

Supporting Information

Experimental Section

Synthesis of $\text{Ag}_4\text{Pt}_2(\text{SPhMe}_2)_8$. 40 mg $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 40 mg AgNO_3 were dissolved in 3 mL CH_3OH by ultrasound. The solutions were poured into 15 mL CH_2Cl_2 at 0 °C. After vigorously stirring for 10 min, 84 μL 2,4-dimethylbenzenethiol was added. After 30 min, 3 mL freshly prepared ice solution of 45 mg NaBH_4 was added into the above solution quickly. The mixture was allowed to stirring overnight. After reaction, the crude product was washed with CH_3OH several times and extracted with CH_2Cl_2 . The crude product was purified by PTLC to obtain $\text{Ag}_4\text{Pt}_2(\text{SPhMe}_2)_8$.

Synthesis of $\text{Ag}_4\text{Pd}_2(\text{SPhMe}_2)_8$. The same as $\text{Ag}_4\text{Pt}_2(\text{SPhMe}_2)_8$, except replacing $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ with Na_2PdCl_4 .

Synthesis of $\text{Ag}_4\text{Ni}_2(\text{SPhMe}_2)_8$. The same as $\text{Ag}_4\text{Pt}_2(\text{SPhMe}_2)_8$, except replacing $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Preparation of supported catalysts. 3 mg $\text{Ag}_4\text{M}_2(\text{SPhMe}_2)_8$ (M = Ni, Pd, Pt) and 150 mg TiO_2 (TiO_2 was pretreated at 400 °C for 5 h) were mixed in 1 mL CH_2Cl_2 and then dried in air overnight.

Catalytic reactions. 50 mg $\text{Ag}_4\text{M}_2(\text{SPhMe}_2)_8/\text{TiO}_2$ (M = Ni, Pd, Pt) was dispersed in 20 mL H_2O under stirring. Then 0.1 mL $1 \text{ g} \cdot \text{L}^{-1}$ methyl orange or rhodamine B was added and the solution was irradiated with visible light using a Xe lamp. Samples from the solution were taken every 3 minutes and measured with UV-vis spectrometer.

Characterization. X-ray crystallography analysis of $\text{Ag}_4\text{Pt}_2(\text{SPhMe}_2)_8$ was collected on a Bruker D8 VENTURE. UV-vis absorption spectra were carried out on a Shimadzu UV-1800 spectrophotometer at a medium sampling scan rate. Binding energies of the surface species on the catalysts were determined by X-ray photoelectron spectroscopy (XPS) (Thermo Scientific K-

Alpha) using a Al K α ($h\nu = 1486.6$ eV) as the excitation source. Correction of the charge effect was made with the C 1s peak at 284.8 eV. The electrochemical impedance spectroscopy (EIS) measurement was performed on a CHI660B electrochemical workstation. A conventional three-electrode system was employed for the experiments. A platinum foil and a saturated Ag/AgCl electrode were used as counter electrode (CE) and reference electrode (RE), respectively. Working electrode (WE) was a glassy carbon. All the experiments were carried out in 1 mol·L⁻¹ Na₂SO₄ at room temperature.

Computational Methods

The three Au₄M₂(SPhMe₂)₈ (M = Ni, Pd, and Pt) clusters were modelled at the density functional theory (DFT) level. The full atomistic structural model, comprising a monomer unit of the crystal structure of each Au₄M₂ cluster, was used for all the calculations. All of the DFT calculations were carried out using the Gaussian09 software with the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functionals^{S1} and the aug-cc-pVDZ basis set and pseudopotentials.^{S2-S6} Density of states analysis and the natural population analysis^{S7} were performed to comprehend the electronic structures of the clusters.

Table S1. Binding energies of Ag, Ni, Pd, and Pt in Ag₄M₂ from XPS analysis.

Sample	Binding energy (eV)							
	Ag 3d _{5/2}	Ag 3d _{3/2}	Ni 2p _{3/2}	Ni 2p _{1/2}	Pd 3d _{5/2}	Pd 3d _{3/2}	Pt 4f _{7/2}	Pt 4f _{5/2}
Ag ₄ Ni ₂	368.5	374.5	853.5	870.8	-	-	-	-
Ag ₄ Pd ₂	368.7	374.7	-	-	337.0	342.3	-	-
Ag ₄ Pt ₂	368.9	374.9	-	-	-	-	72.4	75.7

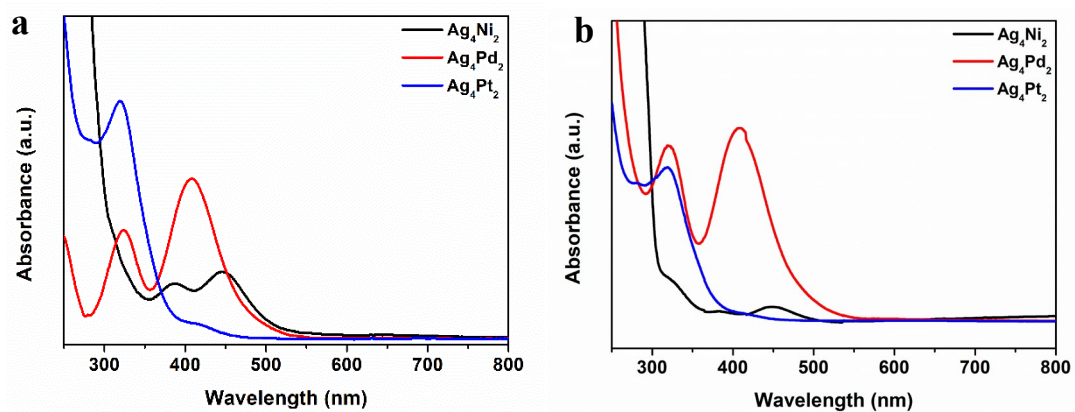


Figure S1. UV-vis absorption spectra of the Ag_4Ni_2 , Ag_4Pd_2 and Ag_4Pt_2 catalysts after photocatalytic degradation processes of (a) methyl orange and (b) rhodamine B. The cluster catalysts were dissolved in CH_2Cl_2 for UV-vis measurement.

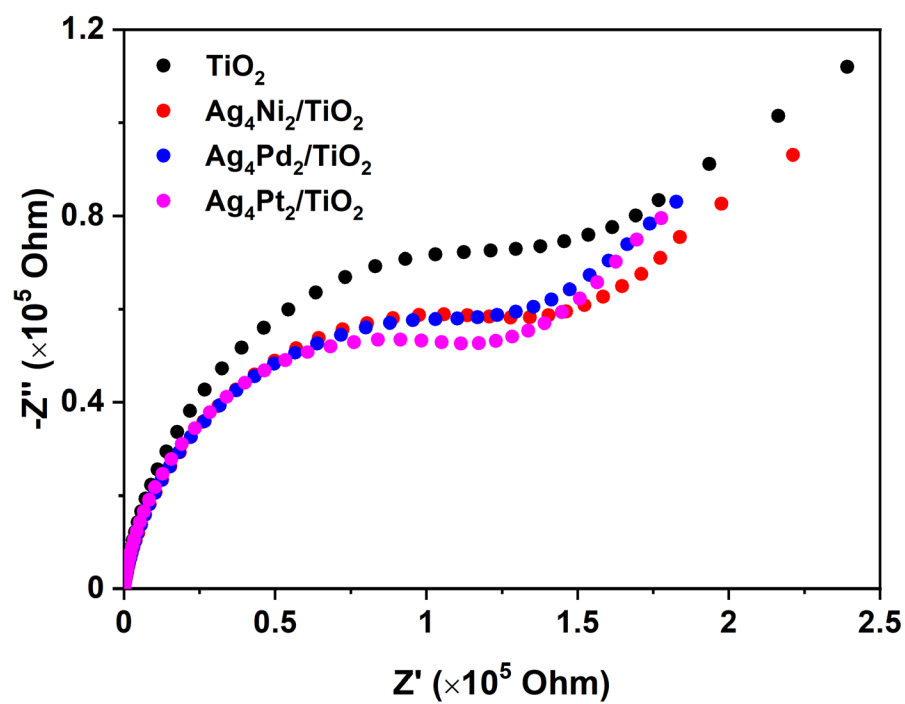


Figure S2. The electrochemical impedance spectroscopy (EIS) of the three $\text{Ag}_4\text{M}_2/\text{TiO}_2$ clusters.

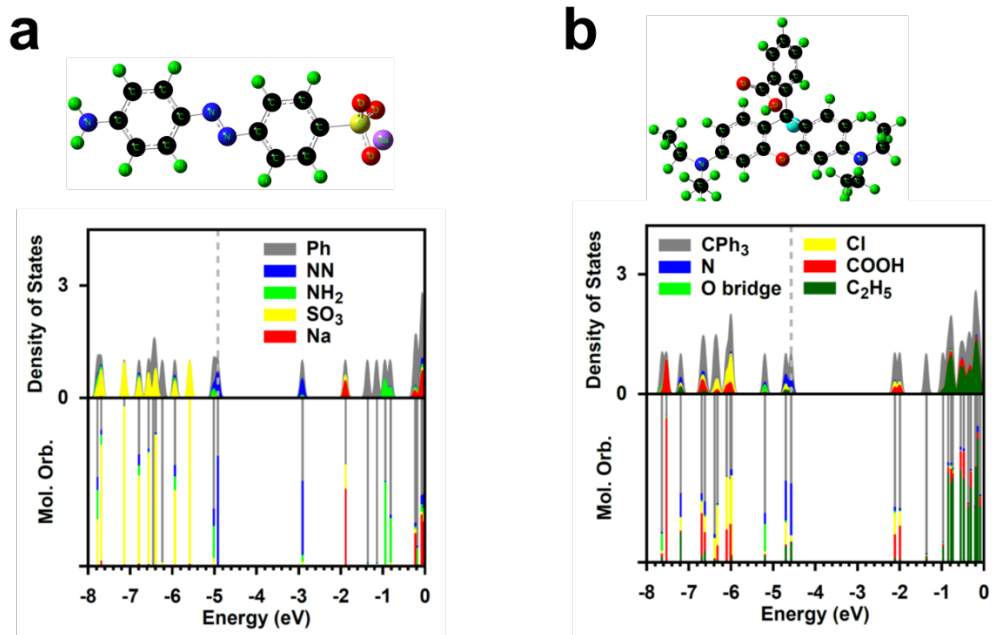


Figure S3. Molecular structure and PDOS for (a) methyl orange and (b) rhodamine B at the DFT PBE/Aug-cc-pVDZ level. Color code for the molecular structures: red = O, yellow = S, black = C, blue = N, green = H, cyan = Cl, and purple = Na.

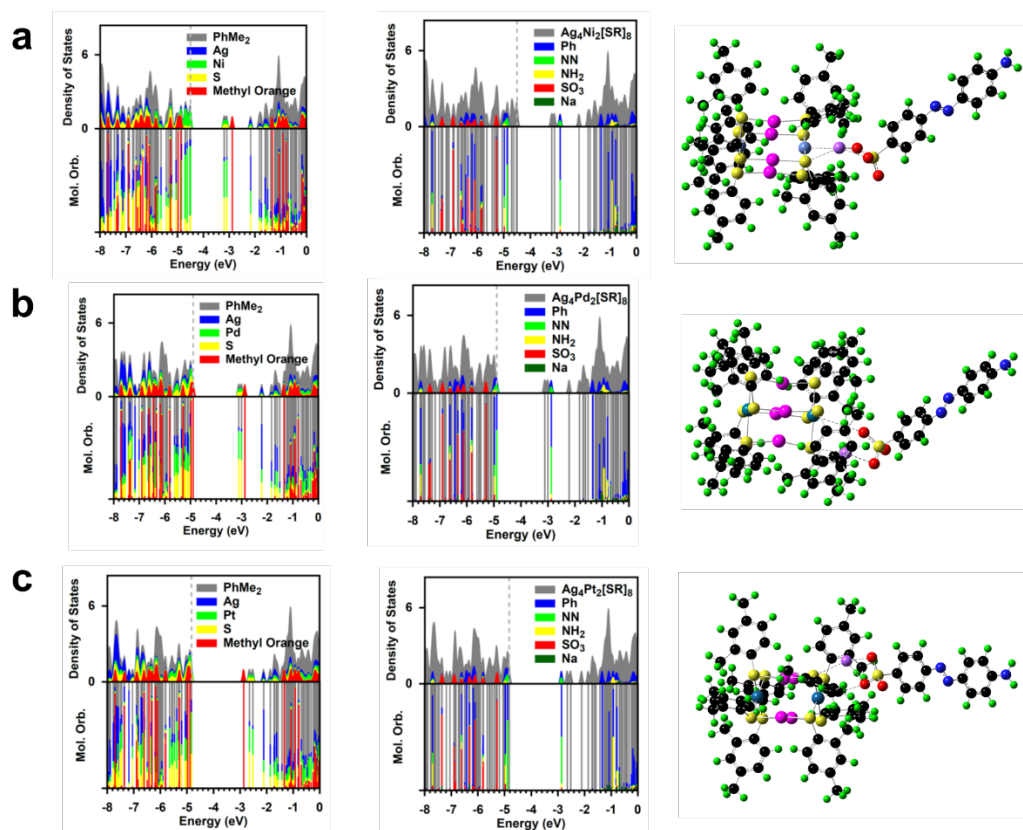


Figure S4. The molecular structure and PDOS for complex of methyl orange with $\text{Ag}_4\text{M}_2(\text{SPhMe}_2)_8$ with M-S as the anchor point at the DFT PBE/Aug-cc-pVDZ level, M = (a) Ni, (b) Pd, and (c) Pt. The fragmental PDOSs for Ag_4M_2 catalyst and methyl orange are shown in the left and middle panels, respectively, and the molecular structure is shown in the right panel.

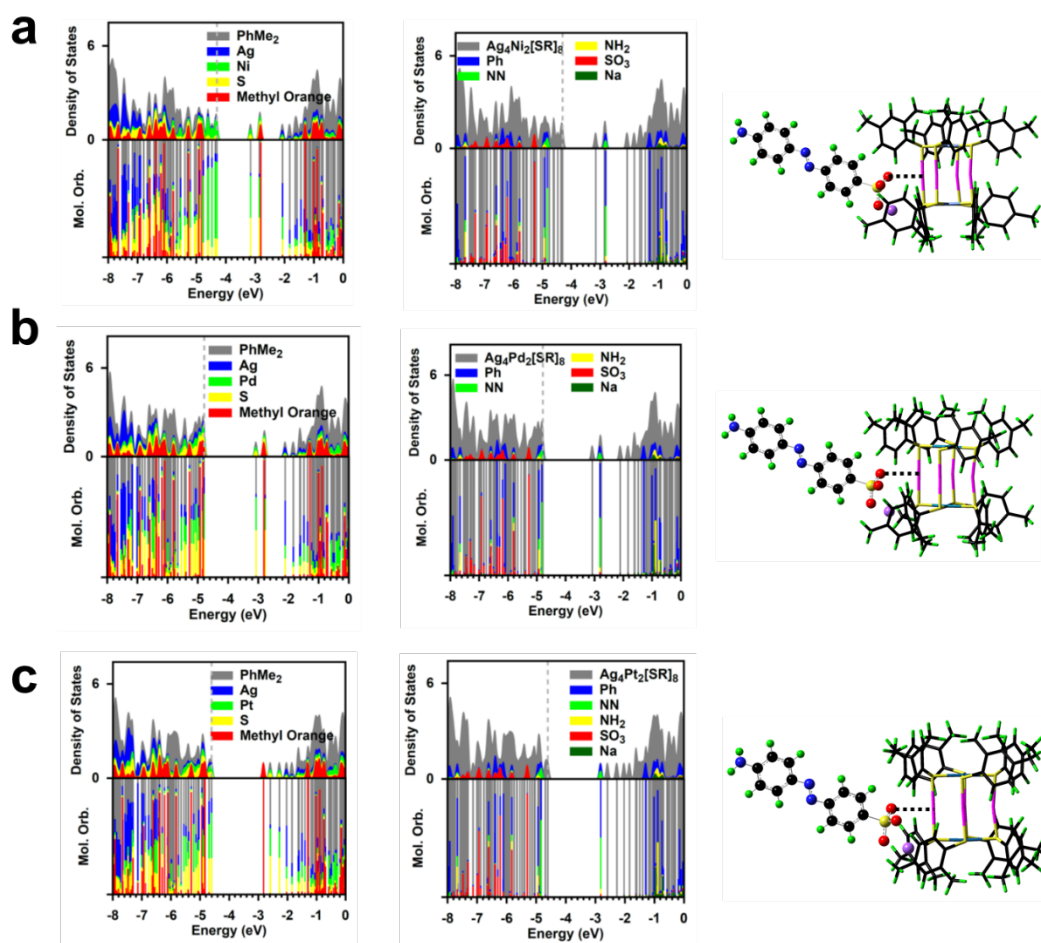


Figure S5. The molecular structure and PDOS for complex of methyl orange with $\text{Ag}_4\text{M}_2(\text{SPhMe}_2)_8$ with Ag as the anchor point at the DFT PBE/Aug-cc-pVDZ level, $\text{M} =$ (a) Ni, (b) Pd, and (c) Pt. The fragmental PDOSs for Ag_4M_2 catalyst and methyl orange are shown in the left and middle panels, respectively, and the molecular structure is shown in the right panel.

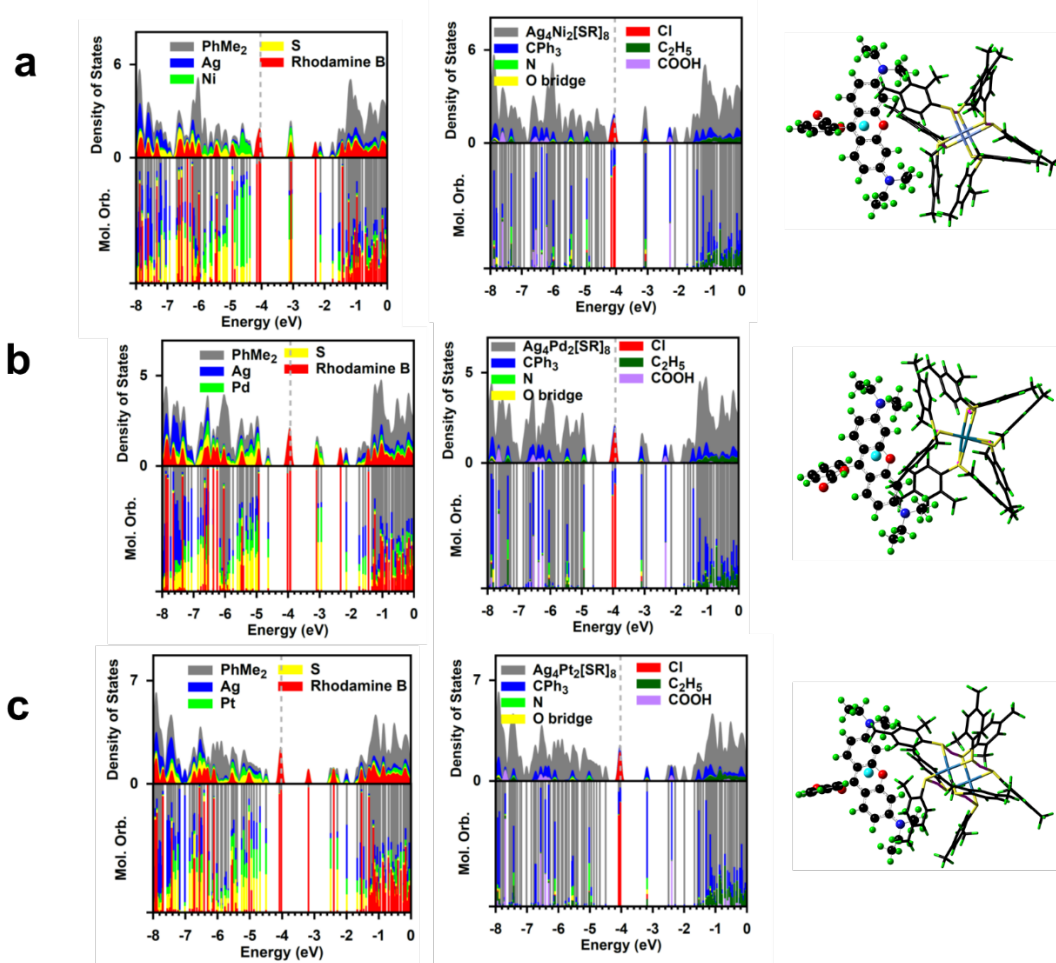


Figure S6. The molecular structure and PDOS for the complex of rhodamine B with $\text{Ag}_4\text{M}_2(\text{SPhMe}_2)_8$ at the DFT PBE/Aug-cc-pVDZ level, M = (a) Ni, (b) Pd, and (c) Pt. The fragmental PDOSs for Ag_4M_2 catalyst and rhodamine B are shown in the left and middle panels, respectively, and the molecular structure is shown in the right panel.

Supporting References

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