ESI

Supporting Information

Polyoxometalates-based Heterometallic Organic-Inorganic Hybrid Materials for Rapid Adsorption and Selective Separation of Methylene Blue from Aqueous Solution

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Supplementary Index

1. Experimental Section

1.1. Materials and Methods

$K_8[\alpha\text{-}SiW_{11}O_{39}]\bullet 13H_2O$ was prepared according to the previous reports.[1] All other reagents and solvents were obtained from commercial sources without further purification.

Powder X-ray diffraction (PXRD) data were performed on a Rigaku/max 2550 diffractometer with Cu Kα radiation Field-emission (λ = 1.5418 Å, continuous, 40 kV, 40 mA, increment = 0.02°). The infrared (IR) spectra (diamond) were recorded on a Nicolet 7600 FT-IR spectrometer within the 4000-500 cm^{-1} region. TGA (thermal gravimetric analysis) was recorded under an air atmosphere with a heating rate of 10 °C/min using a a SDT 2960 Simultaneous DSC-TGA of TA instrument in the temperature range of 23-800 °C. UV−vis spectroscopic studies were collected on a UV-2450 spectrophotometer. The elemental analyses (EA) of C, H, N, S in the solid samples were carried out on a VarioEL analyzer (Elementar Analysensysteme GmbH). The metal Cu and K ions in the solution were analyzed via inductively coupled plasma (ICP) atomic emission spectrometric analysis (POEMS, TJA).

1.2 Syntheses of LnCu-POMs (1-4)

Compounds **1** and **4** were prepared by similar procedure. A mixture of $K_8[\alpha\text{-}SiW_{11}O_{39}]\bullet 13H_2O$ (150 mg), $CuCl_2\bullet 2H_2O$ (68 mg), $LnCl_3\bullet 6H_2O$ (90 mg) (Ln = Dy, **1**; Er, **4**) and en (**1**) or DETA (**4**) were dissolved in distilled water (10 mL) at room temperature. After stirring for 30 min, the suspension was placed into a 20 mL Teflon-lined stainless-steel container and heated at 150 °C for 5 days. After slow cooling to room temperature, blue-purple plate crystals were filtered, washed with distilled water, and dried in fume hood at room temperature to give a yield of 73% for **1** (based on W) $C_{16}H_{111}Cu_4Dy_2K_2N_{16}O_{101.5}Si_2W_{22}$ (*F*w = 6910.45): calcd. (%) C, 2.78; H, 1.62; N, 3.24; found (%) C, 2.59; H, 1.65; N, 3.21; and 60% for **4** (based on W) $C_{16}H_{77}CuErN_{12}O_{85}Si_2W_{22}$ (*F*w = 6129.58) calcd. (%) C, 3.14; H, 1.27; N, 2.74; found (%) C, 3.11; H, 1.50; N, 2.66. IR data (diamond, cm^{-1}) for **1**: 3441 (m), 3307 (s), 3253 (s), 2951 (w), 2891 (w), 1582 (s), 1458 (w), 1394 (w), 1367 (w), 1323 (w), 1281 (w), 1173 (w), 1097 (m), 1044 (m), 994 (m), 936 (m), 860 (m), 753 (m), 683 (m). IR data (diamond, cm^{-1}) for **4**: 3441 (m), 3307 (s), 3278 (s), 3140 (w), 2957 (w), 2891 (w), 2159 (w), 1582 (s), 1458 (m), 1394 (w), 1367 (w), 1323 (w), 1275 (m), 1167 (w), 1103 (m), 1038 (m), 994 (m), 942 (m), 876 (s), 757 (m), 671 (m).

When oxalic acid ($H_2C_2O_4$) was respectively added in the reaction mixtures used for **Dy-1** with en and **Dy-4** with DETA, blue-purple prism crystals of **Dy-2** and **Er-3** were obtained replacing **Dy-1** and **Er-4**, respectively. $C_{26}H_{126}Cu_6Er_2N_{24}O_{97}Si_2W_{22}$ (*F*w = 7144.15) calcd. (%) C, 4.37; H, 1.78; N, 4.71; found (%) C, 4.58; H, 1.49; N, 4.86. IR data (diamond, cm^{-1}) for **Dy-2**: 3550 (w), 3457 (m), 3307 (s), 3253 (s), 3146 (w), 2945 (w), 2881 (w), 2159 (w), 1653 (s), 1588 (s), 1458 (m), 1394 (w), 1361 (w), 1323 (w), 1275 (w), 1167 (w), 1097 (m), 1032 (m), 994 (m), 946 (m), 867 (s), 769

(m), 671 (m). IR data (diamond, cm^{-1}) for **Er-3**: 3550 (w), 3457 (m), 3302 (s), 3248 (s), 3146 (w), 3951 (w), 2887(w), 2159 (w), 1658 (m), 1576 (m), 1458 (m), 1399 (w), 1361 (w), 1319 (w), 1281 (w), 1173 (w), 1097 (w), 1038 (m),994 (m), 866 (s), 769 (m), 671 (m), 537 (w).

1.3 Dye absorption, separation and release

Dye absorption: Freshly prepared **Dy-1**, **Dy-2**, **Er-3** and **Er-4** samples with various qualities (1 mg, 2 mg, 5 mg, 8 mg and 10 mg) were trasferred into the aqueous solution of methylene blue (MB), methyl organge (MO), rhodamine-B (RhB) and Basic Red 2 (BR2) (20 mg/L) with 20 mL, respectively. After soaking for 24 h, the samples were separated through centrifuge to remove the suspended particle. Then the upper clear solutions were analyzed by a UV-vis spectrophotometer. Similarly, dye absorption for **1-4** towards aqueous solution of MB dye after given time intervals were prepared that freshly prepared **1-4** were dispersed in aqueous solution of MB (20 mL, 20 mg/L) for a regular interval time, then UV-vis spectra were also used to determine the adsorption of **1-4** after centrifuge.

Dye separation: Compounds **Dy-1**, **Dy-2**, **Er-3** and **Er-4** were transferred into the mixtures (20 mL) of MB and RhB, MB and MO (*v*:*v* 1/1, 20 mg/L), respectively. At given time intervals, UV-vis spectra were measured to analysis the selective adsorption ability of **1-4**.

Dye release: the **Dy-1**, **Dy-2**, **Er-3** and **Er-4** loaded with MB were activated with a mixed solvent EtOH/H_2O (*v*:*v* 1:1) of NaCl at room temperature, respectively. The regenerated **Dy-1** sample was dried overnight at 80 °C and reused for the next adsorption. The MB solution from MB@Dy-1 in other various solutions have also been used to monitor the release process in UV-vis spectra, such as pure water, pure ethanol solvent, the aqueous solution of NaCl, as well as the mixed solvents of NaCl with ethanol and water for different volume ratio (1:9 and 9:1).

1.4 Single Crystal X-ray structure determination

Single crystals of **1**, **3** and **4** were selected for indexing and data collection on a Bruker Apex II CCD diffractometer with graphite monochromated Mo-K*a* radiation (λ = 0.71073 Å) at 296 K. Data processing was accomplished with the SAINT program. All absorption corrections were applied using the multi-scan program SADABS.[2] All structures were solved by direct methods using SHELXS-97 program of the SHELXTL package and refined by the full-matrix least squares method with SHELXTL-97.[3] All non-hydrogen atoms were easily found from the difference Fourier map and refined using the full-matrix least-squares method on F^2 with anisotropic thermal parameters during the final cycles except of some disordered oxygen and carbon atoms, as follows. The positions of the hydrogen atoms attached to the carbon and nitrogen atoms were refined isotropically as a riding mode. The hydrogen atoms attached to water molecules were not located in all compounds and just put into the final molecular formula. The occupancy factors of O(48), O(3W) and O(15W) in **Dy-1** as well as O(9W) and O(10W) in **Er-4** were reduced to 50% because

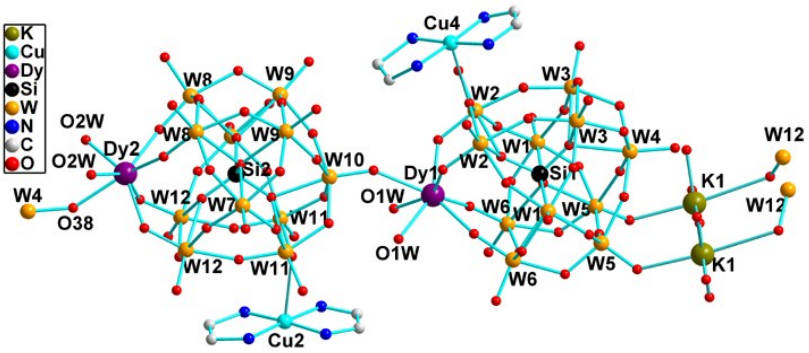
of their large thermal parameters. The program SQUEEZE in PLATON was used to calculate the solvent area and remove their contribution to the overall intensity data in **Dy-1** and **Er-4**. See the CIF file for details. Crystallographic data for **1**, **3** and **4** is summarized in Table S1. Selected bond distances are given in Table S3. The BVS values of all Er, W and O atoms except the lattice water molecules in **Er-4** are listed in Table S2.

Because most of POMs-structures are larger than simple coordination complexes and there are a large amount of weight atoms in their structures, it is very difficult to refine these large structures. Moreover, the quality of crystals are not very good, which usually leads to the case that the quality of intensity data is not perfect, as a result, some atoms have the ADP max/min ratios. Therefore, some disordered atoms have been isotropically refined.

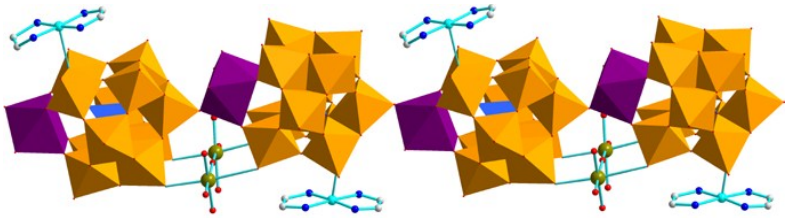
1: The ISOR instruction is used for C1, C2, N8, O17, O22, O23, O36, O38, O48, O58, O29, and O11W.

3: The ISOR instruction is used for Si1, C2, O8, O20, O26, O67, O76, and O6W.

4: The ISOR instruction is used for O53.



(a)



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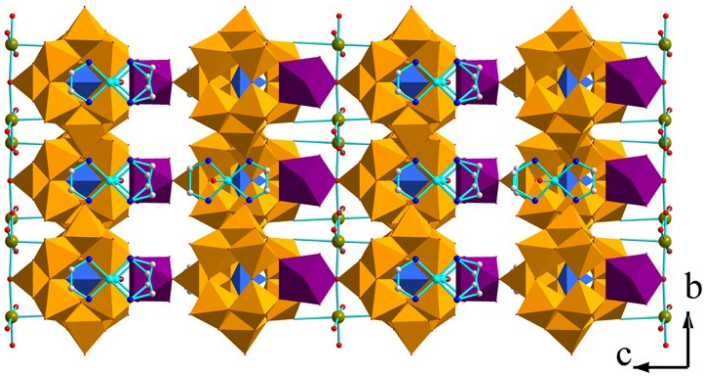


(c)

Fig. S1 (a) Representation of the molecular structure unit of **Dy-1**. The hydrogen atoms, discrete $[Cu(H_2O)(en)_2]^{2+}$ ions, and crystal water molecules are omitted for clarity. (b) The polyhedral view of 1D chain LnCu-POMs of **Dy-1**. (c) The 3D supramolecular architecture along the [100] direction. WO_6 octahedra, gold; SiO_4 tetrahedra, blue; DyO_7 polyhedra, purple; K, dark yellow sphere; C, grey sphere; N, dark blue spheres.

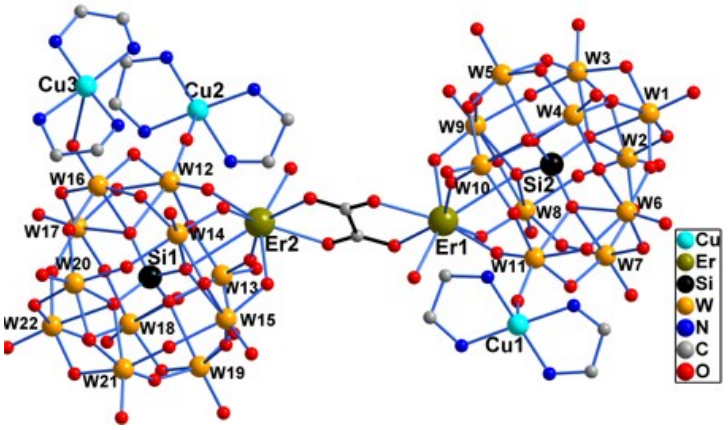
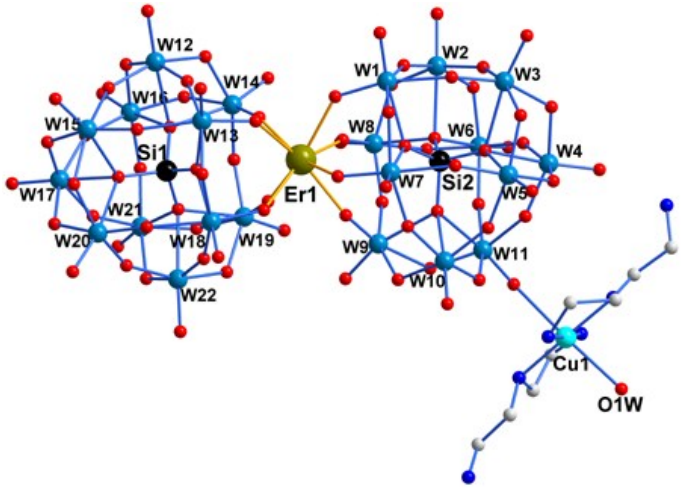
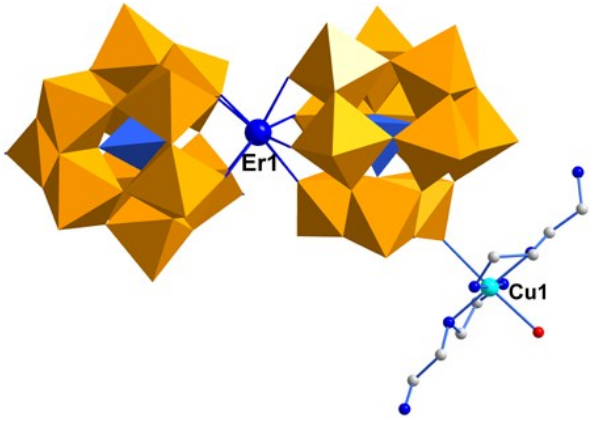


Fig. S2 Representation of the molecular structure unit of **Er-3 (Dy-2)**. The hydrogen atoms, discrete $[Cu(H_2O)(en)_2]^{2+}$ ions, and crystal water molecules are omitted for clarity.



(a)



(b)

Fig. S3 (a) Representation of the molecular structure unit of **Er-4**. The hydrogen atoms, DETA

molecules, and crystal water molecules are omitted for clarity. (b) The polyhedral view of the dimer of **Er-4**.

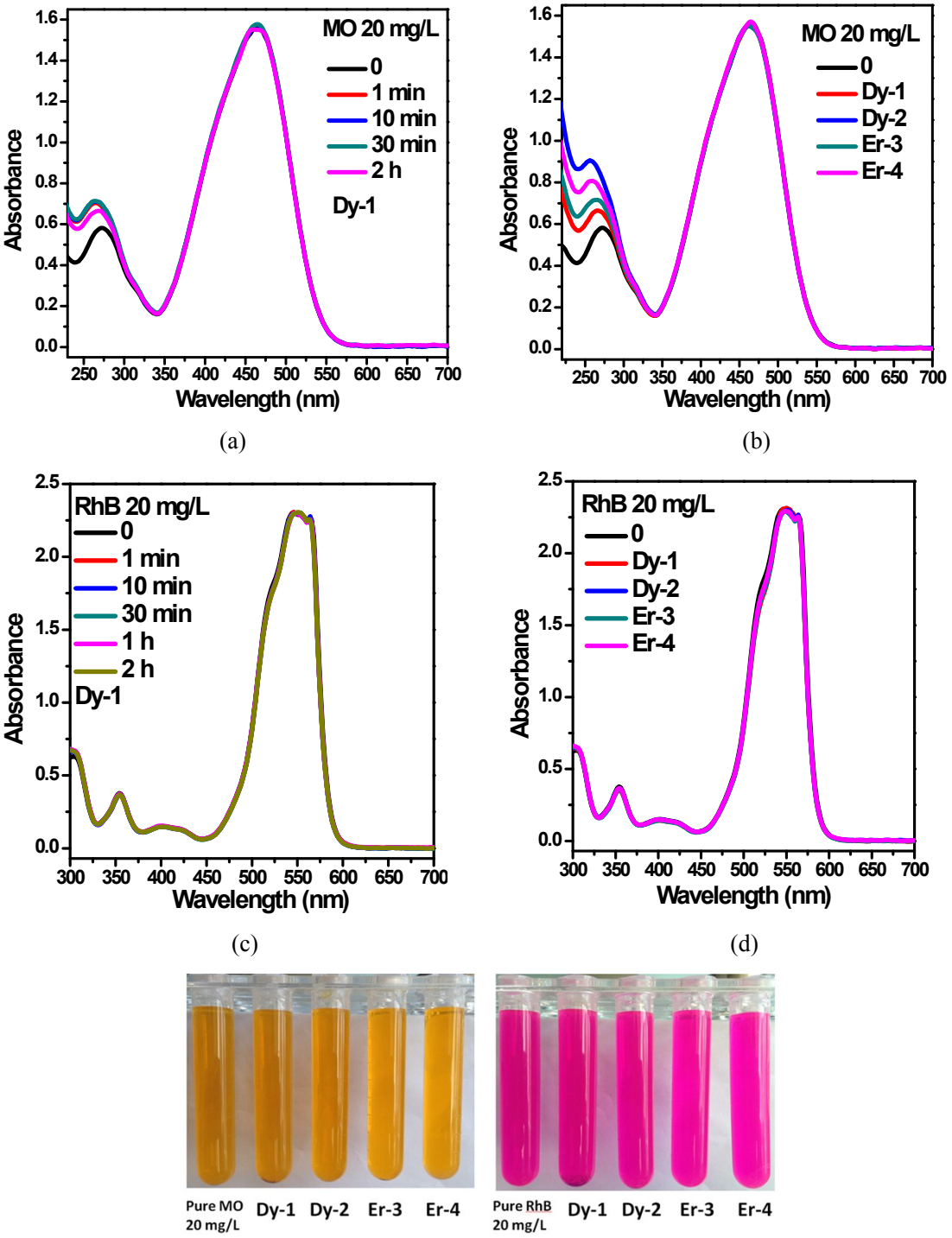
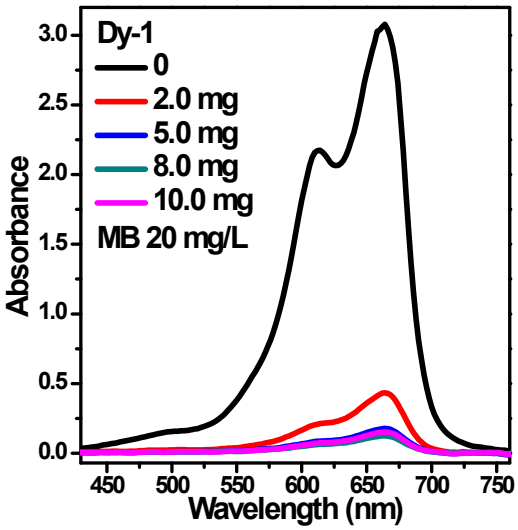
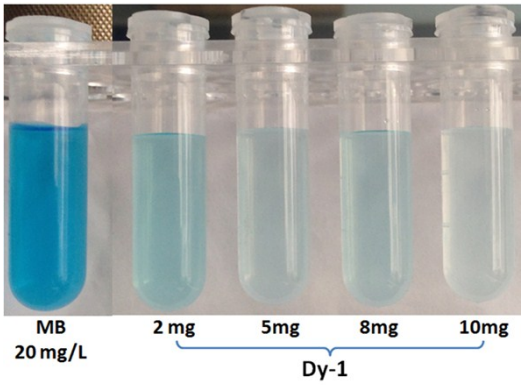
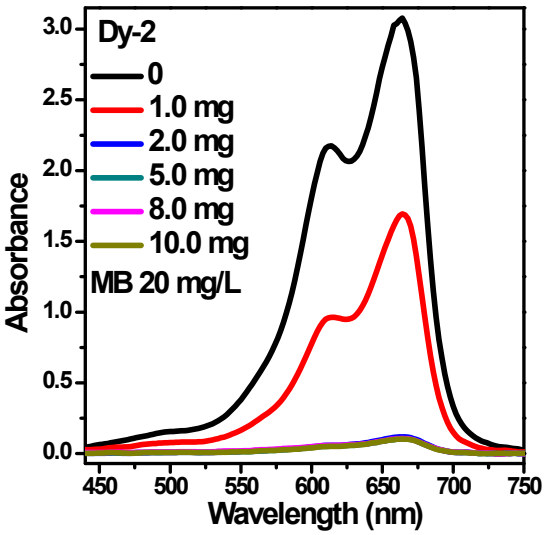
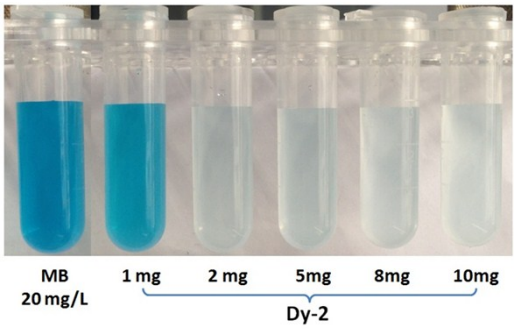


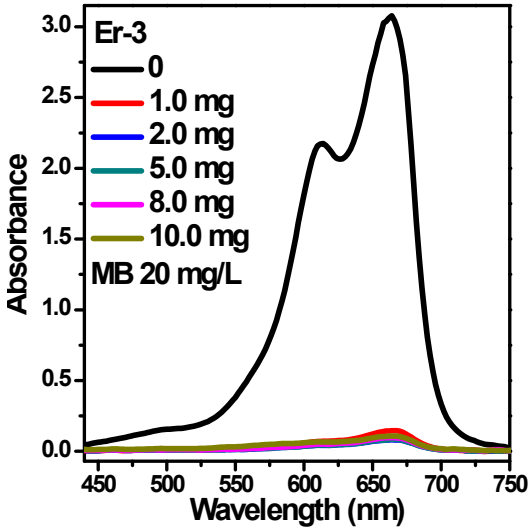
Fig. S4 UV-vis spectra and photographs of aqueous solution of MO (20 mg/L) and RhB (20 mg/L) dyes with **Dy-1** after immersing different time (a and c), as well as with **Dy-1**, **Dy-2**, **Er-3** and **Er-4** (5 mg) after immersing for 24 h.

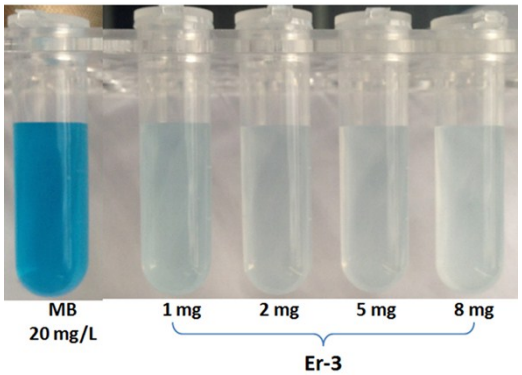

Dy-1
0
2.0 mg
5.0 mg
8.0 mg
10.0 mg
MB 20 mg/L
Absorbance
Wavelength (nm)


MB
20 mg/L
2 mg
5mg
8mg
10mg
Dy-1


Dy-2
0
1.0 mg
2.0 mg
5.0 mg
8.0 mg
10.0 mg
MB 20 mg/L
Absorbance
Wavelength (nm)


MB
20 mg/L
1 mg
2 mg
5mg
8mg
10mg
Dy-2


Er-3
0
1.0 mg
2.0 mg
5.0 mg
8.0 mg
10.0 mg
MB 20 mg/L
Absorbance
Wavelength (nm)


MB
20 mg/L
1 mg
2 mg
5 mg
8 mg
Er-3

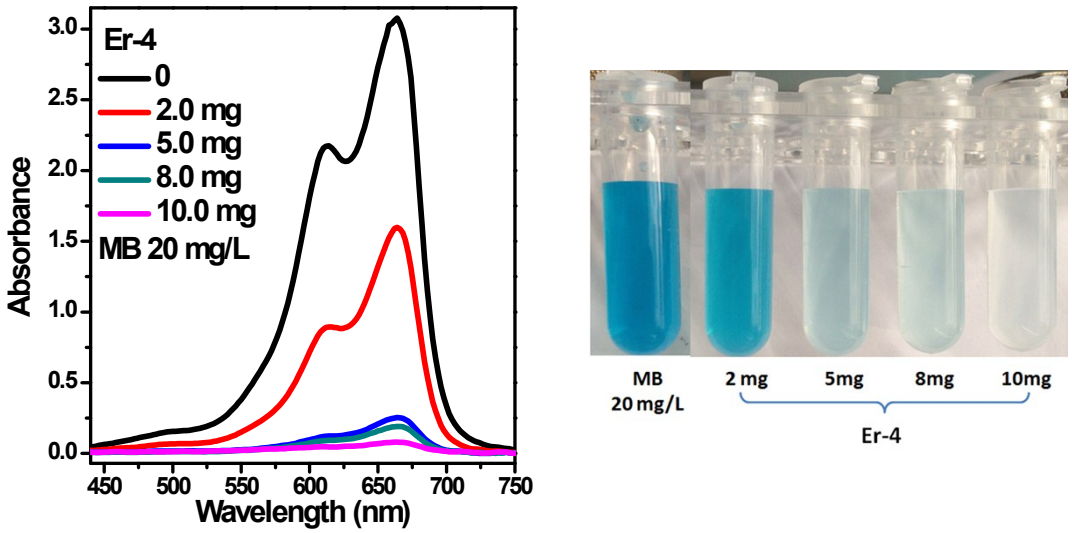


Fig. S5 **Dy-1**, **Dy-2**, **Er-3** and **Er-4** were used to adsorb MB (20 mg/L, 20 mL) in aqueous solution with different quality (mg), as well as the related contrastive photographs of dye solutions before (MB, 20 mg/L) and after with different quality of **1-4**.

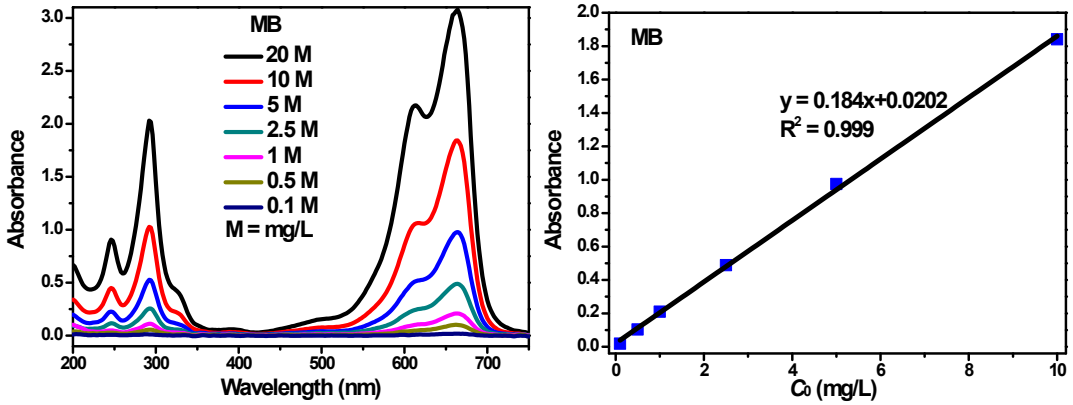
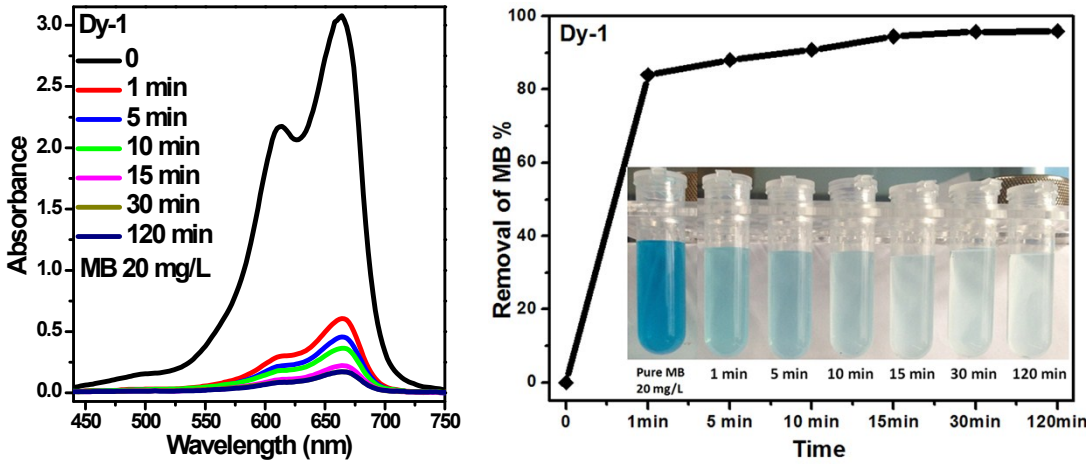
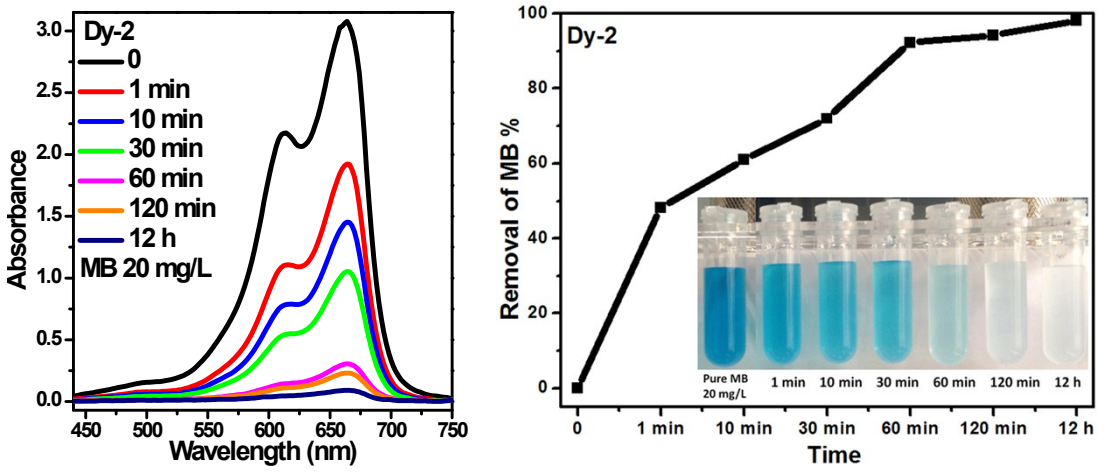


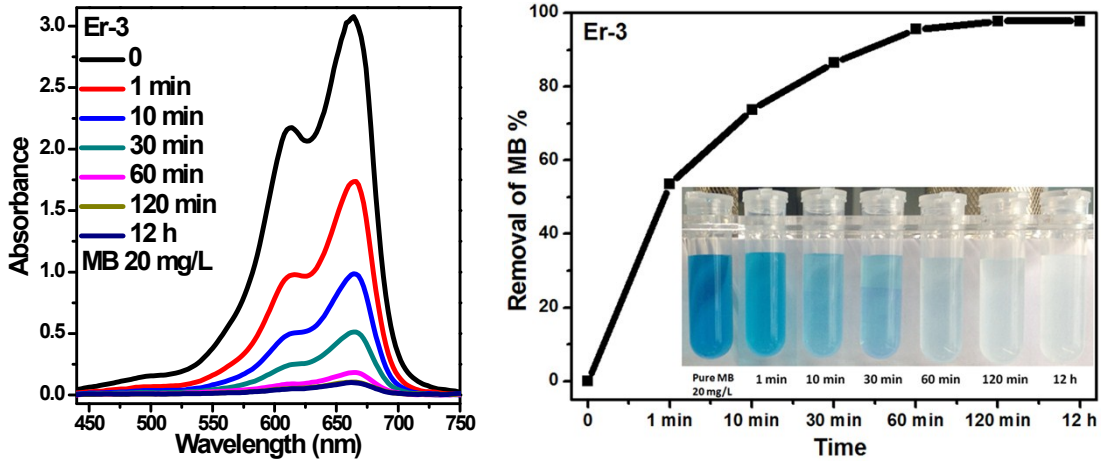
Fig. S6 (a) UV-vis spectra of aqueous solutions of MB dye with different concentrations. (b) The absorbed intensity (blue dots) of MB dye in different concentrations (C_0 = mg/L). The black solid line is the best linear fit.



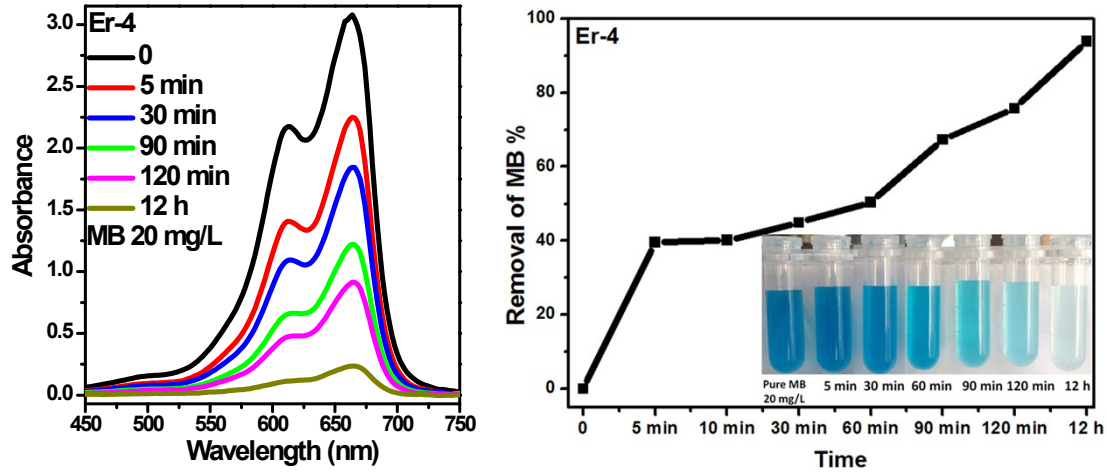
(a) (b)



(c) (d)



(e) (f)



(g) (h)

Fig. S7 (a, c, e and g) The UV-vis spectra of the adsorption rate with **Dy-1**, **Dy-2**, **Er-3** and **Er-4** (5.0 mg) towards MB (20 mg/L, 20 mL). (b, d, f and h) The corresponding removal efficiency on the MB dye for **1-4**. Insert: the comparative photographs after different adsorbed time.

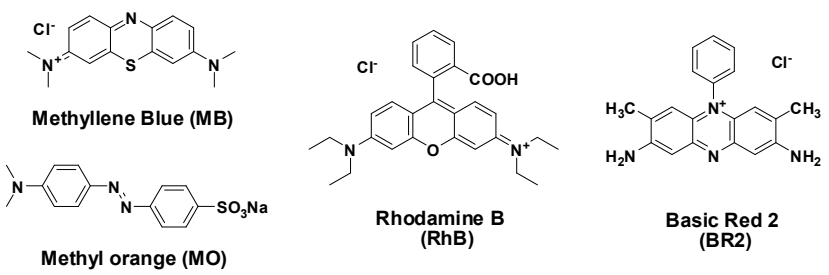


Fig. S8 The structures of dyes, MB, MO, RhB, and BR2.

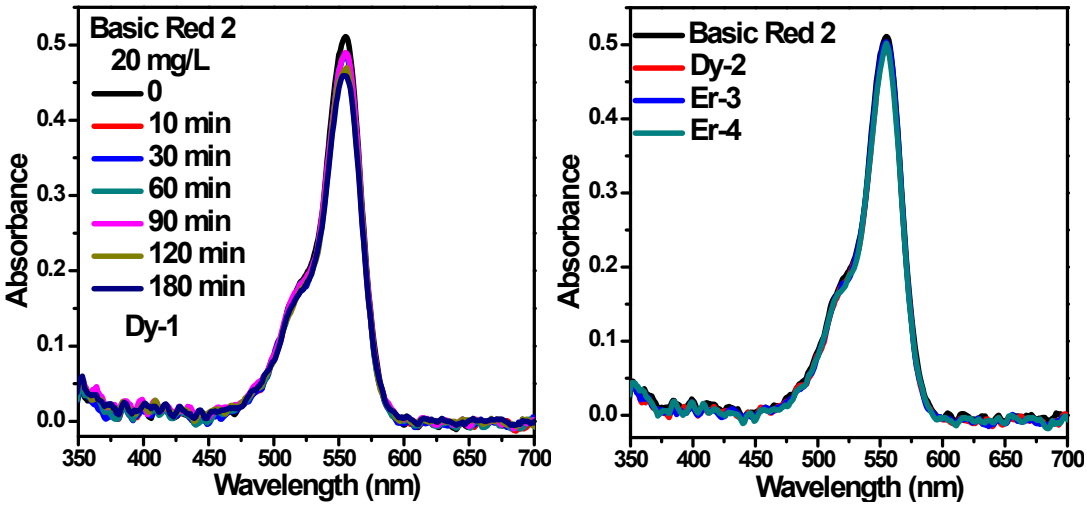
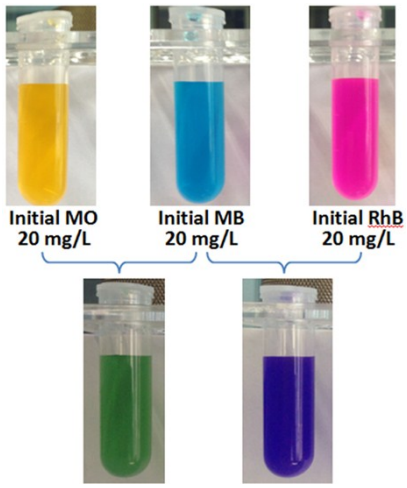
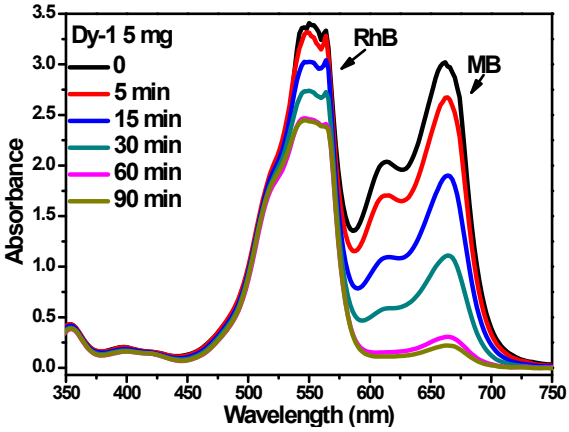


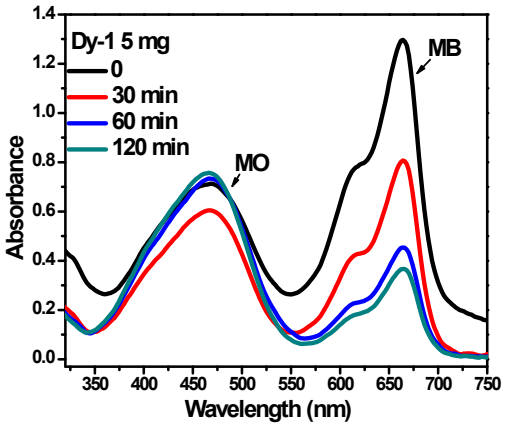
Fig. S9 UV-vis spectra of aqueous solution of BR2 (20 mg/L) dye with **Dy-1** (5 mg) after immersing different time, as well as with **Dy-2**, **Er-3** and **Er-4** (5 mg) after immersing for 24 h.



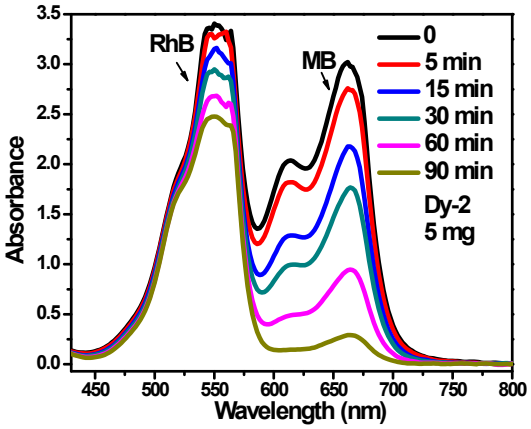
(a)


Dy-1 5 mg
0
5 min
15 min
30 min
60 min
90 min
RhB
MB
Absorbance
Wavelength (nm)

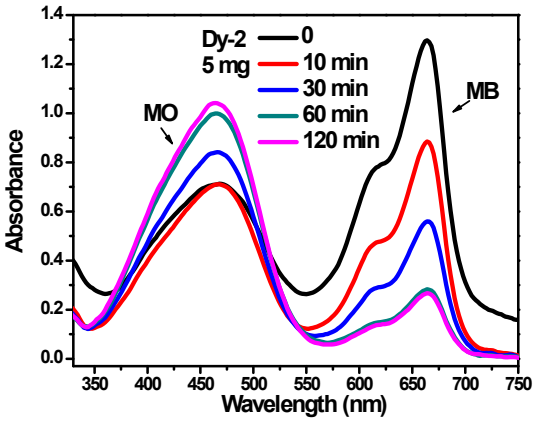
(b)


Dy-1 5 mg
0
30 min
60 min
120 min
MO
MB
Absorbance
Wavelength (nm)

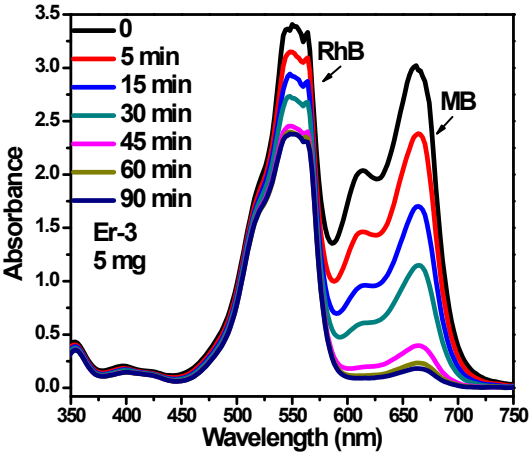
(c)


RhB
MB
0
5 min
15 min
30 min
60 min
90 min
Dy-2
5 mg
Absorbance
Wavelength (nm)

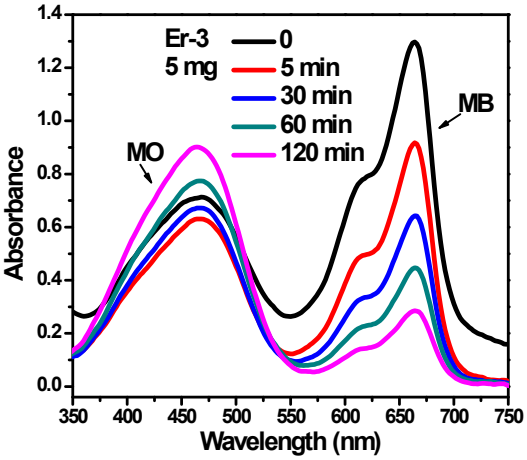
(d)


Dy-2
5 mg
0
10 min
30 min
60 min
120 min
MO
MB
Absorbance
Wavelength (nm)

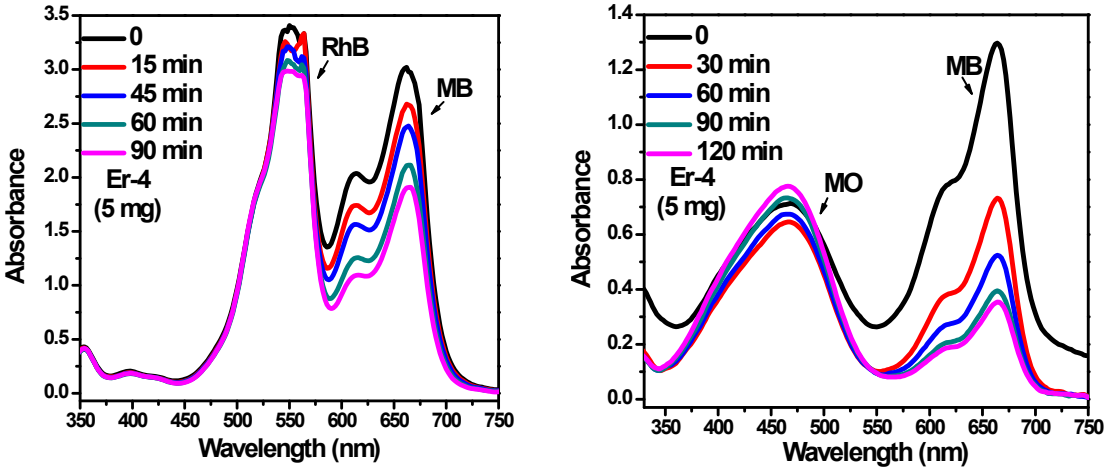
(e)


0
5 min
15 min
30 min
45 min
60 min
90 min
Er-3
5 mg
RhB
MB
Absorbance
Wavelength (nm)

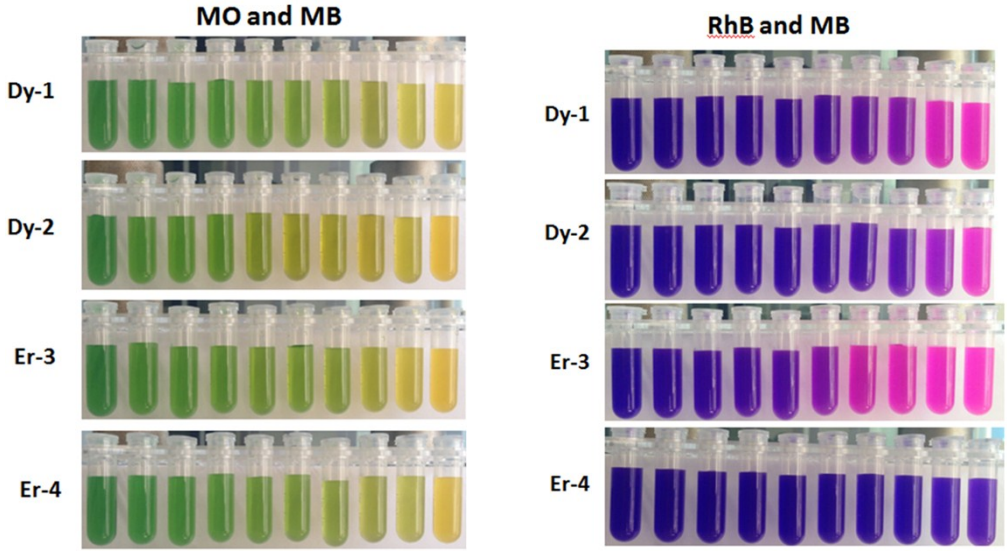
(f)


Er-3
5 mg
0
5 min
30 min
60 min
120 min
MO
MB
Absorbance
Wavelength (nm)

(g)



(h) (i)



(j) (k)

Fig. S10 (a) The photographs of initial MB, MO and RhB solution, as well as the mixed dye solutions of MB and MO, MB and RhB. (b-i) UV-vis spectra of aqueous solution of dyes with **Dy-1** (b and c), **Dy-2** (d and e), **Er-3** (f and g) and **Er-4** (h and i). (b, d, f and h) RhB and MB. (c, e, g and i) MO and MB. (j and k) Photographs of dye selective adsorption of **Dy-1**, **Dy-2**, **Er-3** and **Er-4**.

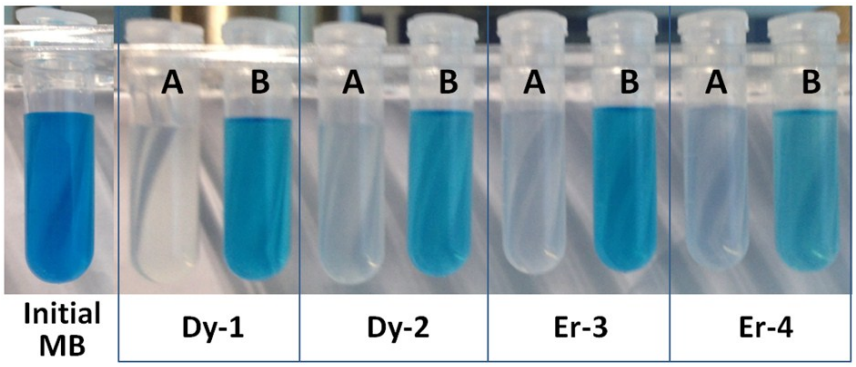


Fig. S11 The contrastive photographs of MB dye solution after adsorption-desorption process for

Dy-1, **Dy-2**, **Er-3** and **Er-4**. A: The solution of MB dye after adsorption with different compounds **1-4**; B: The solution of MB from MB@**Dy-1** (**Dy-2**, **Er-3** and **Er-4**) in ethanol solution of NaCl.

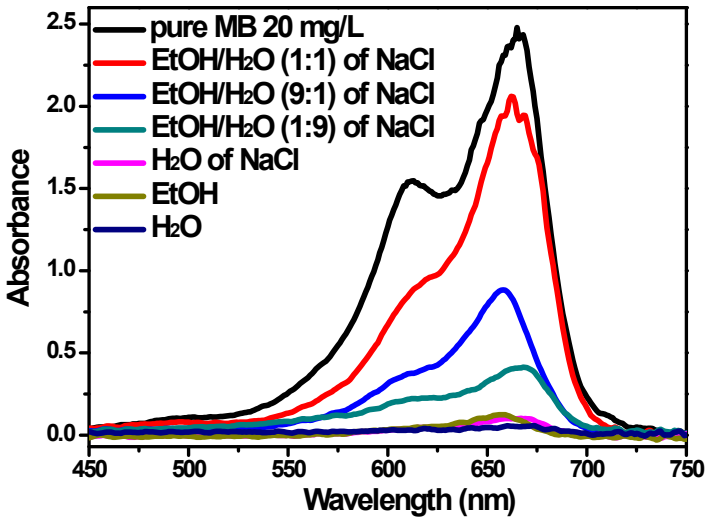


Fig. S12 The UV-vis spectra of desorbed MB solution from MB@Dy-1 using various elution solutions, such as, pure aqueous solution (H_2O), pure ethanol solvent (EtOH), the aqueous solution of NaCl (H_2O of NaCl), the mixed solvents with EtOH and H_2O of NaCl for different volume ratio (EtOH/H_2O (1:1) of NaCl, EtOH/H_2O (9:1) of NaCl, EtOH/H_2O (1:9) of NaCl).

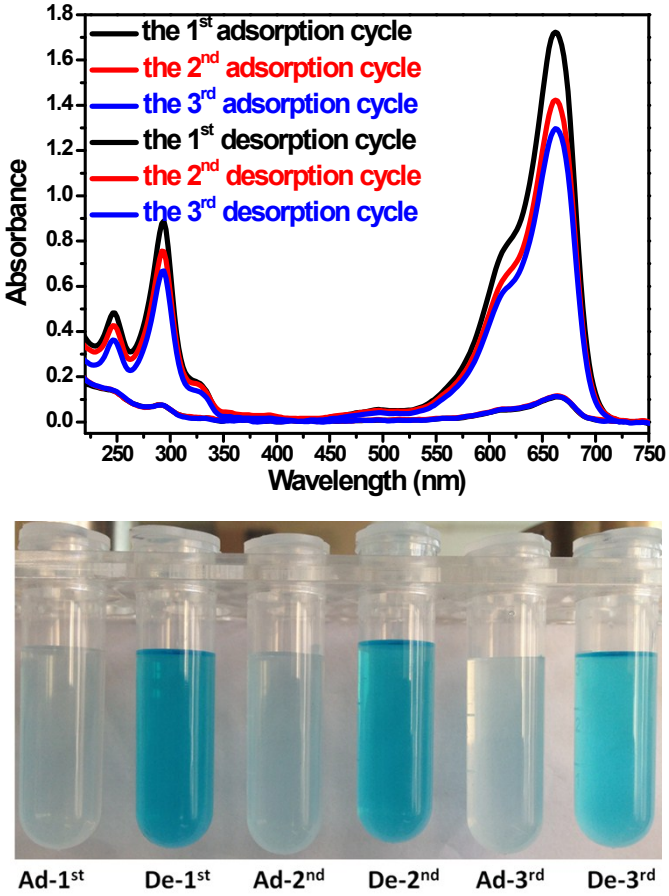


Fig. S13 The UV-vis spectra and photographs of three adsorption and desorption cycles for **Dy-1**,

the first cycle: Ad-1st and De-1st; the second cycle: Ad-2nd and De-2nd; the third cycle: Ad-3rd and De-3rd.

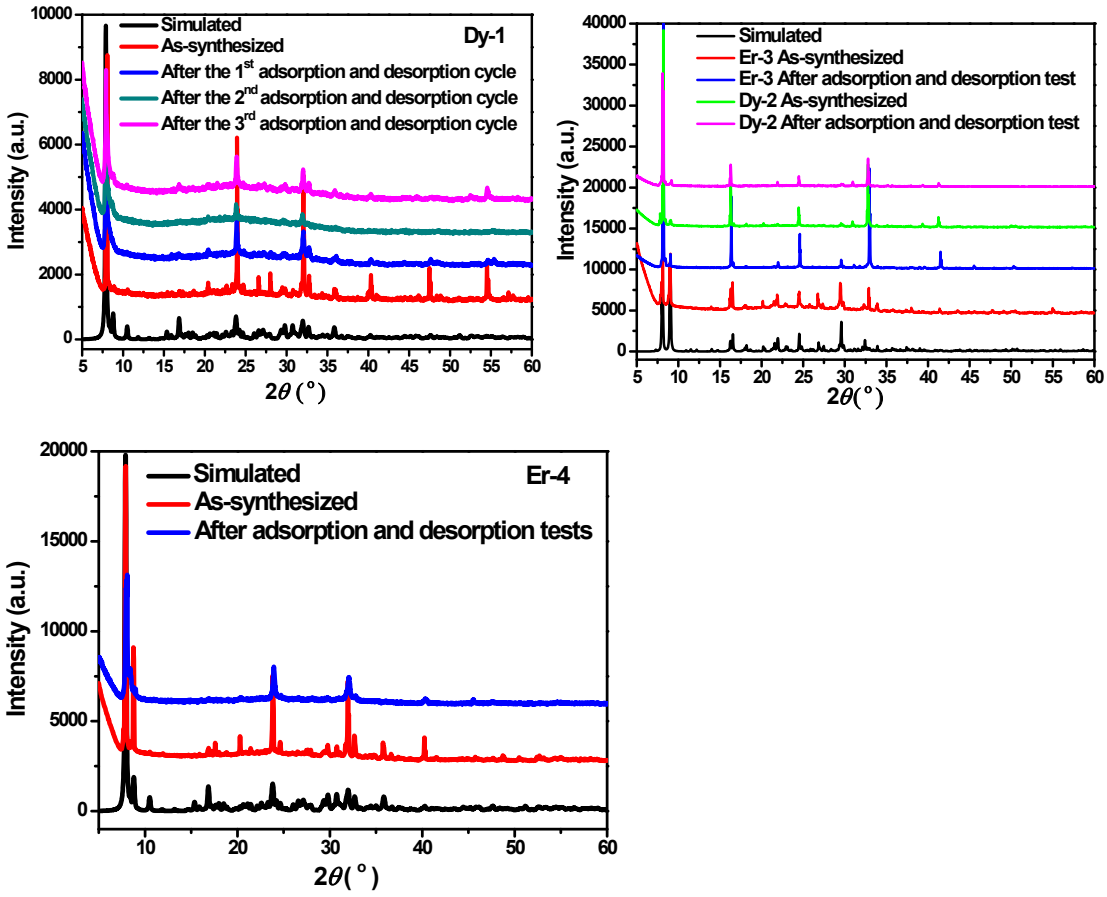
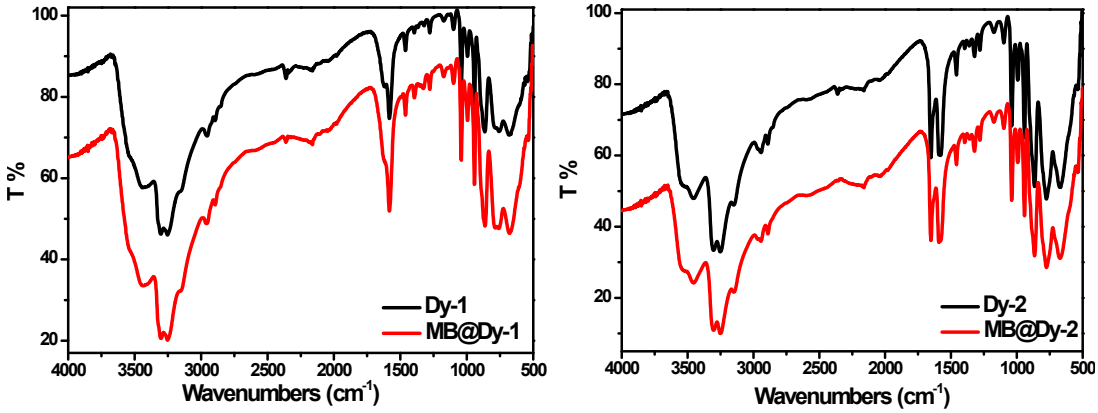


Fig.S14 PXRD patterns for **Dy-1**, **Dy-2**, **Er-3** and **Er-4**.



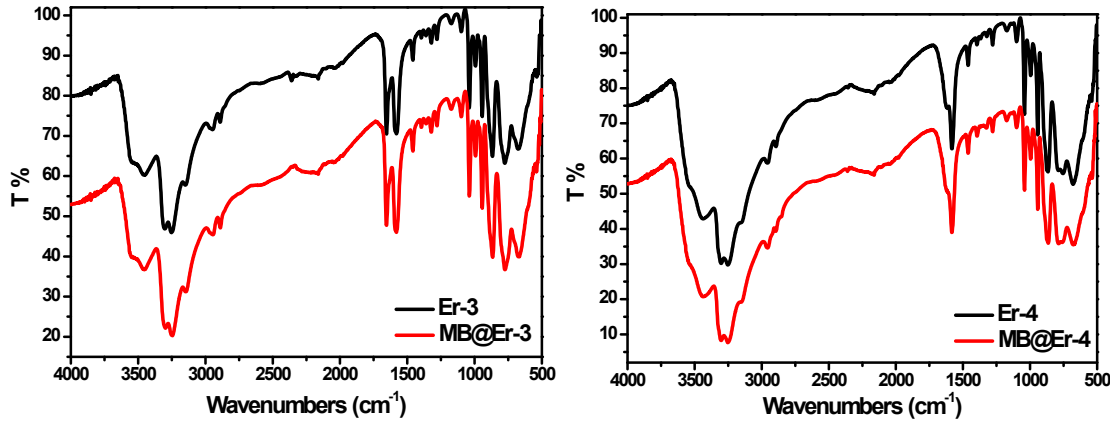


Fig. S15 FT-IR spectra for **Dy-1**, **Dy-2**, **Er-3** and **Er-4**, as well as the related MB@LnCu-POMs (**1-4**).

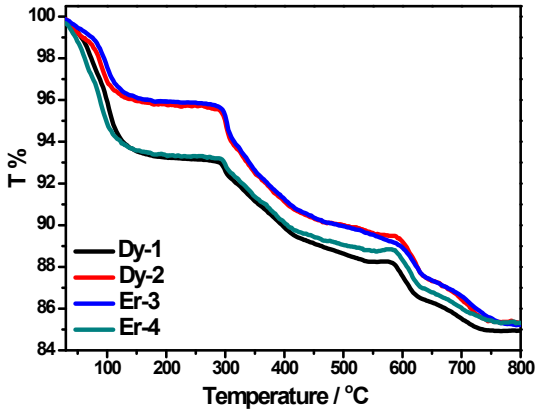


Fig. S16 TGA curves of **Dy-1**, **Dy-2**, **Er-3** and **Er-4**.

The TG curves of compounds **1-4** show three weight loss steps. The first weight loss corresponds to the releases of free and coordinated water molecules (for **Dy-1**: found. 6.50%, calcd. 6.24%; for **Er-3**: found. 3.88%, calcd. 3.28%; for **Er-4**: found. 6.32%, calcd. 5.13%) in the range from room temperature to 153 °C. The total weight loss at 750 °C is 15.1% for **Dy-1**, 14.6% for **Dy-2,** 14.73% for **Er-3**, 14.66% for **Er-4**.

Table S1 Summary of Crystal Data and Structure Results for 1-4.

Compound	**Dy-1**	**Er-3**	**Er-4**
CCDC	1028827	1028828	1028829
Empirical formula	$C_{16}H_{111}Cu_4Dy_2K_2N_{16}O_{101.5}Si_2W_{22}$	$C_{26}H_{126}Cu_6Er_2N_{24}O_{97}Si_2W_{22}$	$C_{16}H_{77}CuErN_{12}O_{85}Si_2W_{22}$
structural formula#	$[K_2(H_2O)_{6.5}][Cu(en)_2]_2[Dy(H_2O)_2SiW_{11}O_{39}]_2$•2$[Cu(H_2O)(en)_2]$•10$H_2O$	$[Cu(en)_2]_3[Er(H_2O)SiW_{11}O_{39}]_2(C_2O_4)$•$[Cu(H_2O)(en)_2]_3$•10$H_2O$	$[Cu(H_2O)(DETA)_2]H_{11}[Er(SiW_{11}O_{39})_2]$•2DETA•6$H_2O$
fw	6910.45	7144.15	6129.58

Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	*C*m	*F*dd2	$P2_1c$
Temperature (K)	296(2)	296(2)	296(2)
λ (Mo Kα), Å	0.71073	0.71073	0.71073
a /Å	20.5847(11)	43.425(3)	19.142(6)
b /Å	13.4613(7)	43.548(3)	24.362(7)
c /Å	22.9069(13)	25.625(2)	21.693(6)
α /°	90	90	90
β /°	101.9730(10)	90	99.006(7)
γ /°	90	90	90
V /Å^3	6209.3(6)	48461(6)	9992(5)
Z	2	16	4
2θ max (deg)	52.18	52.22	52.12
μ(Mo-Kα) mm^{-1}	22.331	23.320	26.379
D, g/cm^3	3.696	3.917	4.075
F(000)	6146	51072	10760
Crystal size (mm^3)	0.42 × 0.31 × 0.27	0.31 × 0.30 × 0.25	0.36 × 0.31 × 0.17
Reflections collected / unique	19627/8892 [R_{int} = 0.0450]	75181/23546[R_{int} = 0.0792]	59396/19612 [R_{int} = 0.0774]
Final *R* indices [$I > 2\sigma(I)$]	$^aR_1$ = 0.0407, $^bwR_2$ = 0.0970	$^aR_1$ = 0.0468, $^bwR_2$ = 0.1039	$^aR_1$ = 0.0461, $^bwR_2$ = 0.0997
R indices (all data)	$^aR_1$ = 0.0497, $^bwR_2$ = 0.1028	$^aR_1$ = 0.0647, $^bwR_2$ = 0.1139	$^aR_1$ = 0.0707, $^bwR_2$ = 0.1077
GOF	1.067	1.028	1.022

$^a R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, $^b wR_2 = \{\sum w[(F_o)^2-(F_c)^2]^2/\sum w[(F_o)^2]^2\}^{1/2}$

#: These formulas were determined by considering crystal structures and other analyses (EA, TGA, and BVS) together.

Table S2. The BVS values of all the atoms except the lattice water molecules in **Er-4**.

Atoms	BVS values	Atoms	BVS values
Er1	2.89	Si1	3.87
Si2	3.98	W1	6.13
W2	6.16	W3	6.25
W4	6.22	W5	6.18

W6	6.26	W7	5.92
W8	5.94	W9	6.17
W10	6.19	W11	6.10
W12	6.11	W13	5.88
W14	6.25	W15	5.90
W16	6.14	W17	6.22
W18	5.94	W19	5.88
W20	6.04	W21	5.97
W22	6.04		
O1	1.71	O2	1.90
O3	1.97	O4	1.89
O5	1.60	O6	1.83
O7	1.76	O8	1.98
O9	1.75	O10	1.78
O11	1.65	O12	2.08
O13	1.85	O14	1.91
O15	1.98	O16	1.91
O17	1.65	O18	1.85
O19	1.86	O20	2.02
O21	1.95	O22	1.94
O23	1.89	O24	2.08
O25	1.88	O26	1.70
O27	2.03	O28	1.93
O29	1.87	O30	1.93
O31	1.92	O32	2.02
O33	2.00	O34	1.89
O35	1.90	O37	1.90
O38	1.70	O39	1.78
O42	1.74	O43	1.67
O44	1.90	O45	1.67
O46	1.54	O47	1.70
O48	1.83	O49	1.92
O50	1.92	O51	2.07
O52	2.04	O53	1.84
O54	1.94	O55	1.76
O56	2.06	O57	1.99
O58	1.60	O59	1.82
O60	1.81	O66	1.81
O67	1.93	O68	1.86
O69	1.74	O70	1.94
O71	1.73	O72	1.80
O73	1.89	O74	1.82
O75	1.98	O76	1.87

O77	1.87	O78	2.08
O79	2.03	O80	1.91
O81	1.83	O91	1.88
O92	1.60	O93	1.57
O94	1.77	O95	1.54

Table S3. Selected bond lengths for **1**, **3** and **4**.

Compound Dy-1			
Cu(1)-N(6)	1.96(3)	Cu(1)-N(5)#2	2.00(2)
Cu(1)-N(6)#2	1.96(3)	Cu(1)-N(5)	2.00(2)
Cu(2)-N(2)	1.98(3)	Cu(2)-N(1)	2.01(3)
Cu(2)-N(2)#2	1.98(3)	Cu(2)-N(1)#2	2.01(3)
Cu(3)-N(8)#2	2.02(3)	Cu(3)-N(7)	2.04(3)
Cu(3)-N(8)	2.02(3)	Cu(3)-N(7)#2	2.04(3)
Cu(3)-O(8W)	2.43(4)	Cu(4)-N(3)	1.92(3)
Cu(4)-N(3)#2	1.92(3)	Cu(4)-N(4)	1.97(3)
Cu(4)-N(4)#2	1.97(3)	Dy(1)-O(7)	2.276(16)
Dy(1)-O(9)#2	2.253(15)	Dy(1)-O(1W)#2	2.360(15)
Dy(1)-O(9)	2.253(15)	Dy(1)-O(1W)	2.360(15)
Dy(1)-O(7)#2	2.276(16)	Dy(1)-O(6)	2.48(2)
Dy(2)-O(44)#2	2.291(16)	Dy(2)-O(2W)	2.35(2)
Dy(2)-O(44)	2.291(16)	Dy(2)-O(2W)#2	2.35(2)
Dy(2)-O(26)#2	2.299(16)	Dy(2)-O(38)#3	2.411(19)
Dy(2)-O(26)	2.299(17)	Dy(2)-O(3W)	2.54(6)
Si(1)-O(11)	1.61(2)	Si(1)-O(12)#2	1.614(16)
Si(1)-O(12)	1.614(16)	Si(1)-O(10)	1.66(2)
Si(2)-O(31)	1.634(16)	Si(2)-O(41)	1.64(2)
Si(2)-O(31)#2	1.634(16)	Si(2)-O(5)	1.65(2)
W(1)-O(14)	1.709(17)	W(1)-O(35)	1.932(16)
W(1)-O(17)#2	1.850(17)	W(1)-O(32)	1.935(16)
W(1)-O(13)	1.870(17)	W(1)-O(12)	2.331(14)
W(2)-O(37)	1.745(16)	W(2)-O(36)	1.970(13)
W(2)-O(9)	1.808(14)	W(2)-O(21)	2.031(15)
W(2)-O(35)	1.897(16)	W(2)-O(10)	2.246(15)
W(3)-O(19)	1.704(18)	W(3)-O(20)	1.922(10)
W(3)-O(21)	1.864(16)	W(3)-O(15)	1.945(14)
W(3)-O(32)	1.894(17)	W(3)-O(11)	2.387(16)
W(4)-O(38)	1.710(19)	W(4)-O(15)	1.906(15)
W(4)-O(16)	1.877(16)	W(4)-O(15)#2	1.906(15)
W(4)-O(16)#2	1.877(16)	W(4)-O(11)	2.32(2)
W(5)-O(39)	1.702(17)	W(5)-O(16)#2	1.965(15)
W(5)-O(8)	1.811(15)	W(5)-O(17)	1.967(18)

W(5)-O(18)	1.900(4)	W(5)-O(12)#2	2.413(16)
W(6)-O(40)	1.700(19)	W(6)-O(13)#2	2.02(2)
W(6)-O(7)	1.788(18)	W(6)-O(8)	2.026(18)
W(6)-O(47)	1.896(8)	W(6)-O(12)#2	2.338(14)
W(7)-O(28)	1.683(17)	W(7)-O(27)	1.945(17)
W(7)-O(43)	1.850(15)	W(7)-O(30)	1.998(18)
W(7)-O(29)	1.886(14)	W(7)-O(31)	2.315(14)
W(8)-O(26)	1.727(17)	W(8)-O(27)	1.960(18)
W(8)-O(25)	1.757(16)	W(8)-O(23)	2.039(15)
W(8)-O(24)	1.927(8)	W(8)-O(31)	2.374(15)
W(9)-O(34)	1.683(17)	W(9)-O(22)	1.911(5)
W(9)-O(23)	1.851(17)	W(9)-O(33)	1.923(16)
W(9)-O(30)	1.855(19)	W(9)-O(31)	2.335(15)
W(10)-O(6)	1.690(19)	W(10)-O(4)#2	1.92(2)
W(10)-O(33)#2	1.914(16)	W(10)-O(4)	1.92(2)
W(10)-O(33)	1.914(16)	W(10)-O(5)	2.331(18)
W(11)-O(2)	1.704(15)	W(11)-O(4)	1.95(2)
W(11)-O(3)	1.800(17)	W(11)-O(29)#2	1.958(14)
W(11)-O(1)	1.917(11)	W(11)-O(5)	2.338(15)
W(12)-O(46)	1.680(15)	W(12)-O(43)#2	1.983(17)
W(12)-O(44)	1.793(16)	W(12)-O(3)	2.067(18)
W(12)-O(45)	1.920(11)	W(12)-O(41)	2.276(15)
Compound Er-3			
Cu(1)-N(7)	1.94(3)	Cu(1)-N(8)	2.00(2)
Cu(1)-N(6)	1.97(3)	Cu(1)-N(1)	2.02(3)
Cu(1)-O(29)	2.280(15)	Cu(2)-O(42)	2.321(14)
Cu(2)-N(21)	1.98(3)	Cu(2)-N(24)	2.05(2)
Cu(2)-N(23)	2.02(2)	Cu(2)-N(22)	2.07(3)
Cu(3)-N(19)	1.96(2)	Cu(3)-N(18)	1.99(2)
Cu(3)-N(20)	1.96(2)	Cu(3)-N(17)	2.01(3)
Cu(4)-N(11)	1.999(17)	Cu(4)-N(9)	2.03(3)
Cu(4)-N(12)	2.011(18)	Cu(4)-N(10)	2.064(16)
Cu(4)-O(2W)	2.374(16)	Cu(5)-O(3W)	2.411(18)
Cu(5)-N(13)	1.981(18)	Cu(5)-N(14)	2.02(2)
Cu(5)-N(16)	1.999(17)	Cu(5)-N(15)	2.028(17)
Cu(6)-N(5)	1.95(2)	Cu(6)-N(3)	1.97(2)
Cu(6)-N(4)	1.97(2)	Cu(6)-N(2)	1.987(19)
Er(1)-O(25)	2.257(15)	Er(1)-O(38)	2.322(13)
Er(1)-O(39)	2.259(14)	Er(1)-O(9W)	2.348(16)
Er(1)-O(31)	2.270(13)	Er(1)-O(41)	2.399(17)
Er(1)-O(35)	2.304(14)	Er(1)-O(115)	2.859(14)
Er(2)-O(76)	2.239(13)	Er(2)-O(10W)	2.380(17)
Er(2)-O(74)	2.261(14)	Er(2)-O(82)	2.383(13)

Er(2)-O(75)	2.263(14)	Er(2)-O(122)	2.397(17)
Er(2)-O(47)	2.279(17)	Er(2)-O(73)	2.863(14)
Si(2)-O(115)	1.602(15)	Si(2)-O(3)	1.630(15)
Si(2)-O(4)	1.628(13)	Si(2)-O(2)	1.636(13)
W(1)-O(14)	1.712(14)	W(1)-O(12)	1.928(13)
W(1)-O(16)	1.896(13)	W(1)-O(7)	1.937(14)
W(1)-O(15)	1.908(14)	W(1)-O(2)	2.332(14)
W(2)-O(5)	1.717(16)	W(2)-O(6)	1.916(14)
W(2)-O(8)	1.795(14)	W(2)-O(9)	1.953(12)
W(2)-O(7)	1.915(14)	W(2)-O(2)	2.349(13)
W(3)-O(10)	1.696(14)	W(3)-O(6)	1.924(15)
W(3)-O(11)	1.809(15)	W(3)-O(12)	1.937(14)
W(3)-O(13)	1.922(16)	W(3)-O(2)	2.368(12)
W(4)-O(18)	1.721(14)	W(4)-O(15)	1.883(14)
W(4)-O(20)	1.846(14)	W(4)-O(19)	1.942(15)
W(4)-O(17)	1.875(14)	W(4)-O(3)	2.401(14)
W(5)-O(22)	1.698(15)	W(5)-O(21)	1.932(13)
W(5)-O(23)	1.883(14)	W(5)-O(17)	1.949(15)
W(5)-O(13)	1.898(15)	W(5)-O(3)	2.354(13)
W(6)-O(27)	1.687(15)	W(6)-O(16)	1.924(12)
W(6)-O(28)	1.860(12)	W(6)-O(32)	1.932(13)
W(6)-O(19)	1.883(15)	W(6)-O(4)	2.390(13)
W(7)-O(33)	1.708(14)	W(7)-O(30)	1.929(11)
W(7)-O(34)	1.875(14)	W(7)-O(32)	1.965(13)
W(7)-O(9)	1.879(11)	W(7)-O(4)	2.350(12)
W(8)-O(37)	1.707(15)	W(8)-O(34)	1.949(13)
W(8)-O(35)	1.754(13)	W(8)-O(8)	2.050(13)
W(8)-O(36)	1.896(14)	W(8)-O(115)	2.277(14)
W(9)-O(40)	1.702(13)	W(9)-O(36)	1.959(14)
W(9)-O(39)	1.796(14)	W(9)-O(11)	2.037(15)
W(9)-O(23)	1.927(14)	W(9)-O(115)	2.305(14)
W(10)-O(24)	1.709(14)	W(10)-O(21)	1.950(13)
W(10)-O(25)	1.798(15)	W(10)-O(20)	2.084(14)
W(10)-O(26)	1.897(12)	W(10)-O(3)	2.328(14)
W(11)-O(31)	1.734(14)	W(11)-O(30)	1.931(13)
W(11)-O(29)	1.758(12)	W(11)-O(28)	2.025(14)
W(11)-O(26)	1.911(13)	W(11)-O(4)	2.311(11)
W(12)-O(42)	1.728(13)	W(12)-O(79)	1.932(13)
W(12)-O(76)	1.763(13)	W(12)-O(48)	2.026(14)
W(12)-O(44)	1.931(15)	W(12)-O(57)	2.356(12)
W(13)-O(43)	1.720(14)	W(13)-O(46)	1.948(13)
W(13)-O(47)	1.745(16)	W(13)-O(45)	2.029(13)
W(13)-O(44)	1.884(15)	W(13)-O(49)	2.341(14)

W(14)-O(69)	1.725(14)	W(14)-O(68)	1.962(16)
W(14)-O(75)	1.794(14)	W(14)-O(71)	1.999(14)
W(14)-O(72)	1.897(15)	W(14)-O(73)	2.312(13)
W(15)-O(80)	1.693(14)	W(15)-O(72)	1.950(16)
W(15)-O(74)	1.790(14)	W(15)-O(65)	2.064(16)
W(15)-O(56)	1.924(16)	W(15)-O(73)	2.318(13)
W(16)-O(70)	1.722(15)	W(16)-O(79)	1.929(13)
W(16)-O(71)	1.833(14)	W(16)-O(77)	1.944(14)
W(16)-O(67)	1.880(11)	W(16)-O(57)	2.294(14)
W(17)-O(78)	1.713(14)	W(17)-O(50)	1.928(14)
W(17)-O(48)	1.860(14)	W(17)-O(59)	1.928(12)
W(17)-O(77)	1.920(13)	W(17)-O(57)	2.379(13)
W(18)-O(53)	1.723(16)	W(18)-O(50)	1.905(14)
W(18)-O(45)	1.902(14)	W(18)-O(51)	1.919(15)
W(18)-O(54)	1.904(14)	W(18)-O(49)	2.396(14)
W(19)-O(52)	1.700(15)	W(19)-O(46)	1.924(13)
W(19)-O(55)	1.880(15)	W(19)-O(51)	1.929(14)
W(19)-O(56)	1.900(17)	W(19)-O(49)	2.332(13)
W(20)-O(66)	1.699(15)	W(20)-O(67)	1.968(12)
W(20)-O(68)	1.897(18)	W(20)-O(64)	1.980(14)
W(20)-O(63)	1.938(14)	W(20)-O(58)	2.374(13)
W(21)-O(62)	1.738(14)	W(21)-O(55)	1.941(15)
W(21)-O(65)	1.793(17)	W(21)-O(61)	1.957(16)
W(21)-O(63)	1.917(15)	W(21)-O(58)	2.332(12)
W(22)-O(60)	1.718(15)	W(22)-O(54)	1.898(15)
W(22)-O(64)	1.864(15)	W(22)-O(61)	1.929(15)
W(22)-O(59)	1.888(12)	W(22)-O(58)	2.378(13)
Compound Er-4			
Er(1)-O(14)	2.325(10)	Er(1)-O(55)	2.368(11)
Er(1)-O(22)	2.343(11)	Er(1)-O(69)	2.397(11)
Er(1)-O(30)	2.356(10)	Er(1)-O(72)	2.400(11)
Er(1)-O(24)	2.362(11)	Er(1)-O(7)	2.401(10)
Cu(1)-N(1)	1.970(14)	Cu(1)-N(4)	2.051(19)
Cu(1)-N(2)	2.006(13)	Cu(1)-N(3)	2.077(13)
Si(1)-O(29)	1.615(11)	Si(1)-O(80)	1.646(11)
Si(1)-O(19)	1.632(11)	Si(1)-O(77)	1.653(10)
Si(2)-O(2)	1.614(10)	Si(2)-O(28)	1.633(10)
Si(2)-O(35)	1.629(10)	Si(2)-O(73)	1.648(11)
W(1)-O(10)	1.704(11)	W(1)-O(78)	1.915(10)
W(1)-O(69)	1.797(10)	W(1)-O(34)	1.933(10)
W(1)-O(26)	2.111(10)	W(1)-O(35)	2.220(9)
W(2)-O(11)	1.722(10)	W(2)-O(78)	1.897(10)
W(2)-O(27)	1.893(10)	W(2)-O(20)	1.928(11)

W(2)-O(31)	1.894(11)	W(2)-O(2)	2.338(10)
W(3)-O(66)	1.733(13)	W(3)-O(13)	1.944(11)
W(3)-O(26)	1.837(10)	W(3)-O(91)	1.971(16)
W(3)-O(20)	1.902(10)	W(3)-O(28)	2.358(10)
W(4)-O(94)	1.730(12)	W(4)-O(50)	1.904(13)
W(4)-O(67)	1.878(11)	W(4)-O(91)	1.925(16)
W(4)-O(75)	1.898(11)	W(4)-O(28)	2.314(9)
W(5)-O(9)	1.707(10)	W(5)-O(13)	1.952(11)
W(5)-O(23)	1.817(11)	W(5)-O(75)	1.956(11)
W(5)-O(56)	1.950(12)	W(5)-O(28)	2.361(9)
W(6)-O(59)	1.704(11)	W(6)-O(27)	1.945(10)
W(6)-O(25)	1.829(11)	W(6)-O(67)	1.988(11)
W(6)-O(12)	1.921(11)	W(6)-O(2)	2.402(10)
W(7)-O(5)	1.748(10)	W(7)-O(33)	1.966(10)
W(7)-O(7)	1.788(11)	W(7)-O(23)	2.116(11)
W(7)-O(34)	1.939(10)	W(7)-O(35)	2.206(9)
W(8)-O(71)	1.702(11)	W(8)-O(31)	1.988(10)
W(8)-O(14)	1.756(10)	W(8)-O(25)	2.111(10)
W(8)-O(32)	1.924(10)	W(8)-O(2)	2.375(10)
W(9)-O(48)	1.711(11)	W(9)-O(74)	1.982(10)
W(9)-O(30)	1.753(10)	W(9)-O(53)	2.111(11)
W(9)-O(32)	1.907(10)	W(9)-O(73)	2.320(11)
W(10)-O(47)	1.728(10)	W(10)-O(74)	1.917(11)
W(10)-O(56)	1.873(12)	W(10)-O(15)	1.923(11)
W(10)-O(33)	1.882(10)	W(10)-O(73)	2.327(9)
W(11)-O(43)	1.722(10)	W(11)-O(15)	1.930(10)
W(11)-O(53)	1.820(12)	W(11)-O(50)	1.963(13)
W(11)-O(12)	1.886(10)	W(11)-O(73)	2.401(10)
W(12)-O(42)	1.708(11)	W(12)-O(79)	1.911(11)
W(12)-O(57)	1.899(16)	W(12)-O(70)	1.917(11)
W(12)-O(37)	1.904(13)	W(12)-O(77)	2.324(10)
W(13)-O(95)	1.750(12)	W(13)-O(44)	1.959(12)
W(13)-O(72)	1.762(11)	W(13)-O(4)	2.110(12)
W(13)-O(57)	1.941(16)	W(13)-O(29)	2.213(10)
W(14)-O(1)	1.711(11)	W(14)-O(70)	1.939(11)
W(14)-O(24)	1.766(12)	W(14)-O(76)	2.095(10)
W(14)-O(16)	1.915(10)	W(14)-O(77)	2.339(10)
W(15)-O(93)	1.724(11)	W(15)-O(68)	1.924(13)
W(15)-O(4)	1.830(12)	W(15)-O(49)	1.970(11)
W(15)-O(79)	1.919(11)	W(15)-O(80)	2.368(10)
W(16)-O(38)	1.731(11)	W(16)-O(37)	1.946(12)
W(16)-O(76)	1.830(11)	W(16)-O(21)	1.958(11)
W(16)-O(51)	1.900(12)	W(16)-O(77)	2.394(10)

W(17)-O(45)	1.715(13)	W(17)-O(8)	1.911(11)
W(17)-O(21)	1.893(11)	W(17)-O(81)	1.921(10)
W(17)-O(49)	1.895(12)	W(17)-O(80)	2.314(10)
W(18)-O(46)	1.763(12)	W(18)-O(52)	1.941(11)
W(18)-O(55)	1.774(11)	W(18)-O(54)	2.089(11)
W(18)-O(44)	1.908(12)	W(18)-O(29)	2.249(10)
W(19)-O(17)	1.721(11)	W(19)-O(3)	1.971(11)
W(19)-O(22)	1.749(10)	W(19)-O(18)	2.100(11)
W(19)-O(16)	1.951(10)	W(19)-O(19)	2.381(10)
W(20)-O(92)	1.737(12)	W(20)-O(68)	1.955(11)
W(20)-O(54)	1.824(12)	W(20)-O(81)	1.973(10)
W(20)-O(60)	1.930(11)	W(20)-O(80)	2.320(11)
W(21)-O(58)	1.724(12)	W(21)-O(8)	1.935(11)
W(21)-O(18)	1.828(11)	W(21)-O(6)	1.945(10)
W(21)-O(51)	1.908(11)	W(21)-O(19)	2.395(10)
W(22)-O(39)	1.706(11)	W(22)-O(60)	1.915(10)
W(22)-O(3)	1.875(11)	W(22)-O(6)	1.941(11)
W(22)-O(52)	1.881(11)	W(22)-O(19)	2.330(10)

Symmetry transformations used to generate equivalent atoms: Symmetry transformations used to generate equivalent atoms: For **Dy-1** #1 x, y, z+1; #2 x, -y+1, z; #3 x, y, z-1.

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