Supplementary material for

Three cation-templated Cu(I) self-assemblies: synthesis, structures, and photocatalytic properties

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Table S1 Selected bond lengths (Å) and angles (◦) for compounds **1-3**

Bond	Å	Bond	Å	Bond	Å
		1			
Br1- Cu1	2.3803(10)	Br2-Cu1	2.3483(9)	Br3-Cu1	2.3678(11)
		2			
Cu1-Cu1^{1}	2.648(4)	Cu1-I2	2.600(2)	Cu2-I3	2.7028(16)
Cu1-Cu2^{2}	2.974(3)	Cu1-I3	2.715(2)	Cu2-I3^{1}	2.7028(16)
Cu1-Cu2	2.974(3)	Cu2-Cu1^{1}	2.974(3)	Cu2-I4	2.601(3)
Cu1-I1	2.7122(13)	Cu2-Cu2^{2}	2.756(5)	I1-Cu1^{1}	2.7122(13)
Cu1-I1^{2}	2.7122(13)	Cu2-I1	2.714(3)	I3-Cu2^{2}	2.7028(16)
		3			
Cu1-S1	2.4212(9)	Cu1-S2	2.3882(9)	Cu1-N1^{2}	1.983(3)
Cu1-N23	1.996(3)	S1-C1	1.657(3)	S2-C2	1.659(3)
N1-Cu1^{2}	1.983(3)	N1-C1	1.147(4)	N2-Cu1^{4}	1.996(3)
N2-C2	1.151(4)				
Angle	°	Angle	°	Angle	°
		1			
Br2-Cu1-Br1	123.38(4)	Br2-Cu1-Br3	123.72(4)	Br3-Cu1-Br1	112.65(4)
		2			
Cu1^{1}-Cu1-Cu2	63.57(5)	I1^{2}-Cu1-I1	120.40(8)	I3-Cu1-Cu2^{2}	56.51(6)
Cu1^{1}-Cu1-Cu2^{2}	63.57(5)	I1-Cu1-I3	105.34(6)	Cu1-Cu2-Cu1^{1}	52.86(9)
Cu1^{1}-Cu1-I1^{2}	60.78(4)	I1^{2}-Cu1-I3	105.34(6)	Cu2^{2}-Cu2-Cu1^{1}	62.40(5)
Cu1^{1}-Cu1-I1	60.78(4)	I2-Cu1-Cu1^{1}	136.94(5)	Cu2^{2}-Cu2-Cu1	62.40(5)
Cu1^{1}-Cu1-I3	111.33(5)	I2-Cu1-Cu2	148.04(6)	I1-Cu2-Cu1^{1}	56.74(6)
Cu2-Cu1-Cu2^{2}	55.21(11)	I2-Cu1-Cu2^{2}	148.04(6)	I1-Cu2-Cu1	56.74(6)
I1-Cu1-Cu2^{2}	104.85(8)	I2-Cu1-I1^{2}	107.03(5)	I1-Cu2-Cu2^{2}	111.07(6)
I1-Cu1-Cu2	56.78(6)	I2-Cu1-I1	107.03(5)	I3^{1}-Cu2-Cu1	102.43(9)

$I1^{2}$-Cu1-Cu2	104.86(8)	I2-Cu1-I3	111.73(8)	$I3^{1}$-Cu2-$Cu1^{1}$	56.90(6)
$I1^{2}$-Cu1-$Cu2^{2}$	56.78(6)	I3-Cu1-Cu2	56.51(6)	I3-Cu2-$Cu1^{1}$	102.43(9)
I3-Cu2-Cu1	56.90(6)	I4-Cu2-$Cu1^{1}$	149.52(7)	Cu1-I1-$Cu1^{1}$	58.43(7)
I3-Cu2-$Cu2^{2}$	59.34(5)	I4-Cu2-Cu1	149.52(7)	Cu1-I1-Cu2	66.48(7)
$I3^{1}$-Cu2-$Cu2^{2}$	59.34(5)	I4-Cu2-$Cu2^{2}$	136.92(7)	$Cu1^{1}$-I1-Cu2	66.48(7)
I3-Cu2-I1	105.64(7)	I4-Cu2-I1	112.01(10)	$Cu2^{2}$-I3-Cu1	66.59(7)
$I3^{1}$-Cu2-I1	105.64(7)	I4-Cu2-I3	108.01(7)	Cu2-I3-Cu1	66.59(7)
I3-Cu2-$I3^{1}$	117.57(10)	I4-Cu2-$I3^{1}$	108.01(7)	$Cu2^{2}$-I3-Cu2	61.32(10)
		3			
$N1^{2}$-Cu1-S1	101.73(7)	$N2^{3}$-Cu1-S1	113.48(8)	C2-S2-Cu1	102.31(10)
$N1^{2}$-Cu1-S2	113.49(8)	$N2^{3}$-Cu1-S2	106.25(8)	C1-N1-$Cu1^{2}$	157.8(2)
$N1^{2}$-Cu1$N2^{3}$	117.62(10)	C1-S1-Cu1	98.16(10)	C2-N2-$Cu1^{4}$	174.2(2)
N1-C1-S1	179.3(3)	N2-C2-S2	178.0(3)	S2-Cu1-S1	103.53(3)

Table S2. Structural parameters for the hydrogen bonds in **1**.

Hydrogen Bonds				
DH⋯A	d(D-A) Å	d(H-A) Å	d(D-A) Å	D-H-A/°
N2H2A⋯Br1[a]	0.86	2.68	3.457(5)	151.3
N4H4A⋯Br3[b]	0.87	2.55	3.346(4)	152.7

weak interactions					
DH⋯A	d(H-A) Å	DH⋯A	d(H-A) Å	DH⋯A	d(H-A) Å
N2-H2A⋯Br1	2.68	N2-H2B⋯Br1	3.03	C13-H13⋯Br3	2.79
C9-H9⋯Br2	2.84	C8-H8B⋯Br3	2.91	C8-H8A⋯Br1	2.92
C5-H5⋯Br1	2.96	C18-H18⋯Br2	2.79	C14-H14⋯Br3	2.99 Å
N4-H4B…Br2	2.97	N4-H4A…Br3	2.55		

symmetry code [a]1 - x, -1/2 + y, 1/2 - z; [b]2 - x, 1 - y, 1 - z

Table S3

Geometrical Coordinates of optimized complex $[MAPB][Cu_4I_8]$

C	-1	4.62825800	-4.46872800	-5.03665900
C	-1	4.62818200	4.46877500	-5.03665900
C	-1	4.50048300	-3.29293100	-4.43565900
C	-1	4.50042800	3.29297500	-4.43565800
C	-1	4.35804900	-5.66208900	-4.35435000
C	-1	4.35795300	5.66213100	-4.35434900
C	-1	3.97350900	-5.54008700	-3.02701700

C	-1	3.97341500	5.54012300	-3.02701600
C	-1	4.03438400	-1.85293000	-2.50393900
C	-1	4.03435200	1.85296600	-2.50393900
C	-1	3.83707900	-4.30722200	-2.49208800
C	-1	3.83700700	4.30725500	-2.49208800
C	-1	6.10971400	-1.76256000	-1.22576800
C	-1	6.10968400	1.76263100	-1.22576800
C	-1	4.76332900	-1.84343200	-1.19015500
C	-1	4.76329800	1.84348100	-1.19015500
C	-1	4.07885000	1.85749900	-0.00005400
C	-1	6.76742900	-1.67203700	-0.00006800
C	-1	4.07888200	-1.85746200	0.00004600
C	-1	6.76740100	1.67212000	0.00003200
C	-1	4.76334200	-1.84343300	1.19013900
C	-1	4.76331100	1.84348200	1.19013900
C	-1	6.10972700	-1.76256000	1.22573800
C	-1	6.10969700	1.76263200	1.22573800
C	-1	3.83710600	-4.30722200	2.49208100
C	-1	3.83703300	4.30725500	2.49208100
C	-1	4.03441000	-1.85292800	2.50393100
C	-1	4.03437800	1.85296500	2.50393100
C	-1	3.97354100	-5.54008700	3.02700900
C	-1	3.97344700	5.54012200	3.02701000
C	-1	4.35809500	-5.66209000	4.35433800
C	-1	4.35799900	5.66213100	4.35433800
C	-1	4.50053100	-3.29293000	4.43564600
C	-1	4.50047500	3.29297500	4.43564600
C	-1	4.62831100	-4.46872800	5.03664400
C	-1	4.62823500	4.46877500	5.03664400
Cu	-1	-3.77019700	0.00000200	-1.32391300
Cu	-1	-1.49578100	-1.37468200	-0.00002500
Cu	-1	-1.49580500	1.37462500	-0.00002500
Cu	-1	-3.77018300	0.00000200	1.32398700
H	0	4.91222100	-4.49873200	-6.08429500
H	0	4.91214600	4.49878300	-6.08429500
H	0	4.61592100	-6.91661700	-5.91716200
H	0	4.61580300	6.91666300	-5.91716100
H	0	4.68628100	-2.36241500	-4.95855300
H	0	4.68624600	2.36246300	-4.95855200
H	0	4.13187200	-7.66223000	-4.46141800
H	0	4.13174400	7.66226900	-4.46141800
H	0	4.46511800	-1.14096200	-3.20836900
H	0	4.46509400	1.14100600	-3.20837200
H	0	3.69061900	-6.40572700	-2.43791100

H	0	3.69051200	6.40575800	-2.43791100
H	0	2.96508700	-1.64121400	-2.38375200
H	0	2.96505900	1.64123200	-2.38374800
H	0	6.66887700	-1.71994700	-2.15570700
H	0	6.66887900	1.72002600	-2.15568500
H	0	3.43846300	-4.16279000	-1.49386600
H	0	3.43839000	4.16281800	-1.49386700
H	0	2.98687600	1.91471600	0.00002800
H	0	7.85124900	-1.57242900	-0.00011700
H	0	2.98690900	-1.91469600	0.00012200
H	0	7.85122300	1.57253000	-0.00002000
H	0	3.43853300	-4.16277600	1.49385900
H	0	3.43846300	4.16280200	1.49385900
H	0	6.66887400	-1.72014400	2.15567300
H	0	6.66881300	1.72022600	2.15569600
H	0	2.96519400	-1.63952400	2.38376100
H	0	2.96516500	1.63954200	2.38376600
H	0	3.69092500	-6.40574900	2.43780600
H	0	3.69081500	6.40578000	2.43780700
H	0	4.46607300	-1.14121800	3.20811800
H	0	4.46605900	1.14126200	3.20811600
H	0	4.13203500	-7.66224600	4.46137500
H	0	4.13190500	7.66228400	4.46137600
H	0	4.68718100	-2.36246900	4.95831600
H	0	4.68713700	2.36251600	4.95831700
H	0	4.61590700	-6.91665400	5.91714400
H	0	4.61579200	6.91670100	5.91714400
H	0	4.91270000	-4.49871800	6.08416300
H	0	4.91262300	4.49876900	6.08416300
I	-1	-5.54520700	-0.00001300	-3.22340300
I	-1	-1.24060100	0.00002400	-2.31142600
I	-1	-4.02287000	-2.35360000	-0.00001100
I	-1	-4.02291000	2.35350000	-0.00001100
I	-1	0.28658200	-3.27853300	-0.00003400
I	-1	0.28652700	3.27850600	-0.00003400
I	-1	-1.24057700	0.00002400	2.31147400
I	-1	-5.54517300	-0.00001300	3.22349700
N	-1	4.46942700	-6.83202700	-4.92326100
N	-1	4.46931100	6.83207100	-4.92326100
N	-1	4.16362700	-3.20821500	-3.16256800
N	-1	4.16357300	3.20825400	-3.16256800
N	-1	4.16366100	-3.20821600	3.16255800
N	-1	4.16360700	3.20825400	3.16255900
N	-1	4.46947900	-6.83202700	4.92324800

N	-1	4.46936400	6.83207100	4.92324800

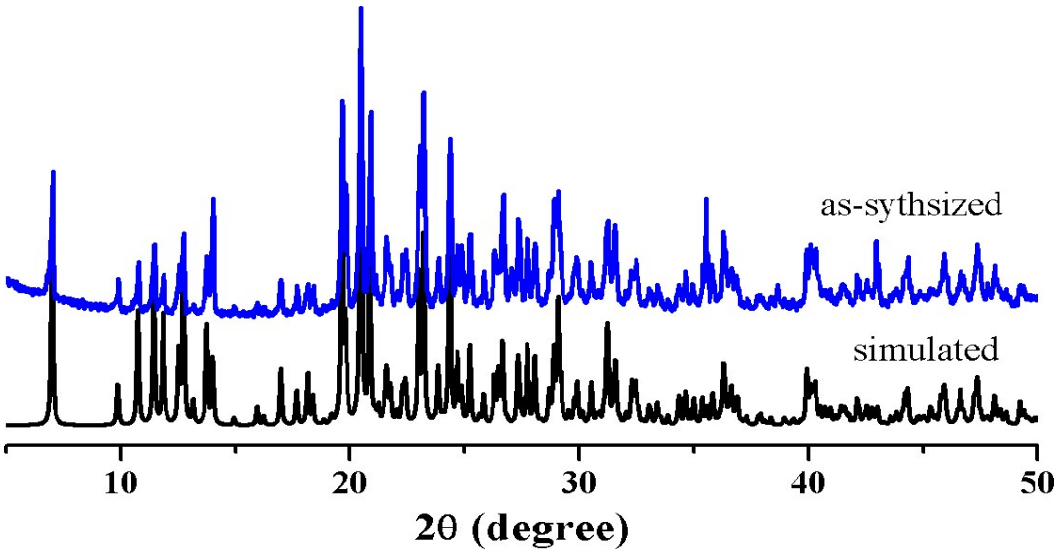

Fig. S1 PXRD patterns for compound 1 and simulated spectra of compound 1 from single crystal data.

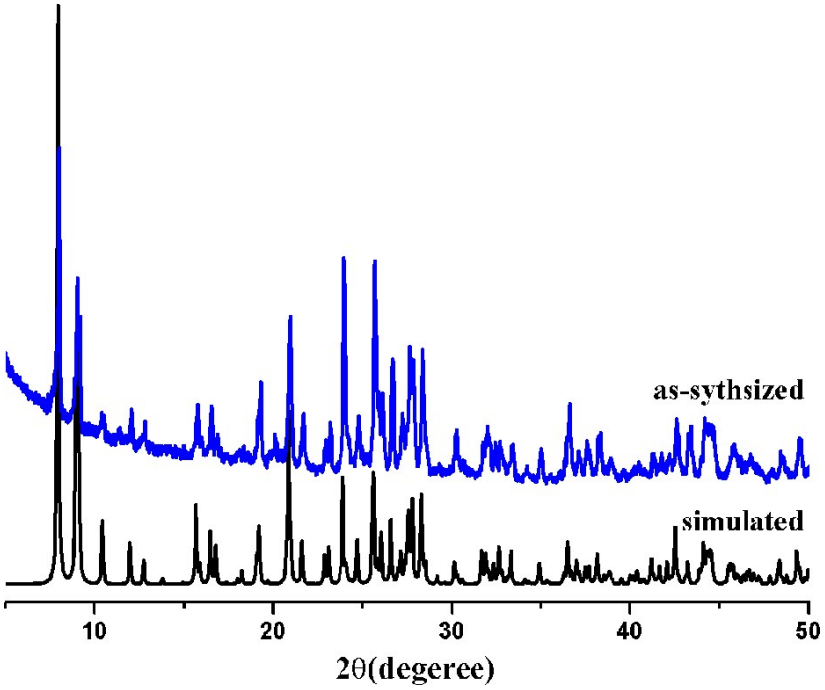

Fig. S2 PXRD patterns for compound 2 and simulated spectra of compound 2 from single crystal data.

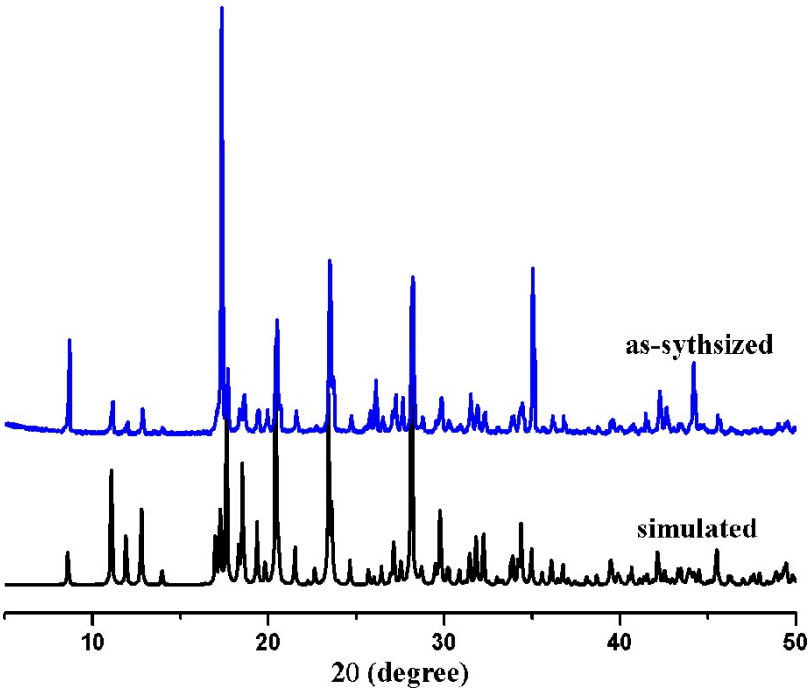

Fig. S3 PXRD patterns for compound 3 and simulated spectra of compound 3 from single crystal data.

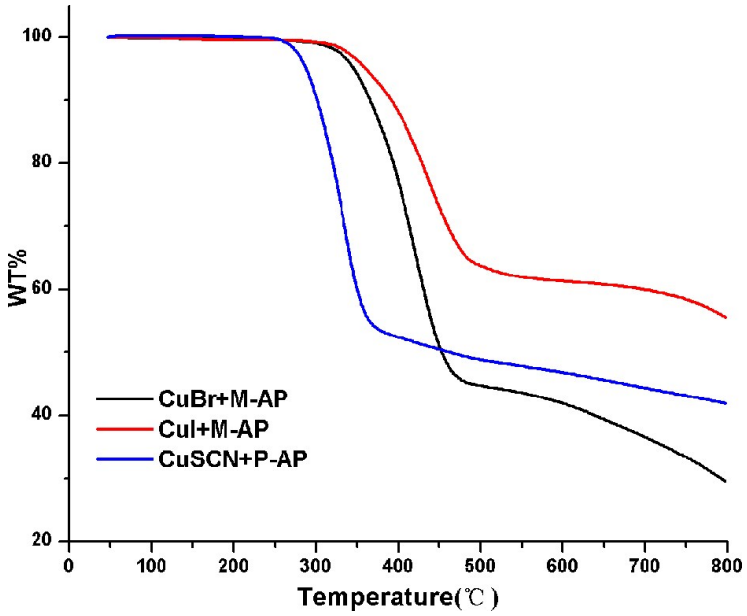

Fig. S4 Thermal gravimetric analysis (TGA) curves for as-synthesized compound **1-3**.

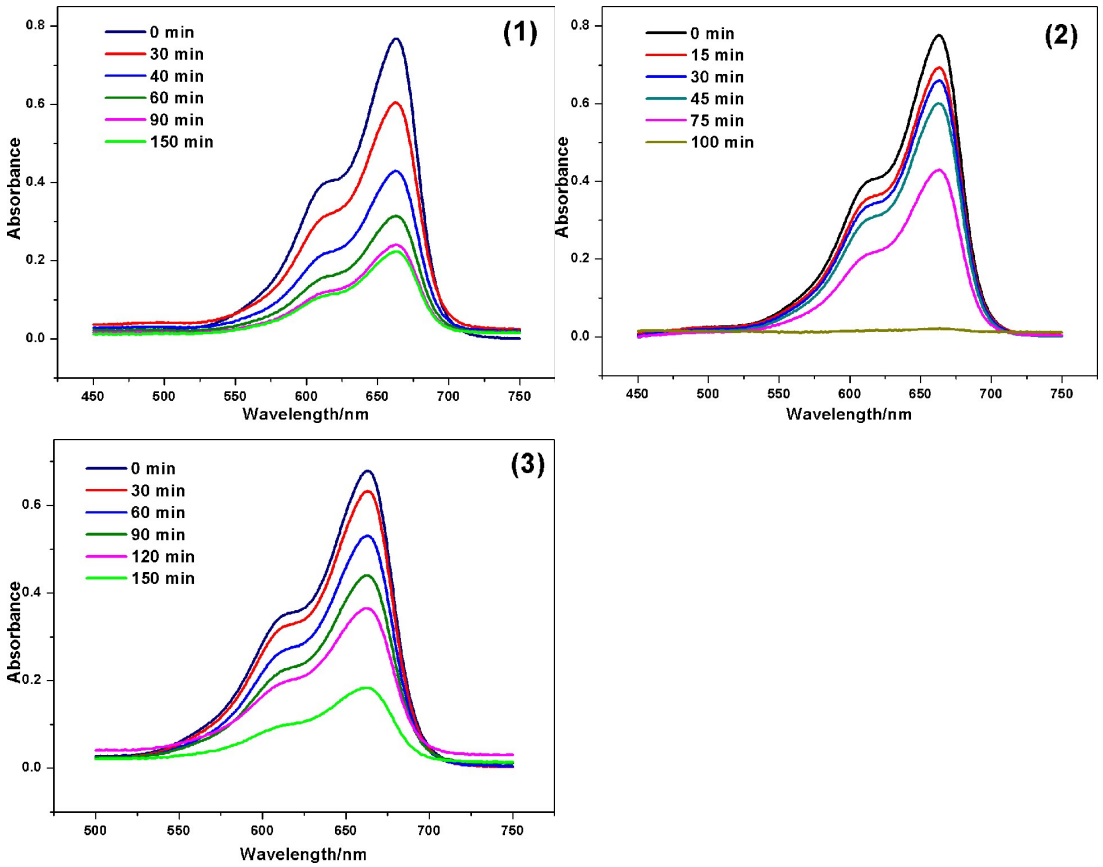

Fig. S5 UV-Vis absorption spectra of methylene blue solution in presence of **1-3** for different time periods.

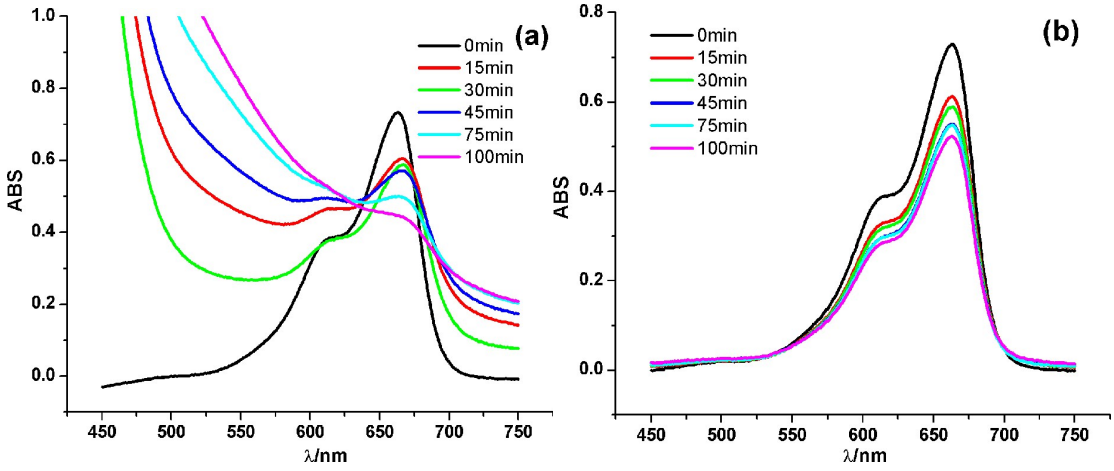

Fig. S6 UV-Vis absorption spectra of methylene blue solution in the trapping experiment of active species during the photocatalytic reaction:(a) 0.1M BQ(a quencher of $\bullet O^{2-}$); (b) 0.1M IPA(a quencher of $\bullet OH$)