

Electronic Supplementary Information

[Co(2,2'-bipy)₃]Ag₃I₆ with hole structure facilitates dye adsorption and photocatalytic reduction

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Table of contents

Table S1. Selected bond lengths (Å) and angles (°) of compound 1	S3
Table S2. Hydrogen bond lengths (Å) and angles (°) of compound 1	S4
Table S3. Summary of structures of silver halogenides directed by transition metal cations and their photocatalytic properties	S5
Figures	S8
Fig. S1 The photo of crystals of 1	S8
Fig. S2 Variance of UV-vis spectra with time for RhB in the presence of compound 1	S8
Fig. S3 Simulated, after adsorption and after release powder XRD patterns of compound 1	S9
Fig. S4 Experimental and simulated powder XRD patterns of compound 1	S9
Fig. S5 Variance of $\ln(C_0/C)$ value with reaction time for the degradation of RhB by compound 1	S10
.....	S10
Fig. S6 Radical-trapping experiments for the degradation of RhB by compound 1	S10
References.....	S11

Table S1. Selected bond lengths (Å) and angles (°) of compound **1**.

Ag(1)–I(1)	2.9023(6)	Ag(1)–I(2)	2.9305(6)
Ag(1)–Ag(1)#1	3.3491(7)	Co(1)–N(1)	1.927(4)
Co(1)–N(2)	1.931(4)		
I(1)–Ag(1)–I(1)#1	108.49(19)	I(1)–Ag(1)–I(1)#2	100.20(2)
I(1)#1–Ag(1)–I(1)#2	109.26(19)	I(1)–Ag(1)–I(2)	114.40(2)
I(1)#1–Ag(1)–I(2)	112.00(19)	I(1)#2–Ag(1)–I(2)	111.80(19)
Ag(1)–I(1)–Ag(1)#1	70.30(14)	Ag(1)–I(1)–Ag(1)#2	113.93(2)
Ag(1)–I(1)–Ag(1)#2	70.70(14)	N(1)–Co(1)–N(1)#1	93.59(16)
N(1)–Co(1)–N(1)#2	93.59(16)	N(1)#1–Co(1)–N(1)#2	93.58(16)
N(1)–Co(1)–N(2)	83.66(16)	N(1)–Co(1)–N(2)#1	88.42(15)
N(1)–Co(1)–N(2)#2	176.70(15)	N(1)#1–Co(1)–N(2)	176.70(15)
N(1)#2–Co(1)–N(2)	88.42(15)	N(1)#1–Co(1)–N(2)#1	83.66(16)
N(1)#1–Co(1)–N(2)#2	88.42(15)	N(1)#2–Co(1)–N(2)#1	176.70(15)
N(1)#2–Co(1)–N(2)#2	83.66(16)	N(2)#1–Co(1)–N(2)	94.42(16)
N(2)#2–Co(1)–N(2)	94.42(16)	N(2)#1–Co(1)–N(2)#2	94.42(16)

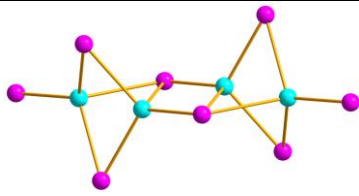
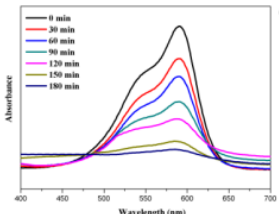
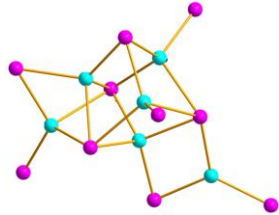
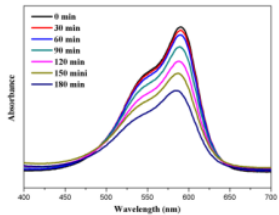
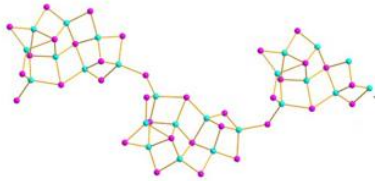
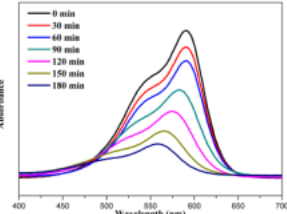
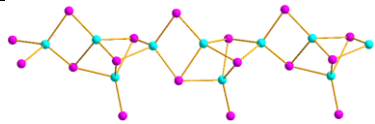
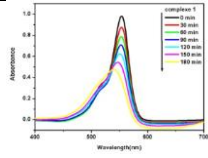
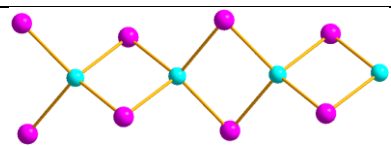
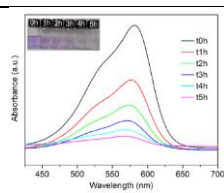
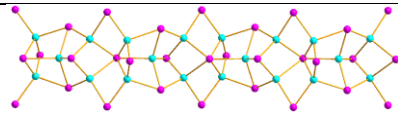
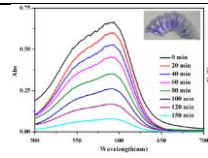
Symmetry transformations used to generate equivalent atoms: #1 $x-y+2/3, x+1/3, -z+1/3$; #2 $-y+1, x-y+1, z$; #3 $y-1/3, -x+y+1/3, -z+1/3$; #4 $-x+y, -x+1, z$.

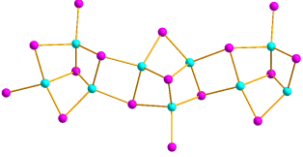
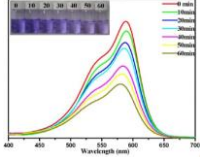
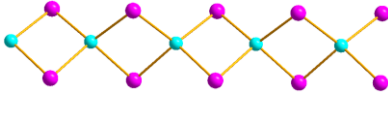
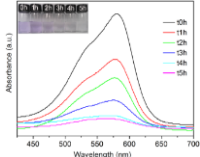
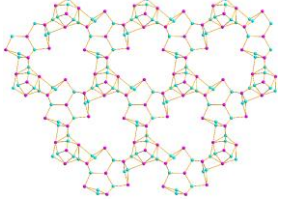
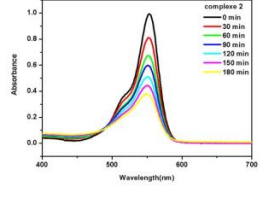
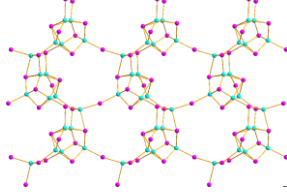
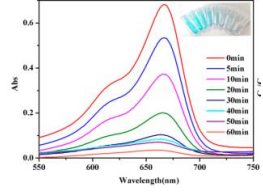
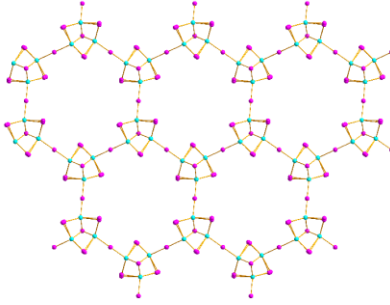
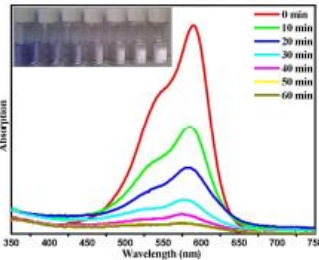
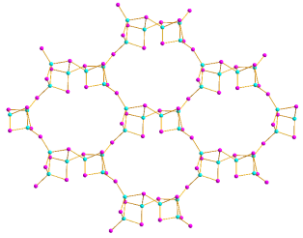
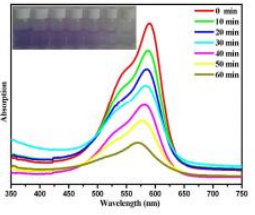
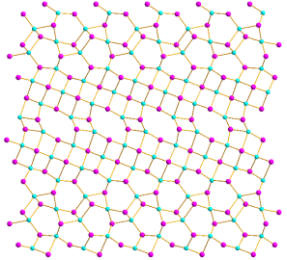
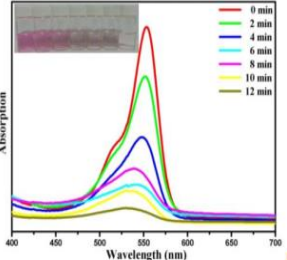
Table S2. Hydrogen bond lengths (Å) and angles (°) of compound **1**.

D–H···A	d(H···A)	d(D···A)	<(DHA)
C(1)–H(1)···N(1)#1	2.46	2.971(6)	114.0
C(2)–H(2)···I(2)	3.17	3.867(5)	134.0
C(4)–H(4)···I(1)	3.22	3.845(5)	127.0
C(4)–H(4)···I(2)	3.33	3.847(5)	118.0
C(10)–H(10)···N(2)#2	2.52	3.021(6)	114.0

Symmetry transformations used to generate equivalent atoms: #1 $-y+1, x-y+1, z$; #2 $-x+y, -x+1, z$; #3 $-x+1, -y+1, -z+1$; #4 $x, y, z+1$.

Table S3. Summary of structures of silver halogenides directed by transition metal cations and their photocatalytic properties.

Compound formulae	Anion structure	Photocatalytic property	Ref
[TM(phen) ₃]Ag ₂ I ₄ ·3 DMF (TM = Co, Ni, Zn)			1
[TM(phen) ₃]Ag ₃ I ₅ ·D MF (TM = Co, Ni, Zn)			1
[TM(phen) ₃] ₂ Ag ₈ I ₁₂ ·7DMF (TM = Co, Ni, Zn)			1
[Co(phen) ₃](Ag ₃ I ₅)·2CH ₃ CN			2
[Cu(phen) ₂ (Br)]AgB r ₂			3
[Ni(DMSO) ₆][Ag ₅ I ₇]			4

[TM(2,2-bipy) ₃]Ag ₃ I ₅ (TM = Mn, Fe, Co, Ni, Zn)			5
[Fe(phen) ₂ (Cl) ₂] ₂ Ag ₂ Br ₄			3
[M(phen) ₃] ₂ Ag ₁₁ I ₁₅ ·H ₂ O (M = Co, Cu)			2
[V(DMSO) ₅ (H ₂ O)] [Ag ₆ I ₈]			4
K _x [TM(2,2-bipy) ₃] ₂ Ag ₆ I ₁₁ (TM = Mn, Fe, Co, Ni, Zn; x = 0.89–1)			6
[(Ni(2,2-bipy) ₃)[H-2,2-bipy]Ag ₃ I ₆			6
[TM(2,2-bipy) ₃] ₂ Ag ₁₃ Br ₁₇ (T M = Ni, Co, Zn, Fe)			7

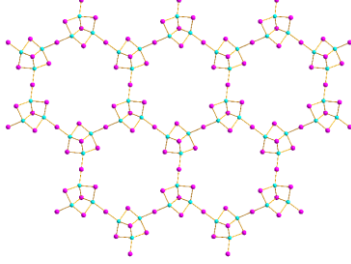
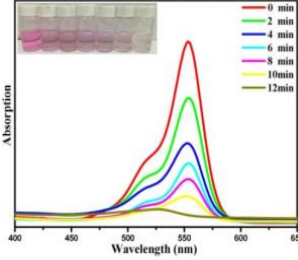
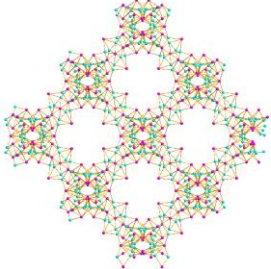
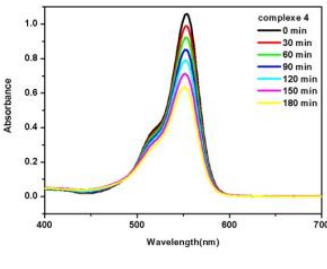
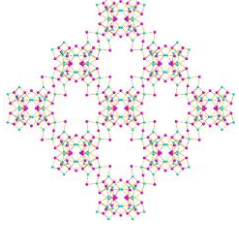
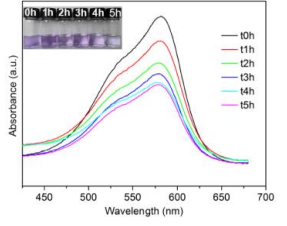
<p>$K[Co(2,2-$ $bipy)_3]_2Ag_6Br_{11}$</p>			<p>7</p>
<p>$[M(phen)_3]_2Ag_{13}I_{17}$ (M = Co, Cd)</p>			<p>2</p>
<p>$[TM(phen)_3]_2Ag_{13}Br$ $_{17} \cdot 2dmsO \cdot 3H_2O$ (TM = Fe, Co, Ni)</p>			<p>3</p>



Fig. S1 The photo of crystals of compound **1**.

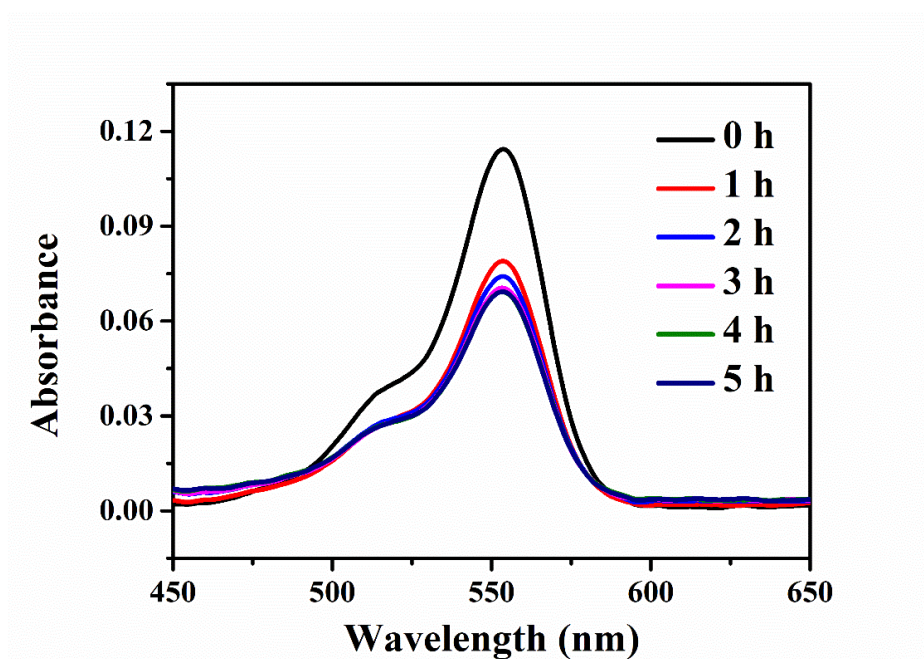


Fig. S2 Variance of UV-vis spectra with time for RhB in the presence of compound **1**.

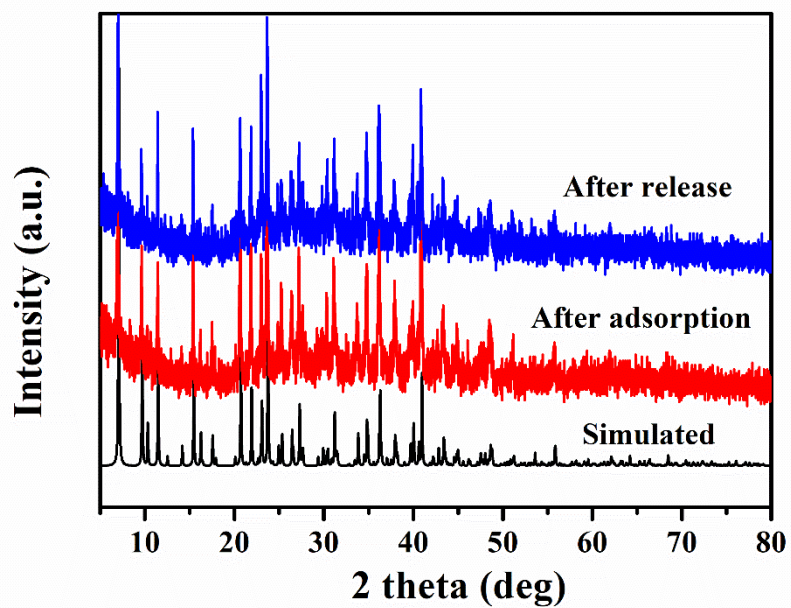


Fig. S3 Simulated, after adsorption and after release powder XRD patterns of compound **1**.

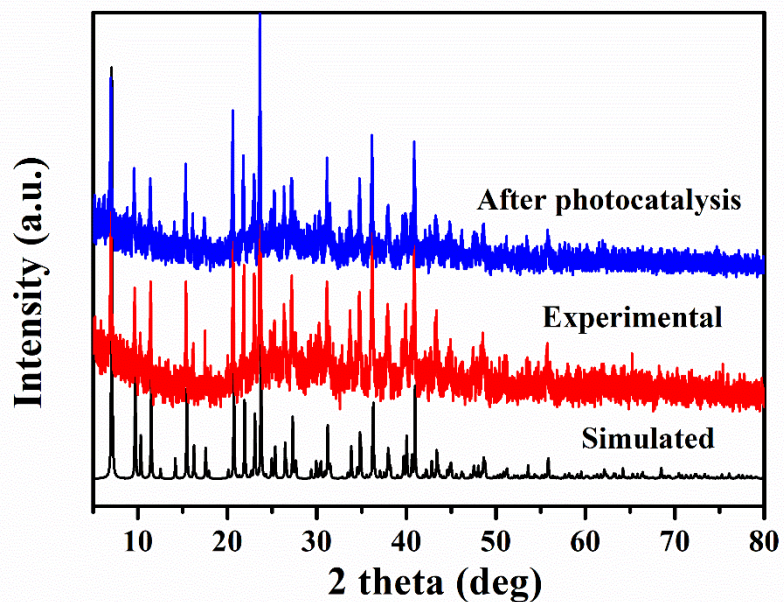


Fig. S4 Experimental and simulated powder XRD patterns of compound **1**.

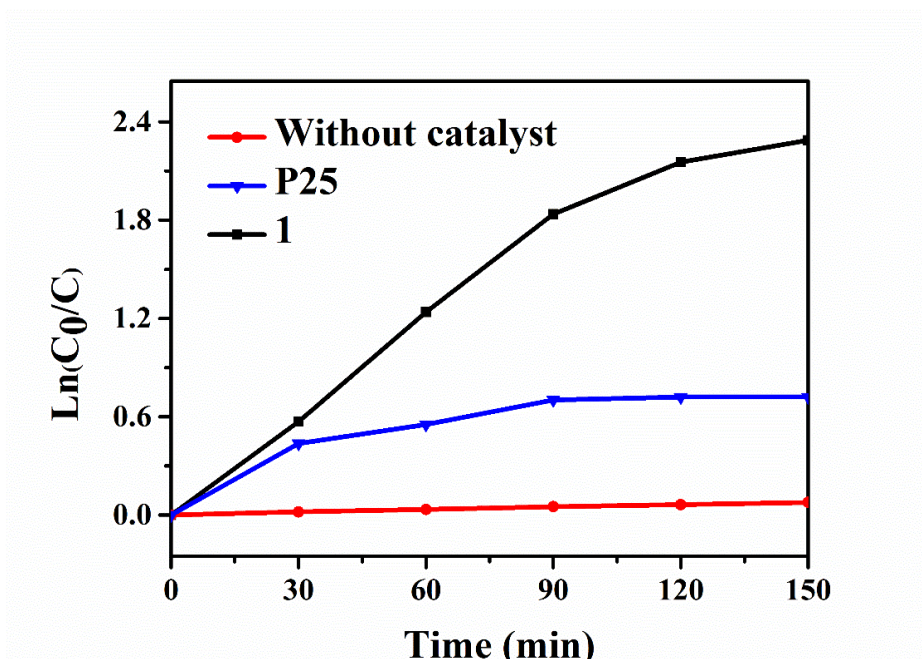


Fig. S5 Variance of $\ln(C_0/C)$ value with reaction time for the degradation of RhB by compound 1.

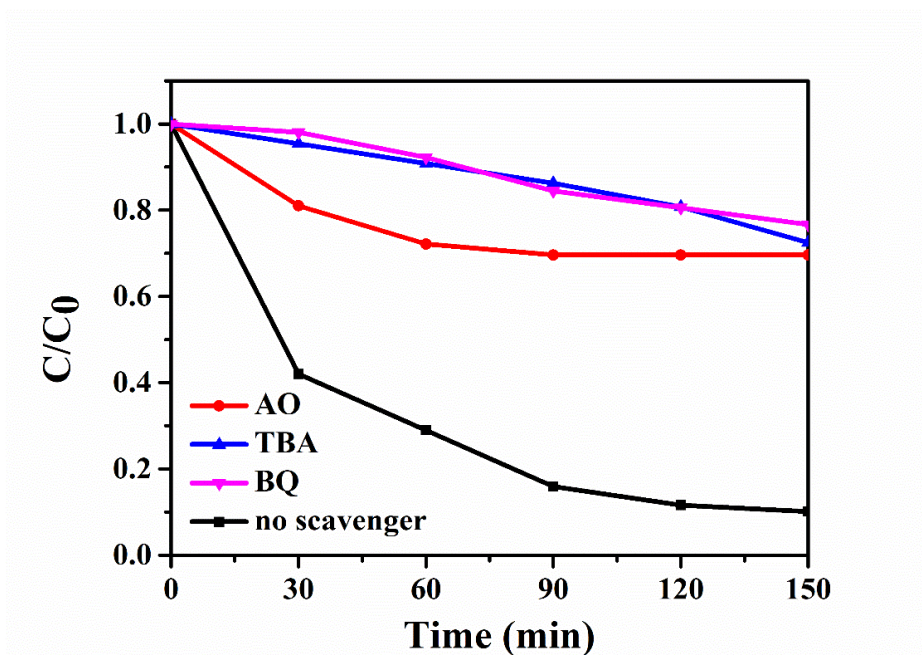


Fig. S6 Radical-trapping experiments for the degradation of RhB by compound 1.

References

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