Metallo-supramolecular grid-type architectures for highly and selectively efficient adsorption of dyes in water

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X-ray crystallography

Structure determination was performed on a Bruker ApexII CCD diffractometer equipped with graphite-monochromatic Mo-Kα radiation (λ = 0.71073 Å) at 293K. Empirical absorption corrections were applied using the SADABS program[1]. The structure of **1** and **2** was solved by direct methods and refined anisotropically by full-matrix least squares techniques on F^2 values, using the SHELX-97 program[2]. Hydrogen atoms were added on appropriate positions in theory and refined with isotropic thermal parameters riding on those parent atoms. The corresponding crystallographic and refinement data for **1** and **2** are listed in Table S1.

Table S1. Crystallographic data and structure refinements for complexes **1** and **2**.

	1	**2**
Empirical formula	$Cu_{5.5}C_{60}H_{49}I_2N_{27}O_5$	$Cu_{15}C_{191}H_{111}Cl_6N_{89}O_{24}$
Formula weight	1831.53	5202.49
Temperature/K	293(2)	293(2)
Crystal system	monoclinic	triclinic
Space group	*C*2/*c*	*P*-1
a/Å	25.089(2)	18.962(10)
b/Å	19.3049(14)	22.560(12)
c/Å	30.127(3)	26.860(14)
α/°	90.00	105.080(7)
β/°	113.501(11)	102.600(7)
γ/°	90.00	98.885(8)
Volume/Å^3	13382(2)	10552(10)
Z	8	1
ρ_{calc}/mg·mm^{-3}	1.818	1.637

m/mm^{-1}	2.712	1.641
F(000)	7228.0	5218.0
Theta range/°	5.14 to 50.04°	1.64 to 57.66°
Index ranges(*h, k, l*)	$-29 \le h \le 29$, $-22 \le k \le 22$, $-35 \le l \le 35$	$-25 \le h \le 25$, $-30 \le k \le 30$, $-35 \le l \le 35$
Reflections collected	43158	147484
Independent reflections	11794[*R*(int) = 0.1555]	53368[R(int) = 0.0594]
Data/restraints/parameters	11794/2862/903	53368/12642/3029
Goodness-of-fit on F^2	1.029	1.113
Final *R* indexes [$I \ge 2\sigma$ (I)]	R_1[a)] = 0.1120, wR_2[b)] = 0.2648	R_1[a)] = 0.0943, wR_2[b)] = 0.2714
Final *R* indexes [all data]	R_1 = 0.1670, wR_2 = 0.3101	R_1 = 0.1832, wR_2 = 0.3493

a) $R = \Sigma||F_0|-|F_c||/\Sigma|F_0|$, b) $wR = [\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[(wF_0^2)^2]]^{1/2}$

Table S2. Selected bond lengths /Å and bond angles /° for complex **1**.

Cu1-N4	2.006(11)	Cu4-N11	1.963(11)
Cu1-N5	2.003(11)	Cu4-N22	2.008(11)
Cu1-N6	1.991(11)	Cu4-N23	2.002(10)
Cu1-N16A	1.972(11)	Cu4-N24	2.029(11)
Cu1-N18A	2.365(12)	Cu5-N26	1.971(11)
Cu2-N8	1.955(11)	Cu5-N26A	1.971(11)
Cu2-N9	2.120(12)	Cu5-N27	2.087(12)
Cu2-N19	2.110(12)	Cu5-N27A	2.087(12)
Cu2-N20	1.971(11)	Cu6-I1	2.509(2)
Cu3-N13	2.055(11)	Cu6-I2B	2.578(2)
Cu3-N13A	2.055(11)	Cu6-I2	2.561(2)
Cu3-N14	2.104(11)	Cu7-N1	2.128(11)
Cu3-N14A	2.104(11)	Cu7-N1A	2.128(11)
Cu3-N15	2.080(11)	Cu7-N2	1.951(11)
Cu3-N15A	2.080(11)	Cu7-N2A	1.951(11)
Cu4-N10	2.422(12)		
N4-Cu1-N18A	100.1(4)	N23-Cu4-N24	77.6(4)
N5-Cu1-N4	78.1(5)	N24-Cu4-N10	99.8(4)
N5-Cu1-N18A	123.2(4)	N26A-Cu5-N26	132.9(7)
N6-Cu1-N5	78.3(4)	N26-Cu5-N27	81.8(5)
N6-Cu1-N18A	96.5(4)	N26A-Cu5-N27	125.2(4)
N16A-Cu1-N4	99.9(4)	N26-Cu5-N27A	125.2(4)
N16A-Cu1-N6	101.1(4)	N27A-Cu5-N27	114.3(7)
N16A-Cu1-N18A	75.0(4)	I1-Cu6-I2B	118.73(8)

N8-Cu2-N9	81.1(5)	I1-Cu6-I2	123.72(8)
N8-Cu2-N19	123.2(5)	I2-Cu6-I2B	117.47(7)
N8-Cu2-N20	138.4(4)	N1-Cu7-N1A	120.5(7)
N19-Cu2-N9	113.8(4)	N2-Cu7-N1A	121.2(4)
N20-Cu2-N9	122.1(5)	N2A-Cu7-N1	121.2(4)
N20-Cu2-N19	81.4(4)	N2-Cu7-N1	81.0(4)
N13A-Cu3-N13	93.9(6)	N2-Cu7-N2A	137.2(7)
N13A-Cu3-N14	105.0(4)	N23-Cu4-N22	77.6(4)
N13-Cu3-N14	75.6(4)	N23-Cu4-N24	99.8(4)
N13-Cu3-N14A	105.0(4)	N24-Cu4-N10	132.9(7)
N13A-Cu3-N14A	75.6(4)	N26A-Cu5-N26	81.8(5)
N13A-Cu3-N15	92.6(4)	N26-Cu5-N27	125.2(4)
N13-Cu3-N15A	92.6(4)	N26A-Cu5-N27	125.2(4)
N15A-Cu3-N14A	75.9(4)	N26-Cu5-N27A	114.3(7)
N15-Cu3-N14A	103.6(4)	N27A-Cu5-N27	118.73(8)
N15-Cu3-N14	75.9(4)	I1-Cu6-I2B	123.72(8)
N15A-Cu3-N14	103.6(4)	I1-Cu6-I2	117.47(7)
N15-Cu3-N15A	94.8(6)	I2-Cu6-I2B	120.5(7)
N11-Cu4-N10	73.1(4)	N1-Cu7-N1A	121.2(4)
N11-Cu4-N22	100.6(4)	N2-Cu7-N1A	121.2(4)
N11-Cu4-N24	101.0(4)	N2A-Cu7-N1	81.0(4)
N22-Cu4-N10	96.0(4)	N2-Cu7-N1	137.2(7)
N23-Cu4-N10	124.8(4)	N2-Cu7-N2A	77.6(4)

Symmetry transformations used to generate equivalent atoms: A 1- *x*, + *y*, 1/2- *z*; B 1/2- *x*, 3/2- *y*, 1- *z*.

Table S3 The BVS calculation result of complex **1**

Cu site	Cu^{I}	Cu^{II}
Cu1	1.490	2.271
Cu2	1.231	1.876
Cu3	1.622	2.472
Cu4	1.447	2.205
Cu5	1.254	1.910
Cu6	0.913	1.134
Cu7	1.238	1.886

Table S4 Selected bond lengths /Å and bond angles /° for complex **2**.

Cu1-N2	1.954(6)	Cu4-N33	2.016(6)
Cu1-O6	2.354(7)	Cu5-N22	2.131(6)

Cu1-N19A	2.027(6)	Cu5-N23	1.952(6)
Cu1-N20A	1.953(6)	Cu5-N24	2.001(6)
Cu1A-N19	2.027(6)	Cu5-N35	1.942(6)
Cu1A-N20	1.953(6)	Cu5-N36	2.273(7)
Cu2-N10	2.055(6)	Cu6-N25	1.999(6)
Cu2-N11	1.919(6)	Cu6-N27	2.229(6)
Cu2-N10A	2.055(6)	Cu6-N44	1.954(6)
Cu2-N11A	1.919(6)	Cu6-N45	2.329(7)
Cu3-N4	2.041(6)	Cu7-N16	1.924(6)
Cu3-N5	1.992(6)	Cu7-N18	2.376(6)
Cu3-N6	1.985(5)	Cu7-N40	1.991(7)
Cu3-N28	2.299(6)	Cu7-N41	1.981(6)
Cu3-N29	1.968(6)	Cu7-N42	1.983(7)
Cu4-N14	2.072(6)	Cu8-N8	1.968(6)
Cu4-N15	2.233(6)	Cu8-N9	2.133(6)
Cu4-N31	2.055(6)	Cu8-N37	2.144(8)
Cu4-N32	1.993(6)	Cu8-N38	1.962(7)
N1-Cu1-O6	86.1(3)	N22-Cu5-N36	97.6(2)
N2-Cu1-N1	81.5(2)	N23-Cu5-N22	80.6(2)
N2-Cu1-N19A	98.9(3)	N23-Cu5-N24	79.5(2)
N2-Cu1-O6	97.4(3)	N23-Cu5-N36	119.1(3)
N19A-Cu1-O6	89.6(3)	N24-Cu5-N36	98.5(3)
N20A-Cu1-N1	99.4(3)	N35-Cu5-N22	101.3(2)
N20A-Cu1-O6	92.4(3)	N35-Cu5-N24	95.6(2)
N11A-Cu2-N10	99.2(2)	N35-Cu5-N36	77.4(3)
N11-Cu2-N10	80.8(2)	N25-Cu6-N27	79.0(2)
N11-Cu2-N10A	99.2(2)	N25-Cu6-N45	116.8(3)
N4-Cu3-N28	105.7(2)	N27-Cu6-N45	116.9(3)
N5-Cu3-N4	80.0(2)	N44-Cu6-N27	121.4(3)
N5-Cu3-N28	128.6(2)	N44-Cu6-N45	76.6(3)
N6-Cu3-N5	78.3(2)	N16-Cu7-N18	75.4(2)
N6-Cu3-N28	90.0(2)	N16-Cu7-N40	100.8(3)
N29-Cu3-N4	100.8(2)	N16-Cu7-N42	99.3(3)
N29-Cu3-N6	97.6(2)	N40-Cu7-N18	97.3(3)
N29-Cu3-N28	76.2(2)	N41-Cu7-N18	117.5(2)
N14-Cu4-N15	77.0(2)	N41-Cu7-N40	78.1(3)
N31-Cu4-N14	102.3(2)	N41-Cu7-N42	79.1(3)
N31-Cu4-N15	90.4(2)	N42-Cu7-N18	101.4(3)
N32-Cu4-N15	96.2(2)	N8-Cu8-N9	80.7(2)
N32-Cu4-N31	78.1(2)	N8-Cu8-N37	128.9(3)
N32-Cu4-N33	77.6(3)	N9-Cu8-N37	100.1(3)
N33-Cu4-N14	102.6(2)	N38-Cu8-N9	115.5(3)
N33-Cu4-N15	98.3(2)	N38-Cu8-N37	79.9(3)

Symmetry transformations used to generate equivalent atoms: A - *x*, 1- *y*, 1- *z*.

Dye adsorption experiments of complex 1

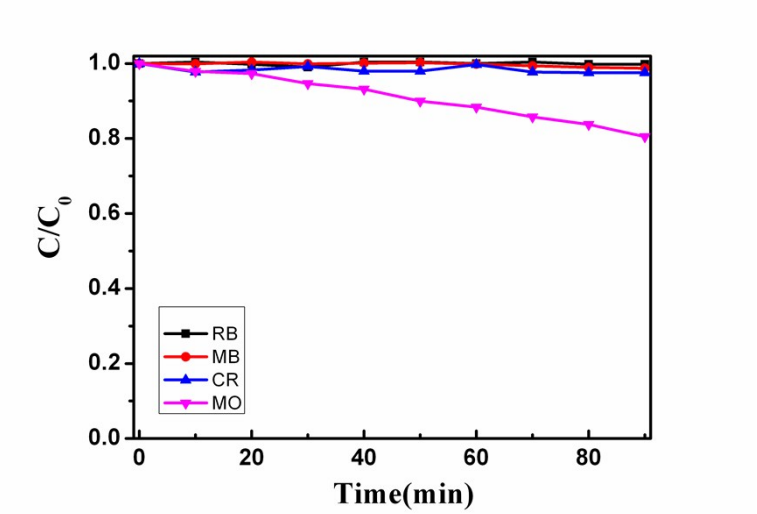

Figure.S1 Concentration changes of MB, RB, MO, and CR with time in the presence of **1**

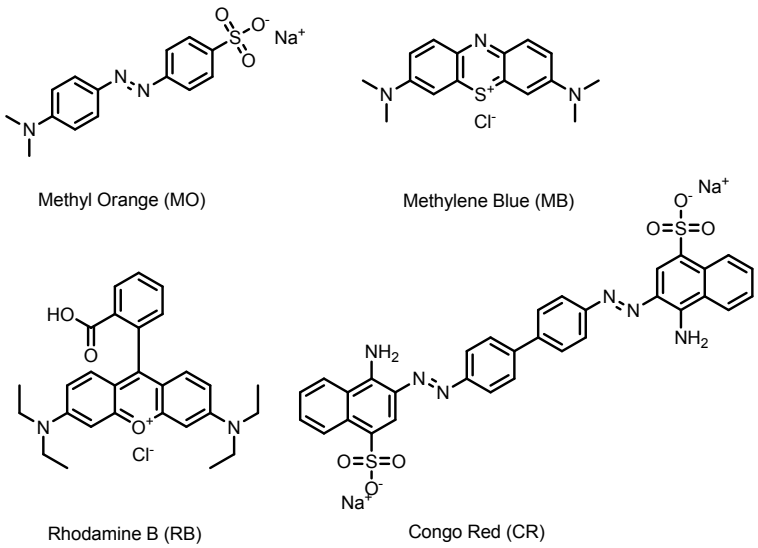

Figure S3 Molecular structure of selected dyes.

1. WI, *Bruker Analytical X‐ray Systems*, Inc.: Madison, 1998.
2. G. M. Sheldrick, *Acta Crystallogr A*, 2008, **64**, 112-122.

We also provide the IR spectra of complex **2**, complex **2** loaded with MO and MO, respectively (Figure S3). Although the difference of IR spectra before and after adsorption is unconspicuous, due to the fact that the typical absorption peaks of complex **2** and MO (such as C=N groups of complex **2** at about 1600 cm^{-1} and N=N of MO molecules at the same position) overlap each other, the slight changes of some peaks at 1600, 1100 and 1000 cm^{-1} can serve as an

auxiliary evidence of the adsorption process.

IR spectra data

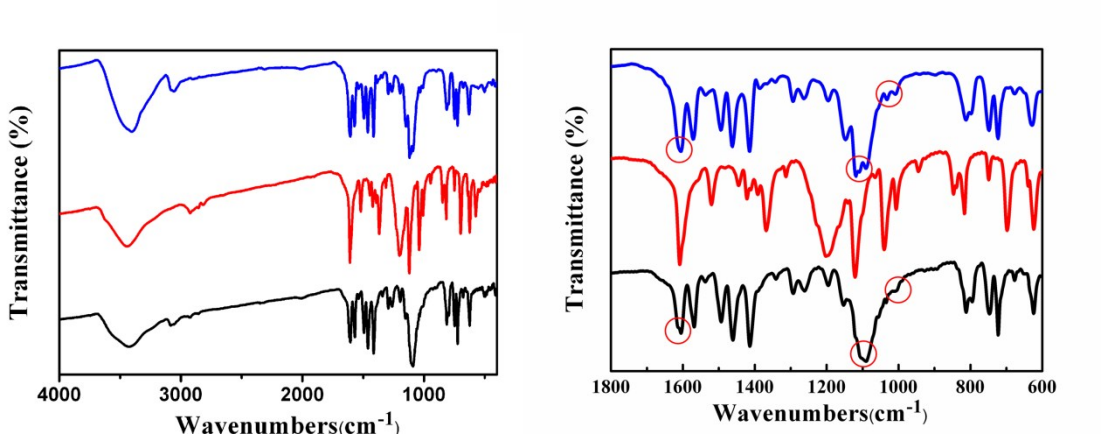

Figure.S3 IR spectra of **2** (black), MO (red) and **2** loaded with MO (blue)

Table S5 The BVS calculation result of complex **2**

Cu site	Cu^{I}	Cu^{II}
Cu1	1.891	2.845
Cu2	1.410	2.150
Cu3	1.505	2.292
Cu4	1.403	2.141
Cu5	1.501	2.289
Cu6	1.033	1.575
Cu7	1.577	2.406
Cu8	1.197	1.823