

Supporting information

Interlinking supertetrahedral chalcogenolate clusters with bipyridines to form two-dimensional coordination polymers for photocatalytic degradation of organic dye

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Experimental Sections

Materials and measurements

All the solvents and chemicals of PhSH, PhSeSePh, Cd(NO₃)₂·4H₂O, AgNO₃, and 4,4'-trimethylenedipiperidine (tmdp) were purchased from Sigma-Aldrich and used without further purification. [Cd₄(SPh)₈]_n^[1] and [Cd₄(SePh)₈]_n^[2] were prepared by the literature procedures. All syntheses were carried out under air atmosphere at room temperature. All elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyzer. Thermal gravimetric analysis (TGA) data was recorded on a Mettler Toledo TGA/SDTA851e thermogravimetric analyzer under N₂ flow. Infrared spectra were recorded on a Bruker Tensor 27 spectrometer with the ATR mode. UV/vis absorption and solid-state diffuse reflectance spectra were recorded on a Shimadzu UV3600 UV/VIS/NIR spectrometer. BaSO₄ as 100 % reflectance references was used in the recordings of the solid-state diffuse spectra. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker Focus D8 diffractometer.

Preparation of Cd₆Ag₄(SPh)₁₆(DMF)₃(CH₃OH) (1)

To a well stirred solution of [Cd₄(SPh)₈] (99 mg, 0.075 mmol) in 4 mL DMF, AgNO₃ (25 mg, 0.15 mmol) was added. A mixture with small amount of white precipitate was then formed. After the mixture stirred overnight, the white precipitate was removed by filtration. The colorless filtrate was collected and carefully layered with 10 mL of CH₃OH. Colorless crystals of **1** were obtained in 3 days. Yield: 94 mg (61 % based on [Cd₄(SPh)₈]). Anal. Calcd. for C₁₀₆H₁₀₅N₃O₄S₁₆Ag₄Cd₆: C, 41.02; H, 3.41; N, 1.35%. Found: C, 41.37; H, 3.32; N, 1.31%.

Preparation of Cd₆Ag₄(SePh)₁₆(DMF)₃(CH₃OH) (2**)**

The method was similar to that used for **1** except using [Cd₄(SePh)₈] (128 mg, 0.075 mmol) instead of [Cd₄(SPh)₈]. Colorless crystals of **2** were obtained in a week. Yield: 105 mg (54 % based on [Cd₄(SePh)₈]). Anal. Calcd. for C₁₀₆H₁₀₅N₃O₄Se₁₆Ag₄Cd₆: C, 33.03; H, 2.75; N, 1.09 %. Found: C, 33.87; H, 2.66; N, 1.14 %.

Preparation of Cd₆Ag₄(SPh)₁₆(tmdp)₂ (3**)**

To a colorless solution of **1** (46 mg, 0.015 mmol) in 3 mL DMF, tmdp (18 mg, 0.1 mmol) was added under stirring. The mixture was stirred overnight. Colorless crystals of **3** were obtained in 3 days by slow evaporation of the yellow filtration. Yield: 35 mg (73 % based on **1**). Anal. Calcd. for C₁₂₂H₁₀₈N₄S₁₆Ag₄Cd₆: C, 45.10; H, 3.35; N, 1.72%. Found: C, 45.92; H, 3.33; N, 1.68%.

Preparation of Cd₆Ag₄(SePh)₁₆(tmdp)₂ (4**)**

The method was similar to that used for **3** by using **2** (58 mg, 0.015 mmol) instead of **1**. Yellow crystals of **4** were obtained. Yield: 42 mg (70 % based on **2**). Anal. Calcd. for C₁₂₂H₁₀₈N₄O₄Se₁₆Ag₄Cd₆: C, 36.64; H, 2.72; N, 1.40%. Found: C, 36.81; H, 2.76; N, 1.34%.

X-ray crystallography

Crystallographic data was collected on a Bruker SMART Apex 2K CCD diffractometer with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 296 K. Data reduction was

performed with SAINT software.^[3] SADABS was used for absorption corrections.^[4] Structures were solved by direct methods using SHELXS software package.^[5,6] All non-hydrogen atoms were refined anisotropically. Crystallographic data and experimental details for **1**, **2**, **3**, and **4** were summarized in Table S1. The unit cells include disordered solvent molecules (DMF or methanol) which could not be modeled as discrete atomic sites. We employed PLATON/SQUEEZE to calculate the diffraction contribution of the solvent molecules to generate a set of solvent-free diffraction intensities. The calculated moiety formulas and sum formulas for 1, 2, 3, 4 are given in Table S1.

Table S1. Crystal data and structure refinement details of the clusters and the coordination polymers

Compound	1 · DMF	2 · 2 DMF · MeOH	3 · 4 DMF	4 · 5 DMF
Molecular formula	C ₁₀₉ H ₁₁₂ N ₄ O ₅ S ₁₆ Ag ₄ Cd ₆	C ₁₁₃ H ₁₂₃ N ₅ O ₇ Se ₁₆ Ag ₄ Cd ₆	C ₁₃₄ H ₁₃₆ N ₈ O ₄ S ₁₆ Ag ₄ Cd ₆	C ₁₃₇ H ₁₄₃ N ₉ O ₅ Se ₁₆ Ag ₄ Cd ₆
Formula weight	3176.86	4032.40	3541.34	4364.84
Crystal system	triclinic	Triclinic	monoclinic	monoclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> (Å)	17.0418(3)	18.2015(14)	20.1772(3)	20.4073(5)
<i>b</i> (Å)	17.8011(3)	20.1673(17)	25.6535(4)	25.9530(6)
<i>c</i> (Å)	20.4041(3)	21.5676(19)	53.9920(9)	54.7443(16)
α (°)	92.7800(10)	67.211(6)	90.00	90
β (°)	91.3500(10)	86.452(6)	98.1050(10)	97.956(2)
γ (°)	101.3720(10)	68.354(5)	90	90
<i>V</i> (Å ³)	6057.71(17)	6753.8(10)	27668.0(8)	28715.2(13)
<i>Z</i>	2	2	8	8
ρ (g cm ⁻³)	1.742	1.983	1.700	2.019
μ (mm ⁻¹)	1.987	5.851	1.751	5.513
<i>F</i> (000)	3132	3824	12800	16704
<i>T</i> /K	296(2)	296(2)	296(2)	296(2)
No. of total reflns.	21305	23761	24365	25303
GOF	0.998	0.979	1.008	0.938
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> >2 σ (<i>I</i>)]	0.0376, 0.0896	0.0849, 0.1838	0.0610, 0.1486	0.0736, 0.1774
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0572, 0.1006	0.2560, 0.2152	0.1288, 0.1698	0.1977, 0.2088

Photocatalysis measurement

The clusters and coordination polymers were applied as photocatalysts for degradation of Rhodamine B (RhB) in aqueous solution under visible light illumination. A 50 W Xenon lamp fitted with a cut-off filter ($\lambda > 380$ nm) was used as a light source. Typically, 20 mg of the photocatalyst was dispersed in 10 mL of RhB aqueous solution (4.18×10^{-5} M, 20 mg L^{-1}). The mixture was stirred for 1 h in the dark to afford a homogeneous suspension before the analysis. The suspension was then irradiated by light during stirring. Aliquots of 1 mL were withdrawn from the suspension at an interval of 5 or 30 min. The dispersed catalyst in the withdrawn mixture was removed by centrifugation and the concentration of RhB in the clear sample solution was analyzed by the UV/vis spectrometer.

For the cyclic photocatalysis test, 40 mg of **1** was used as the catalyst. After photocatalytic degradation of the dye solution, the catalyst was collected by centrifugation and washed by water and acetone several times. The recycled solid was used as the catalyst for photocatalytic degradation of the dye solution again for the evaluation of its cyclic photocatalytic performance.

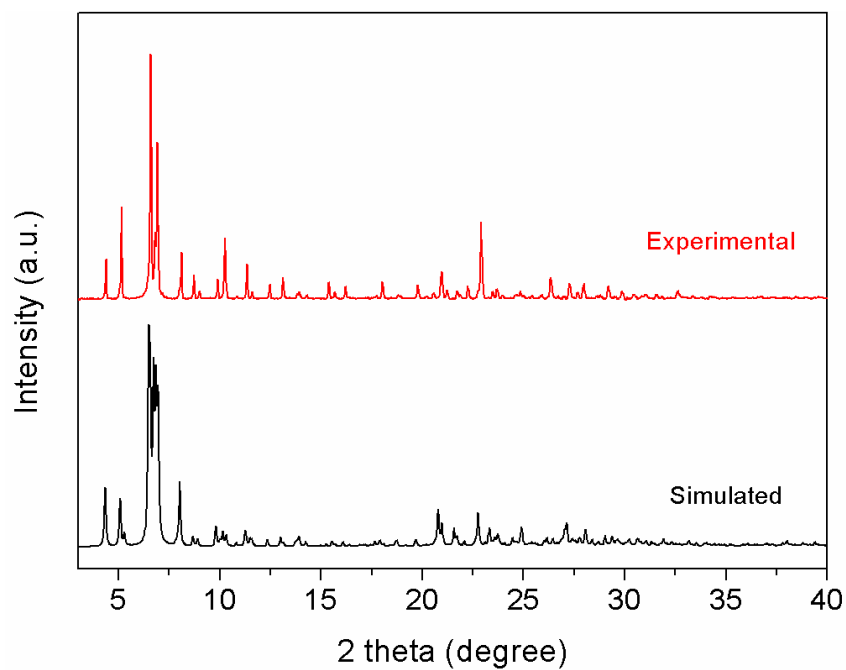


Fig. S1 Experimental and simulated powder X-ray diffraction patterns of $\text{Cd}_6\text{Ag}_4(\text{SPh})_{16}(\text{DMF})_3(\text{CH}_3\text{OH})$ (**1**).

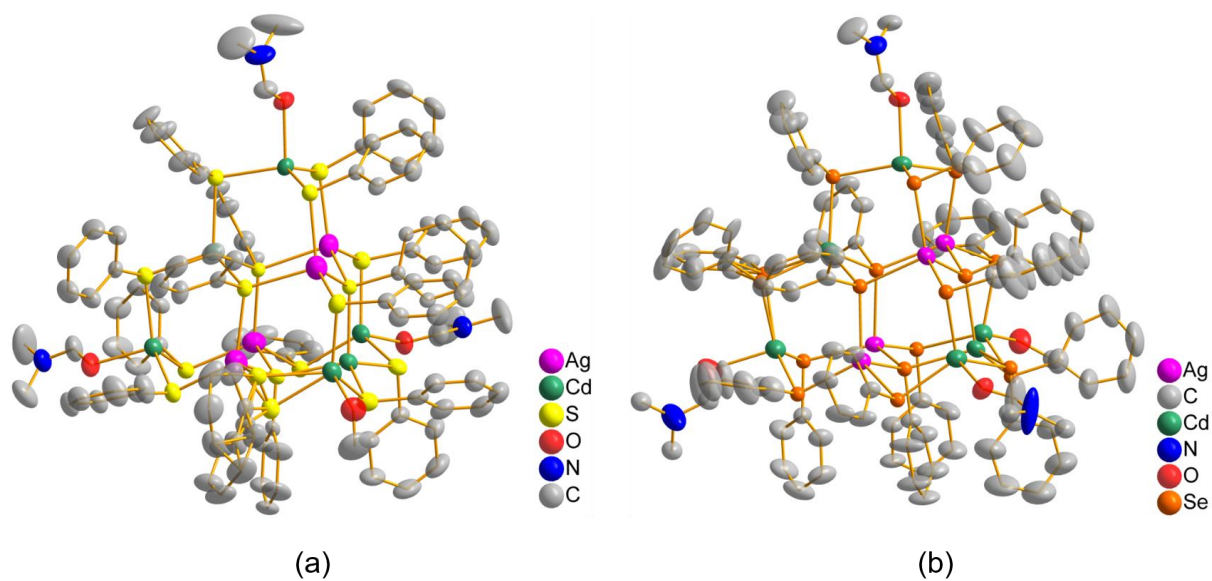


Fig. S2 Molecular structure of (a) $\text{Cd}_6\text{Ag}_4(\text{SPh})_{16}(\text{DMF})_3(\text{CH}_3\text{OH})$ and (b) $\text{Cd}_6\text{Ag}_4(\text{SePh})_{16}(\text{DMF})_3(\text{CH}_3\text{OH})$, showing 30 % thermal ellipsoids.

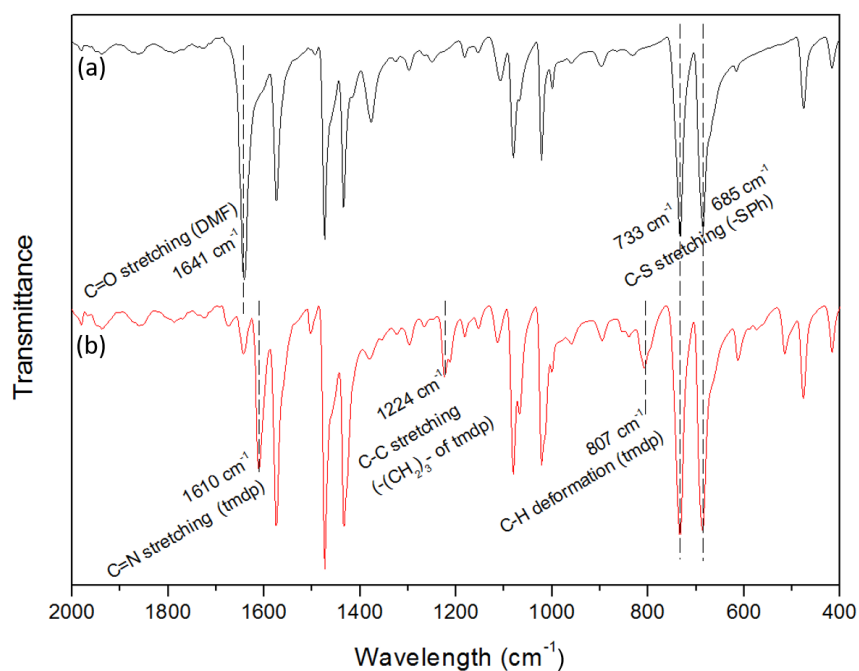


Fig. S3 Infrared spectra of (a) $\text{Cd}_6\text{Ag}_4(\text{SPh})_{16}(\text{DMF})_3(\text{CH}_3\text{OH})$ (**1**) and (b) $\text{Cd}_6\text{Ag}_4(\text{SPh})_{16}(\text{tmdp})_2$ (**3**).

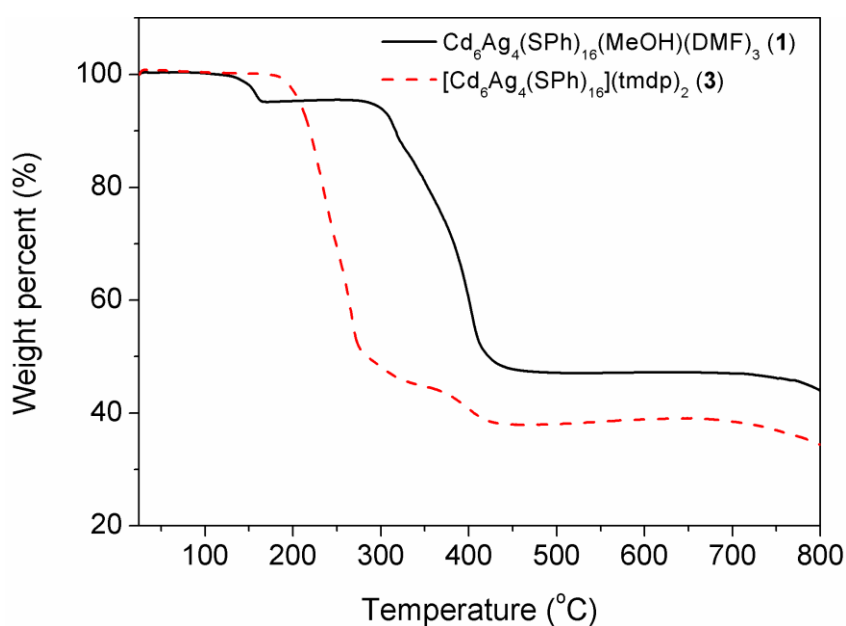


Fig. S4 Thermogravimetric analysis curves of $\text{Cd}_6\text{Ag}_4(\text{SPh})_{16}(\text{DMF})_3(\text{CH}_3\text{OH})$ (**1**) and $\text{Cd}_6\text{Ag}_4(\text{SPh})_{16}(\text{tmdp})_2$ (**3**).

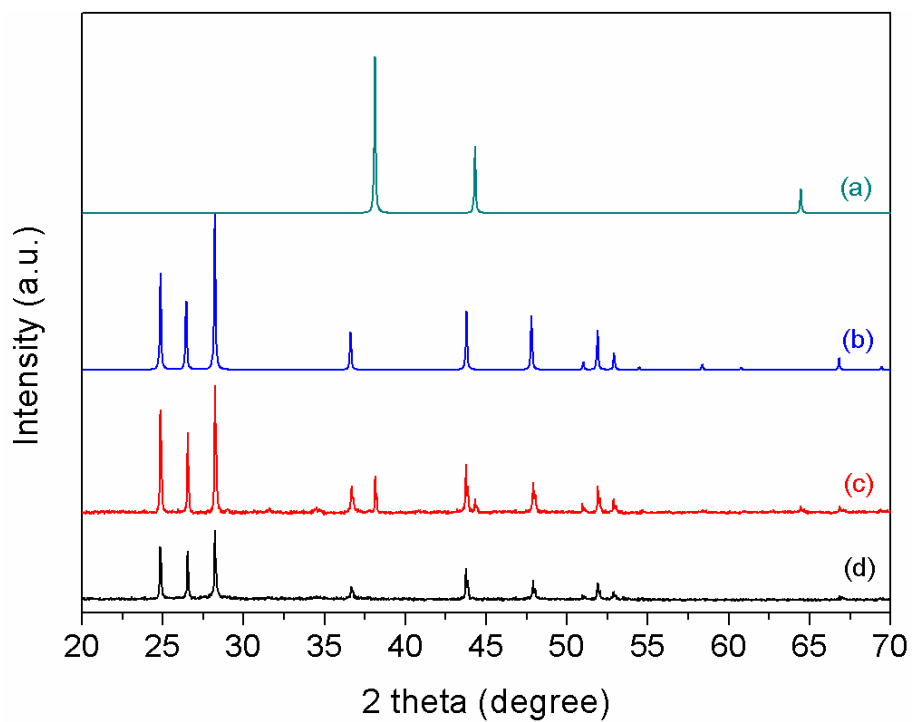


Fig. S5 Powder X-ray diffraction patterns of (a) standard cubic Ag, (b) standard hexagonal CdS, residue of (c) $\text{Cd}_6\text{Ag}_4(\text{SPh})_{16}(\text{DMF})_3(\text{CH}_3\text{OH})$ (**1**) and (d) $\text{Cd}_6\text{Ag}_4(\text{SPh})_{16}(\text{tmdp})_2$ (**3**) after thermogravimetric analysis.

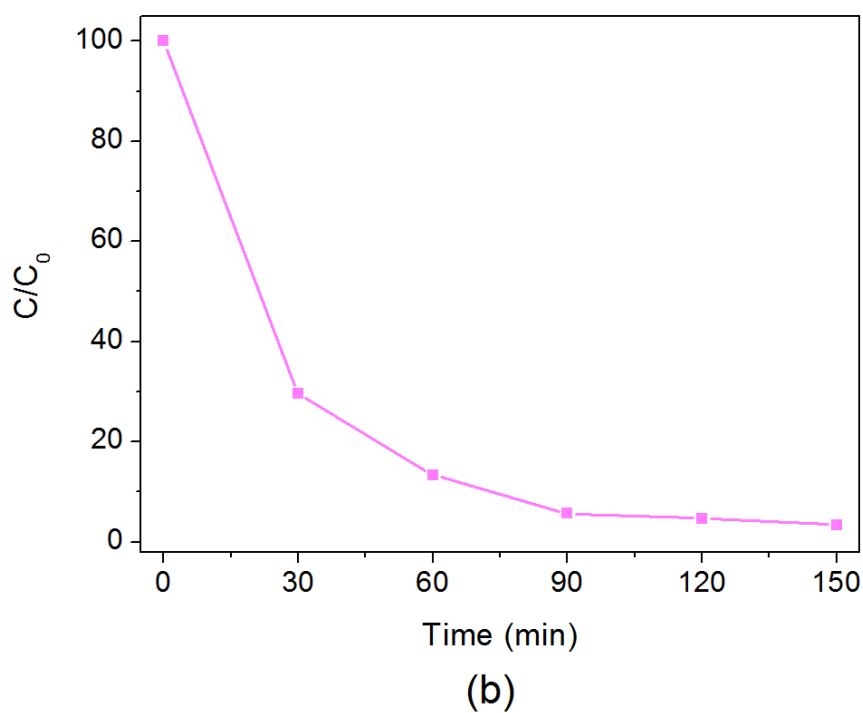
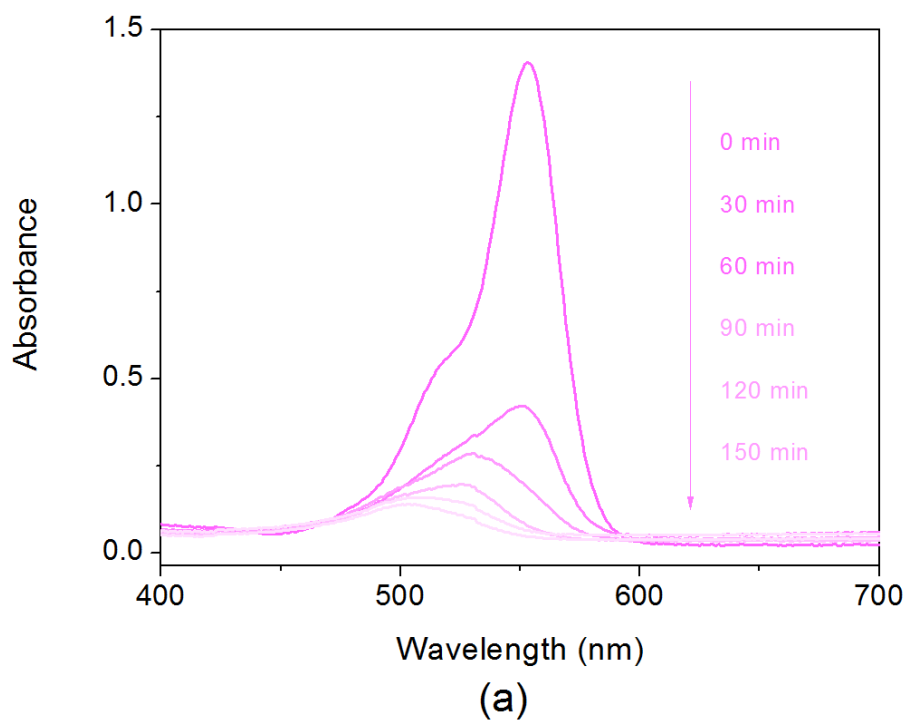


Fig. S6 (a) UV/vis spectra of aqueous rhodamine B during the degradation process photocatalyzed by coordination polymer $\text{Cd}_6\text{Ag}_4(\text{SePh})_{16}(\text{tmdp})_2$ (**4**); (b) Concentration changes of rhodamine B during the photocatalysis process. The concentration of rodamine B was calculated from the UV/vis absorbance at 555 nm.

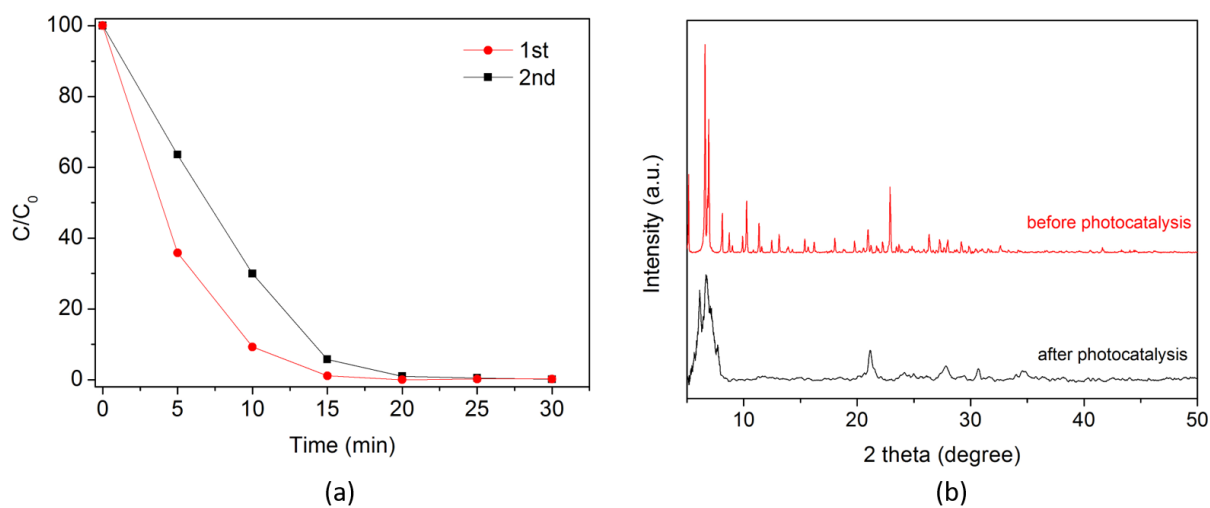


Fig. S7 (a) Cyclic photocatalytic performance of $\text{Cd}_6\text{Ag}_4(\text{SPh})_{16}(\text{DMF})_3(\text{CH}_3\text{OH})$ (**1**) for degradation of RhB; (b) Comparison of PXRD patterns of **1** before and after photocatalysis.

References

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