
N1-C1-H1	122	C2-C1-H1	122
N2-C3-H3	124	C2-C3-H3	124
C5-C6-H6	118	C7-C6-H6	118
C7-C8-H8	120	C9-C8-H8	120

C5-C10-H10	118	C9-C10-H10	118
N5-C13-H13	122	C14-C13-H13	122
N4-C15-H15	125	C14-C15-H15	125
C16-C17-H17	117	C18-C17-H17	117
C17-C18-H18	119	C19-C18-H18	119
C19-C20-H20	119	C21-C20-H20	119
C16-C21-H21	120	C20-C21-H21	120

Symmetry codes: (i) 1-y, 1+x-y, -1/3+z; (ii) -x+y, 1-x, 1/3+z; (iii) -1+y, x, 1-z; (iv) y, 1+x, 1-z; (v) -x, -x+y, 2/3-z; (vi) 1-x, -x+y, 2/3-z; (vii) 1-x, 1-x+y, 2/3-z; (viii) 1+x-y, 2-y, 1/3-z.

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