Supplementary Material (ESI) for CrystEngComm

Coordination polymers based on the octamolybdate and flexible bis(triazole) ligands with different spacer lengths

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Electronic supplementary information

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Table S1 Selected bond lengths (Å) and angles (°) for complexes **1**–**3.**

1

Cu(1)-N(1)	1.964(10)	Cu(1)-N(10a)	1.987(10)
Cu(1)-N(7)	1.999(10)	Cu(1)-N(4b)	2.015(9)
Cu(1)-O(1)	2.413(9)	Mo(1)-O(2)	1.691(9)
Mo(1)-O(1)	1.696(8)	Mo(1)-O(9)	1.915(8)
Mo(1)-O(10c)	1.921(8)	Mo(1)-O(8)	2.264(8)
Mo(1)-O(13)	2.362(7)	Mo(2)-O(3)	1.679(8)
Mo(2)-O(8)	1.735(8)	Mo(2)-O(11)	1.950(7)
Mo(2)-O(12)	1.965(7)	Mo(2)-O(13c)	2.137(7)
Mo(2)-O(13)	2.383(7)	Mo(3)-O(4)	1.684(9)
Mo(3)-O(5)	1.687(8)	Mo(3)-O(9)	1.884(8)
Mo(3)-O(11c)	1.971(7)	Mo(3)-O(12)	2.340(7)
Mo(3)-O(13)	2.388(7)	Mo(4)-O(7)	1.692(8)
Mo(4)-O(6)	1.699(8)	Mo(4)-O(10)	1.878(8)
Mo(4)-O(12)	1.974(7)	Mo(4)-O(13c)	2.335(7)
Mo(4)-O(11c)	2.344(8)	N(1)-Cu(1)-N(10a)	91.9(4)
N(1)-Cu(1)-N(7)	90.8(4)	N(10a)-Cu(1)-N(7)	175.0(4)
N(1)-Cu(1)-N(4b)	173.0(4)	N(10a)-Cu(1)-N(4b)	90.4(4)
N(7)-Cu(1)-N(4b)	87.5(4)	N(1)-Cu(1)-O(1)	99.9(4)
N(10a)-Cu(1)-O(1)	90.8(4)	N(7)-Cu(1)-O(1)	84.6(4)
N(4b)-Cu(1)-O(1)	86.7(4)	O(2)-Mo(1)-O(1)	104.7(5)
O(2)-Mo(1)-O(9)	99.2(4)	O(1)-Mo(1)-O(9)	102.2(4)
O(2)-Mo(1)-O(10c)	97.5(4)	O(1)-Mo(1)-O(10c)	100.4(4)
O(9)-Mo(1)-O(10c)	147.3(3)	O(2)-Mo(1)-O(8)	165.1(4)
O(1)-Mo(1)-O(8)	90.1(4)	O(9)-Mo(1)-O(8)	78.5(3)
O(10c)-Mo(1)-O(8)	78.2(3)	O(2)-Mo(1)-O(13)	94.6(4)
O(1)-Mo(1)-O(13)	160.6(4)	O(9)-Mo(1)-O(13)	76.1(3)
O(10c)-Mo(1)-O(13)	74.7(3)	O(8)-Mo(1)-O(13)	70.5(3)
O(3)-Mo(2)-O(8)	105.7(4)	O(3)-Mo(2)-O(11)	101.6(4)
O(8)-Mo(2)-O(11)	97.0(3)	O(3)-Mo(2)-O(12)	101.5(4)
O(8)-Mo(2)-O(12)	95.7(3)	O(11)-Mo(2)-O(12)	149.5(3)
O(3)-Mo(2)-O(13c)	98.5(4)	O(8)-Mo(2)-O(13c)	155.7(3)
O(11)-Mo(2)-O(13c)	79.1(3)	O(12)-Mo(2)-O(13c)	77.9(3)
O(3)-Mo(2)-O(13)	175.1(4)	O(8)-Mo(2)-O(13)	79.2(3)
O(11)-Mo(2)-O(13)	77.9(3)	O(12)-Mo(2)-O(13)	77.4(3)
O(13c)-Mo(2)-O(13)	76.5(3)	O(4)-Mo(3)-O(5)	105.2(5)
O(4)-Mo(3)-O(9)	102.0(4)	O(5)-Mo(3)-O(9)	101.1(4)
O(4)-Mo(3)-O(11c)	96.8(4)	O(5)-Mo(3)-O(11c)	102.6(4)
O(9)-Mo(3)-O(11c)	144.5(3)	O(4)-Mo(3)-O(12)	162.8(4)
O(5)-Mo(3)-O(12)	89.6(4)	O(9)-Mo(3)-O(12)	83.2(3)
O(11c)-Mo(3)-O(12)	71.0(3)	O(4)-Mo(3)-O(13)	94.4(4)

O(5)-Mo(3)-O(13)	160.3(4)	O(9)-Mo(3)-O(13)	76.0(3)
O(11c)-Mo(3)-O(13)	72.8(3)	O(12)-Mo(3)-O(13)	70.8(2)
O(7)-Mo(4)-O(6)	104.5(4)	O(7)-Mo(4)-O(10)	101.4(4)
O(6)-Mo(4)-O(10)	101.3(4)	O(7)-Mo(4)-O(12)	101.7(4)
O(6)-Mo(4)-O(12)	97.7(4)	O(10)-Mo(4)-O(12)	145.1(3)
O(7)-Mo(4)-O(13c)	159.6(3)	O(6)-Mo(4)-O(13c)	95.8(4)
O(10)-Mo(4)-O(13c)	76.1(3)	O(12)-Mo(4)-O(13c)	73.1(3)
O(7)-Mo(4)-O(11c)	87.8(3)	O(6)-Mo(4)-O(11c)	165.0(4)
O(10)-Mo(4)-O(11c)	84.3(3)	O(12)-Mo(4)-O(11c)	70.9(3)
O(13c)-Mo(4)-O(11c)	71.8(3)		

2

Cu(1)-N(3)	1.969(5)	Cu(1)-N(9)	1.975(5)
Cu(1)-O(14)	1.985(5)	Cu(1)-N(6a)	1.992(5)
Cu(1)-O(1)	2.348(4)	Mo(1)-O(1)	1.706(4)
Mo(1)-O(8)	1.739(4)	Mo(1)-O(12)	1.823(4)
Mo(1)-O(13)	1.890(4)	Mo(1)-O(11)	2.494(4)
Mo(2)-O(3)	1.694(5)	Mo(2)-O(2)	1.701(5)
Mo(2)-O(9)	1.888(4)	Mo(2)-O(11b)	1.995(4)
Mo(2)-O(13b)	2.232(4)	Mo(2)-O(8)	2.368(4)
Mo(3)-O(4)	1.692(5)	Mo(3)-O(5)	1.705(4)
Mo(3)-O(9)	1.939(4)	Mo(3)-O(10)	1.948(4)
Mo(3)-O(12)	2.235(4)	Mo(3)-O(13b)	2.347(4)
Mo(4)-O(7)	1.696(5)	Mo(4)-O(6)	1.699(4)
Mo(4)-O(10)	1.848(4)	Mo(4)-O(11)	1.864(4)
Mo(4)-O(12)	2.506(4)	N(3)-Cu(1)-N(9)	171.5(2)
N(3)-Cu(1)-O(14)	88.7(2)	N(9)-Cu(1)-O(14)	88.1(2)
N(3)-Cu(1)-N(6a)	92.7(2)	N(9)-Cu(1)-N(6a)	89.0(2)
O(14)-Cu(1)-N(6a)	168.7(2)	N(3)-Cu(1)-O(1)	95.07(19)
N(9)-Cu(1)-O(1)	93.14(19)	O(14)-Cu(1)-O(1)	98.4(2)
N(6a)-Cu(1)-O(1)	92.65(19)	O(1)-Mo(1)-O(8)	105.7(2)
O(1)-Mo(1)-O(12)	105.7(2)	O(8)-Mo(1)-O(12)	105.20(19)
O(1)-Mo(1)-O(13)	105.26(19)	O(8)-Mo(1)-O(13)	102.73(18)
O(12)-Mo(1)-O(13)	130.19(18)	O(1)-Mo(1)-O(11)	93.25(19)
O(8)-Mo(1)-O(11)	160.70(18)	O(12)-Mo(1)-O(11)	72.03(16)
O(13)-Mo(1)-O(11)	68.14(15)	O(3)-Mo(2)-O(2)	105.2(2)
O(3)-Mo(2)-O(9)	98.4(2)	O(2)-Mo(2)-O(9)	103.3(2)
O(3)-Mo(2)-O(11b)	93.6(2)	O(2)-Mo(2)-O(11b)	102.8(2)
O(9)-Mo(2)-O(11b)	147.18(18)	O(3)-Mo(2)-O(13b)	96.7(2)
O(2)-Mo(2)-O(13b)	157.9(2)	O(9)-Mo(2)-O(13b)	75.82(16)
O(11b)-Mo(2)-O(13b)	72.48(16)	O(3)-Mo(2)-O(8)	168.3(2)
O(2)-Mo(2)-O(8)	86.2(2)	O(9)-Mo(2)-O(8)	81.12(16)
O(11b)-Mo(2)-O(8)	81.13(17)	O(13b)-Mo(2)-O(8)	71.75(14)
O(4)-Mo(3)-O(5)	104.6(2)	O(4)-Mo(3)-O(9)	98.2(2)
O(5)-Mo(3)-O(9)	97.99(19)	O(4)-Mo(3)-O(10)	96.5(2)

O(5)-Mo(3)-O(10)	101.4(2)	O(9)-Mo(3)-O(10)	151.82(18)
O(4)-Mo(3)-O(12)	160.80(19)	O(5)-Mo(3)-O(12)	94.37(19)
O(9)-Mo(3)-O(12)	81.79(16)	O(10)-Mo(3)-O(12)	76.51(17)
O(4)-Mo(3)-O(13b)	91.58(18)	O(5)-Mo(3)-O(13b)	162.3(2)
O(9)-Mo(3)-O(13b)	72.17(15)	O(10)-Mo(3)-O(13b)	83.56(16)
O(12)-Mo(3)-O(13b)	70.04(14)	O(7)-Mo(4)-O(6)	107.1(2)
O(7)-Mo(4)-O(10)	104.6(2)	O(6)-Mo(4)-O(10)	116.3(2)
O(7)-Mo(4)-O(11)	103.2(2)	O(6)-Mo(4)-O(11)	112.3(2)
O(10)-Mo(4)-O(11)	112.02(19)	O(7)-Mo(4)-O(12)	170.48(19)
O(6)-Mo(4)-O(12)	82.28(18)	O(10)-Mo(4)-O(12)	71.50(16)
O(11)-Mo(4)-O(12)	71.17(17)		

3

Mo(1)-O(2)	1.686(5)	Mo(1)-O(1)	1.702(4)
Mo(1)-O(9)	1.894(4)	Mo(1)-O(8)	1.909(4)
Mo(1)-O(12)	2.357(4)	Mo(1)-O(13a)	2.372(5)
Mo(2)-O(4)	1.684(5)	Mo(2)-O(3)	1.711(4)
Mo(2)-O(8)	1.908(4)	Mo(2)-O(11)	1.916(4)
Mo(2)-O(10)	2.292(4)	Mo(2)-O(13a)	2.380(5)
Mo(3)-O(5)	1.683(5)	Mo(3)-O(12)	1.776(5)
Mo(3)-O(10)	1.777(5)	Mo(3)-O(13)	1.789(5)
Mo(4)-O(6)	1.679(6)	Mo(4)-O(7)	1.684(6)
Mo(4)-O(11a)	1.872(4)	Mo(4)-O(9)	1.888(4)
Mo(4)-O(12)	2.507(5)	Cu(1)-N(9)	1.996(5)
Cu(1)-N(9b)	1.996(5)	Cu(1)-N(3)	2.028(5)
Cu(1)-N(3b)	2.028(5)	Cu(1)-O(1c)	2.439(4)
Cu(1)-O(1d)	2.439(4)	Cu(2)-N(6)	2.000(5)
Cu(2)-N(6e)	2.000(5)	Cu(2)-N(12e)	2.006(5)
Cu(2)-N(12)	2.006(5)	Cu(2)-O(3e)	2.400(4)
Cu(2)-O(3)	2.400(4)	O(2)-Mo(1)-O(1)	103.2(2)
O(2)-Mo(1)-O(9)	99.5(2)	O(1)-Mo(1)-O(9)	101.5(2)
O(2)-Mo(1)-O(8)	100.0(2)	O(1)-Mo(1)-O(8)	100.1(2)
O(9)-Mo(1)-O(8)	146.57(19)	O(2)-Mo(1)-O(12)	163.2(2)
O(1)-Mo(1)-O(12)	93.3(2)	O(9)-Mo(1)-O(12)	73.52(18)
O(8)-Mo(1)-O(12)	80.08(17)	O(2)-Mo(1)-O(13a)	88.1(2)
O(1)-Mo(1)-O(13a)	167.8(2)	O(9)-Mo(1)-O(13a)	80.75(18)
O(8)-Mo(1)-O(13a)	73.09(17)	O(12)-Mo(1)-O(13a)	75.80(18)
O(4)-Mo(2)-O(3)	104.2(2)	O(4)-Mo(2)-O(8)	100.1(2)
O(3)-Mo(2)-O(8)	100.2(2)	O(4)-Mo(2)-O(11)	102.8(2)
O(3)-Mo(2)-O(11)	96.2(2)	O(8)-Mo(2)-O(11)	147.55(18)
O(4)-Mo(2)-O(10)	90.6(2)	O(3)-Mo(2)-O(10)	164.5(2)
O(8)-Mo(2)-O(10)	81.31(18)	O(11)-Mo(2)-O(10)	75.73(18)
O(4)-Mo(2)-O(13a)	165.6(2)	O(3)-Mo(2)-O(13a)	89.6(2)
O(8)-Mo(2)-O(13a)	72.91(17)	O(11)-Mo(2)-O(13a)	79.44(17)
O(10)-Mo(2)-O(13a)	76.00(18)	O(5)-Mo(3)-O(12)	109.3(3)

O(5)-Mo(3)-O(10)	109.8(3)	O(12)-Mo(3)-O(10)	110.3(2)
O(5)-Mo(3)-O(13)	107.9(3)	O(12)-Mo(3)-O(13)	110.5(2)
O(10)-Mo(3)-O(13)	109.0(2)	O(6)-Mo(4)-O(7)	106.1(3)
O(6)-Mo(4)-O(11a)	101.9(2)	O(7)-Mo(4)-O(11a)	103.3(2)
O(6)-Mo(4)-O(9)	100.6(2)	O(7)-Mo(4)-O(9)	104.9(2)
O(11a)-Mo(4)-O(9)	137.0(2)	O(6)-Mo(4)-O(12)	164.5(3)
O(7)-Mo(4)-O(12)	88.5(2)	O(11a)-Mo(4)-O(12)	79.10(17)
O(9)-Mo(4)-O(12)	69.98(17)	N(9)-Cu(1)-N(9b)	180.0
N(9)-Cu(1)-N(3)	90.5(2)	N(9b)-Cu(1)-N(3)	89.5(2)
N(9)-Cu(1)-N(3b)	89.5(2)	N(9b)-Cu(1)-N(3b)	90.5(2)
N(3)-Cu(1)-N(3b)	180.00(19)	N(9)-Cu(1)-O(1c)	89.91(19)
N(9b)-Cu(1)-O(1a)	90.09(19)	N(3)-Cu(1)-O(1c)	81.5(2)
N(3b)-Cu(1)-O(1c)	98.5(2)	N(9)-Cu(1)-O(1d)	90.09(19)
N(9b)-Cu(1)-O(1d)	89.91(19)	N(3)-Cu(1)-O(1d)	98.5(2)
N(3b)-Cu(1)-O(1d)	81.5(2)	O(1c)-Cu(1)-O(1d)	180.0(2)
N(6)-Cu(2)-N(6e)	180.0(3)	N(6)-Cu(2)-N(12e)	88.3(2)
N(6e)-Cu(2)-N(12e)	91.7(2)	N(6)-Cu(2)-N(12)	91.7(2)
N(6e)-Cu(2)-N(12)	88.3(2)	N(12e)-Cu(2)-N(12)	180.0(5)
N(6)-Cu(2)-O(3e)	90.08(18)	N(6e)-Cu(2)-O(3e)	89.92(18)
N(12e)-Cu(2)-O(3e)	89.92(19)	N(12)-Cu(2)-O(3e)	90.08(19)
N(6)-Cu(2)-O(3)	89.92(18)	N(6e)-Cu(2)-O(3)	90.08(18)
N(12e)-Cu(2)-O(3)	90.08(19)	N(12)-Cu(2)-O(3)	89.92(19)
O(3e)-Cu(2)-O(3)	180.0		

Symmetry codes: **[1]:** (a) x, y + 1, z; (b) x – 1, y, z; (c) –x + 2, –y + 1, –z; (d) x + 1, y, z; (e) x, y – 1, z. **[2]:** (a) –x + 1/2, y + 1/2, –z + 1/2; (b) –x + 1, –y + 2, –z; (c) –x, –y + 2, –z + 1; (d) –x + 1/2, y – 1/2, –z + 1/2. **[3]:** (a) –x + 1, –y, –z ; (b) –x, –y + 1, –z; (c) –x, –y, –z; (d) x, y + 1, z; (e) –x + 1, –y, –z + 1.

Fig. S1 Thermogravimetric (TG) curves for **1**–**3**.

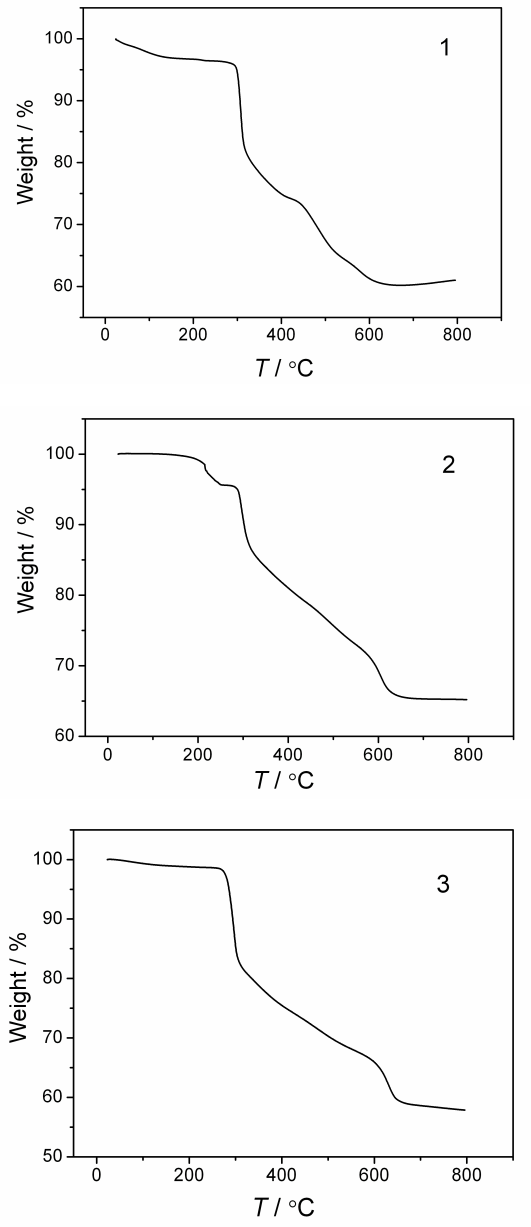

Fig. S2 The PXRD patterns of the simulated from the single-crystal diffraction data (red) and as-synthesized (black) for **1**–**3**.

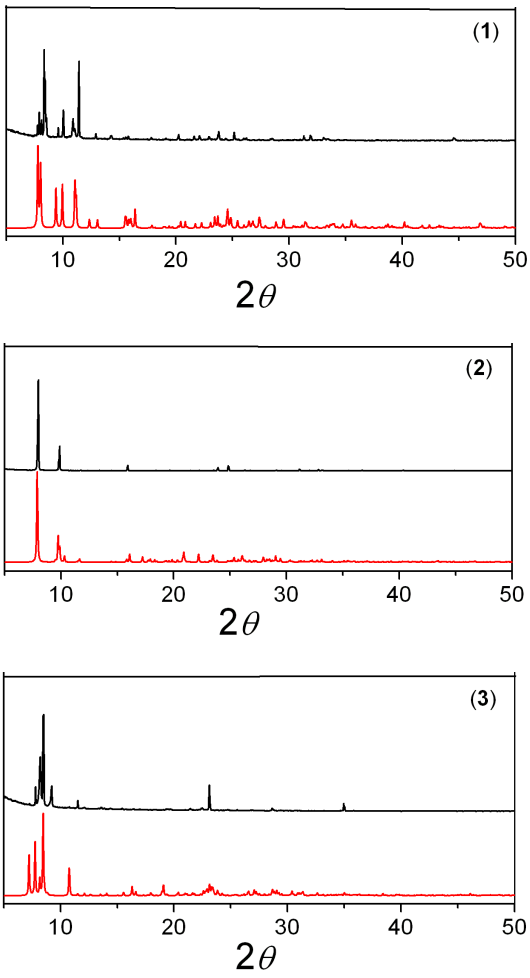

Fig. S3 Cyclic voltammograms of the **2**-CPE in 0.1 M H_2SO_4 at different scan rates (from inner to outer: 200, 240, 280, and 320 $mV \cdot s^{-1}$).

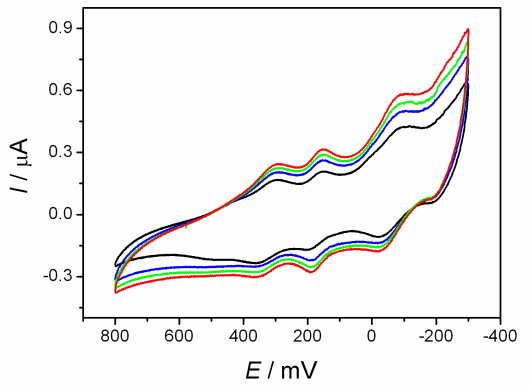

Fig. S4 (a) The **2**-CPE in 0.1 M H_2SO_4 containing 0, 1.5, 2.0 and 2.5 mM $NaBrO_3$. (b) The **2**-CPE in 0.1 M H_2SO_4 containing 0, 0.5, 1.0 and 3.0 mM $NaNO_2$. Scan rate: 80 $mV \cdot s^{-1}$.

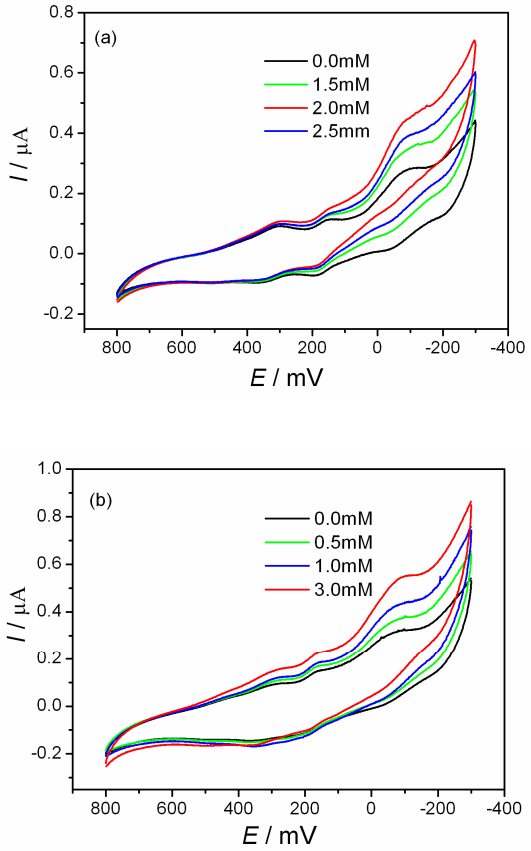

Fig. S5 Cyclic voltammograms of the **3**-CPE in 0.1 M H_2SO_4 at different scan rates (from inner to outer: 100, 140, 180, and 220 $mV \cdot s^{-1}$).

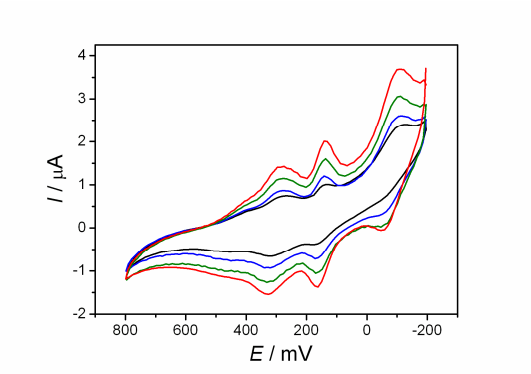

Fig. S6 (a) The **3**-CPE in 0.1 M H_2SO_4 containing 0, 2.0, 3.5 and 5.0 mM $NaBrO_3$. (b) The **3**-CPE in 0.1 M H_2SO_4 containing 0, 1.0, 3.0 and 5.0 mM $NaNO_2$. Scan rate: 80 $mV \cdot s^{-1}$.