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Novel silver-phosphine coordination polymers incorporating Wurster's blue-like radical cations and their photoelectric properties

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Experimental Section

Materials and methods

Ligand **dpppda** was prepared according to a literature method^{S1}. All other chemicals were obtained from commercial sources and used as received. Elemental analyses (EA) for C, H, and N were determined on a Carlo-Erba CHON-S microanalyzer. IR spectra were obtained using a Nicolet is-10 FT-IR spectrometer (KBr disks, 4000–400 cm⁻¹). ¹H and ³¹P{¹H} NMR spectra were recorded at ambient temperature on a Varian UNITY plus-400 spectrometer. Powder X-ray diffraction (PXRD) patterns were collected on a PANalytical Aeris diffractometer (Cu-K α). X-ray photoelectron spectra (XPS) were collected with an ESCALAB 250Xi Spectrometer. UV-Vis spectra were obtained with a Shimadzu UV-2600 spectrometer. The ESR spectra were obtained with an JES-X320 electron spin resonance spectrometer operating at the X-band (frequency 9.148 GHz) for samples sealed inside a 4 mm thick quartz capillary, with irradiation by a Xe light (500 W, equipped with a filter < 400 nm). Electrospray ion mass spectra (ESI-MS) were recorded on an Agilent 1220/6220 mass spectrometer using methanol as mobile phase.

Synthesis of compounds 1 and 2

Synthesis of [Ag₄(μ_3 - η^3 -NO₃)₄(**dpppda**)_n·2CH₂Cl₂ (**1**·2CH₂Cl₂).

To a solution of AgNO₃ (13.6 mg, 0.08 mmol) in 1 mL CH₃OH was added a solution of **dpppda** (18 mg, 0.02 mmol) in 4 mL CH₂Cl₂. The resulting mixture was stirred for 60 min and filtered. Et₂O (40 mL) was layered onto the filtrate at ambient temperature for 3 days to form blue crystals of **1**·2CH₂Cl₂, which were collected by filtration and desolvated *in vacuo*. Yield for **1**: 11 mg (68% based on **dpppda**). Anal. Calcd. For C₅₈H₅₂Ag₄N₆O₁₂P₄: C, 44.02; H, 3.29; N, 5.31, Found: C, 43.75; H, 3.603; N, 5.142 (%). IR (KBr disk): 3040(w), 2924(w), 2415(w), 1755(w), 1615(w), 1606(w), 1500(s), 1375(s), 1080(w), 980(w), 856(w), 735(m), 690(m) cm⁻¹.

Synthesis of [Ag₄(μ - η^2 -NO₃)₂(μ - η , η^2 -NO₃)₂(**dpppda**)_n (**2**).

To a solution of AgNO₃ (13.6 mg, 0.08 mmol) in 1 mL CH₃OH was added a solution of **dpppda** (18 mg 0.02 mmol) in 2 mL CHCl₃. The resulting mixture was stirred for 300 min and filtered. Et₂O (40 mL) was layered onto the filtrate at ambient temperature for 2 days to form dark-green crystals of **2**, which were collected by filtration, washed with Et₂O and dried *in vacuo*. Yield for **2**: 12 mg (38% based on **dpppda**). Anal. Calcd for C₅₈H₅₂Ag₄N₆O₁₂P₄: C, 44.02; H, 3.29; N, 5.31. Found: C, 43.53; H, 3.402; N, 5.095(%). IR (KBr disk) 3050(w), 2910(w), 2420(w), 1615(w), 1505(m), 1450(m), 1370(s), 1260(m), 1130(w), 990(w), 720(m), 680(m) cm⁻¹.

Single crystal X-ray crystallography

Single crystals of **1**·2CH₂Cl₂ and **2** suitable for single crystal X-ray crystallography were obtained directly from the above preparations. Each crystal was mounted on a glass fiber with grease and cooled in a liquid nitrogen stream to 223K. Crystallographic measurements were carried out on an Agilent Xcalibur (**1**·2CH₂Cl₂) and a Rigaku Mercury (**2**) CCD X-ray diffractometer using graphite monochromated Cu K α (λ = 1.54178 Å, for **1**·2CH₂Cl₂) and Mo K α (λ = 0.71073 Å, for **2**) and radiations. The programs CrysAlisPro (Agilent Technologies, Ver. 1.171.36.28, for **1**·2CH₂Cl₂) and Crystalclear (Rigaku and MSc, Ver. 1.3, for **2**) were used for the refinement of cell parameters and the reduction of collected data, while absorption corrections (multi-scan) were applied.

The crystal structures were solved by direct methods and refined on F^2 by full-matrix least squares methods with the SHELXTL-2016 program package. The solvated CH_2Cl_2 molecule in $1 \cdot 2\text{CH}_2\text{Cl}_2$ was disordered over two positions with equal occupancies. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were added theoretically. Relevant crystal data, collection parameters, and refinement results can be found in Table S1.

Electrode Preparation and Photocurrent Measurement.

Photoelectrodes were prepared using the powder-coating method^{S2}. Compounds **1** and **2** were ground and pressed uniformly on a cleaned indium tin oxide (ITO) glass ($10 \text{ } \Omega/\text{square}$) with an effective area of 0.2 cm^2 ($0.4 \text{ cm} \times 0.5 \text{ cm}$). A 150 W Xenon lamp equipped with a UV filter ($< 400\text{nm}$) was located 20 cm away from the surface of the ITO electrode and employed as the light source. The cyclic voltammetry and photocurrent experiments were performed on a CHI-630E electrochemistry workstation in a three-electrode system, with the sample-coated ITO glass as the working electrode, a Pt plate as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. The supporting electrolyte solution was a 0.1 mol/L Na_2SO_4 aqueous solution. During the photocurrent experiment, the lamp was kept on continuously, and a manual shutter was used to block the exposure of the sample to the light in 20s time intervals.

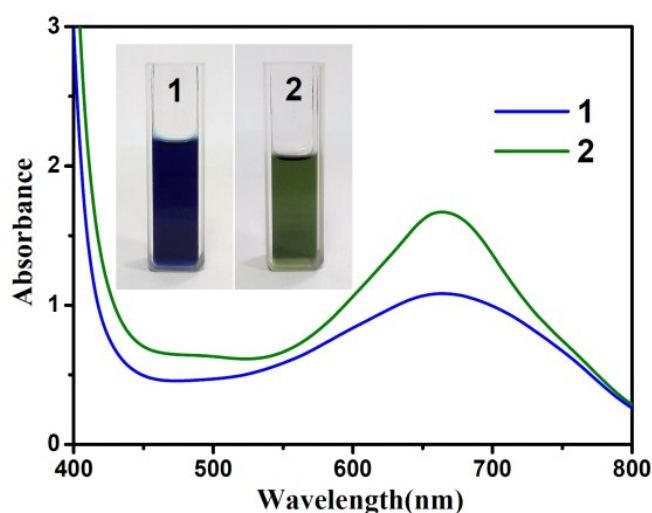
Density functional theory (DFT) calculations for HOMO–LUMO analysis.

The HOMO and LUMO energies of **1** and **2** were calculated with the Gaussian 09 program using the Cartesian coordinates at their solid-state structures^{S3}. The LanL2DZ relativistic effective core potential was used for the Ag atom and the 6-31G(d,p) basis set was used for the other atoms (P, C, N, O and H)^{S4}. Calculations with the B3LYP functional were estimated^{S5}. Test calculations with Stuttgart-Dresden (SDD) ECPs basis set for Ag atoms in M06 calculations give a similar result to that obtained by the LanL2DZ basis set.

Table S1. Summary of crystal data and structure refinement parameters for **1**·2CH₂Cl₂ and **2**.

Compound	1 ·2CH ₂ Cl ₂	2
empirical formula weight	C ₅₈ H ₅₂ Ag ₄ N ₆ O ₁₂ P ₄ , 2CH ₂ Cl ₂	C ₅₈ H ₅₂ Ag ₄ N ₆ O ₁₂ P ₄
crystal system	monoclinic	Monoclinic
space group	<i>C2/c</i>	<i>P2₁/c</i>
<i>a</i> (Å)	28.2415(8)	11.096(2)
<i>b</i> (Å)	13.1850(3)	23.934(5)
<i>c</i> (Å)	19.6699(5)	11.876(2)
β (°)	114.578(3)	108.96(3)
<i>V</i> (Å ³)	6660.7(3)	2982.8(12)
ρ_{calc} (g cm ⁻³)	1.745	1.760
<i>Z</i>	4	2
μ (mm ⁻¹)	12.215	1.468
<i>F</i> (000)	3480.0	1572.0
<i>R</i> ₁ ^a	0.0800	0.0570
<i>wR</i> ₂ ^b	0.2333	0.0989
<i>GOF</i> ^c	1.042	1.092

^a $R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$. ^b $wR_2 = \frac{\{\sum w(F_o^2 - F_c^2)^2\}}{\{\sum w(F_o^2)^2\}}^{1/2}$. ^c $GOF = \frac{\{\sum w((F_o^2 - F_c^2)^2)/(n-p)\}}{1/2}$, where *n* = number of reflection and *p* = total number of parameters refined.

**Fig. S1** UV-Vis spectra of reaction solutions during the syntheses of **1** and **2**. The solutions were prepared by stirring the mixture of AgNO₃ (13.6 mg) and dppda (18 mg) in 1 mL CH₃OH and 4 mL CH₂Cl₂ (60minutes, for **1**) or in 1 mL CH₃OH and 2 mL CHCl₃ (300minutes, for **2**), and then filtered.

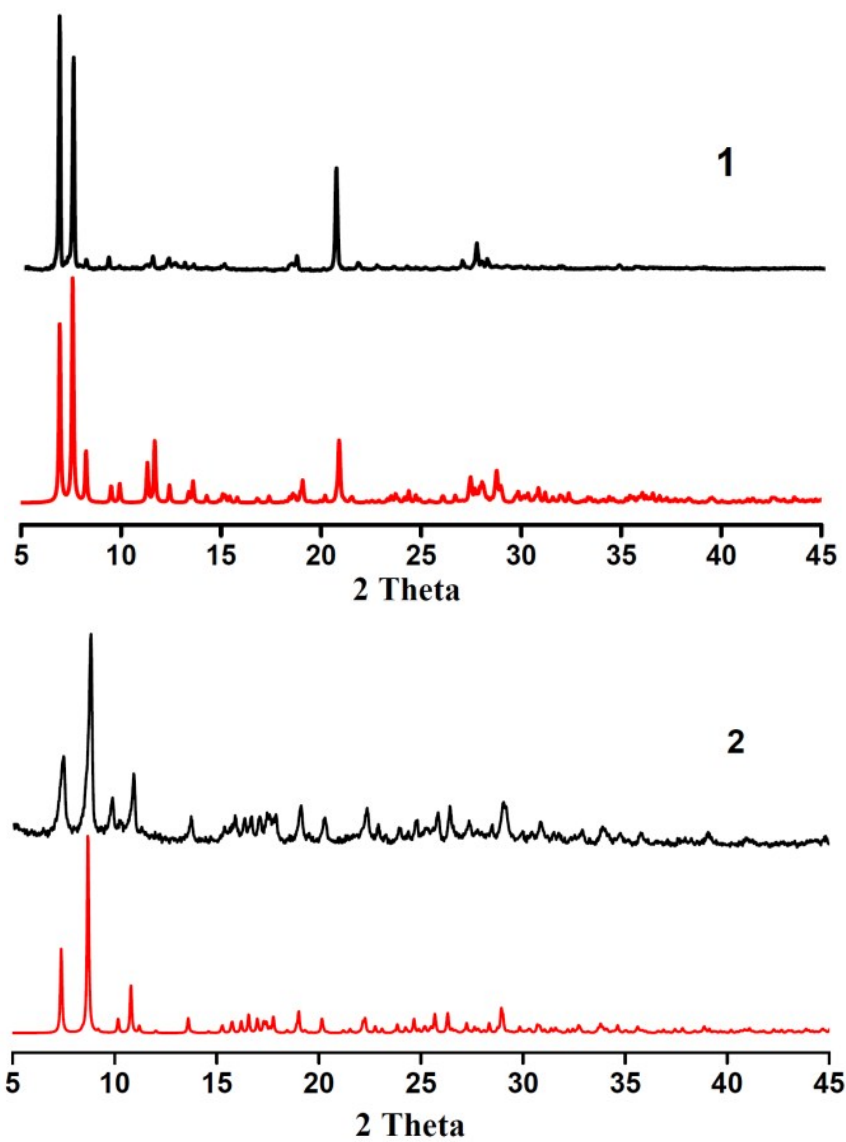


Fig. S2 PXRD patterns for **1** and **2**: simulated from single crystal data (Red) and as-synthesized sample (Black).

Table S2 The energies (eV) of the frontier molecular orbitals of **1**, **2** from DFT calculations.

	HOMO-1	HOMO	LUMO	LUMO+1	$\Delta E_{LUMO-HOMO}$	λ
	eV	eV	eV	eV	eV	nm
1	-5.57	-4.19	-3.27	-2.31	0.92	1348
2	-5.50	-4.28	-3.22	-2.42	1.06	1170

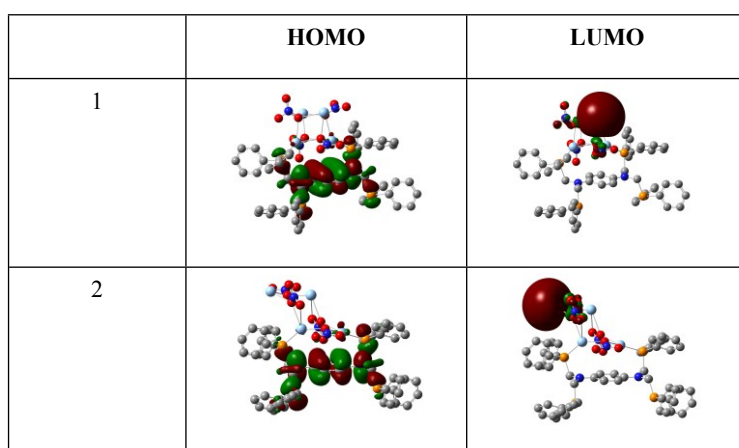


Fig. S3 Molecular orbital distribution of HOMO and LUMO for **1**, **2**.

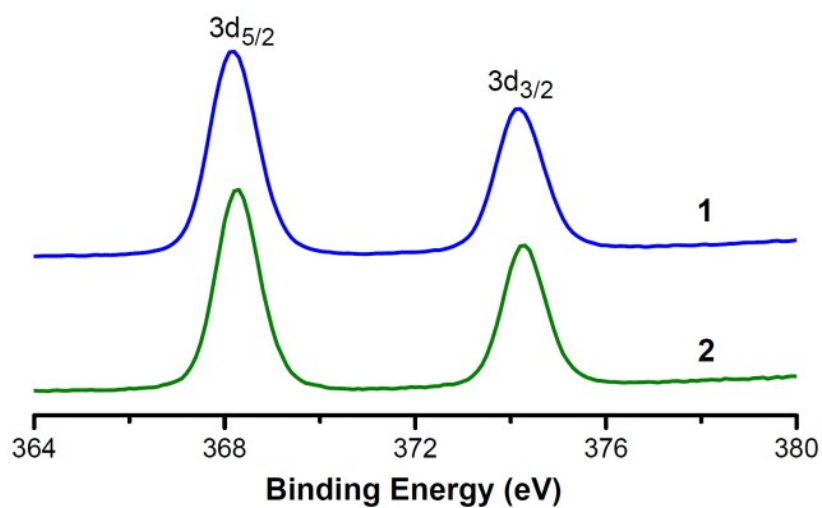


Fig. S4 Ag 3d XPS spectra of compounds **1** and **2**.

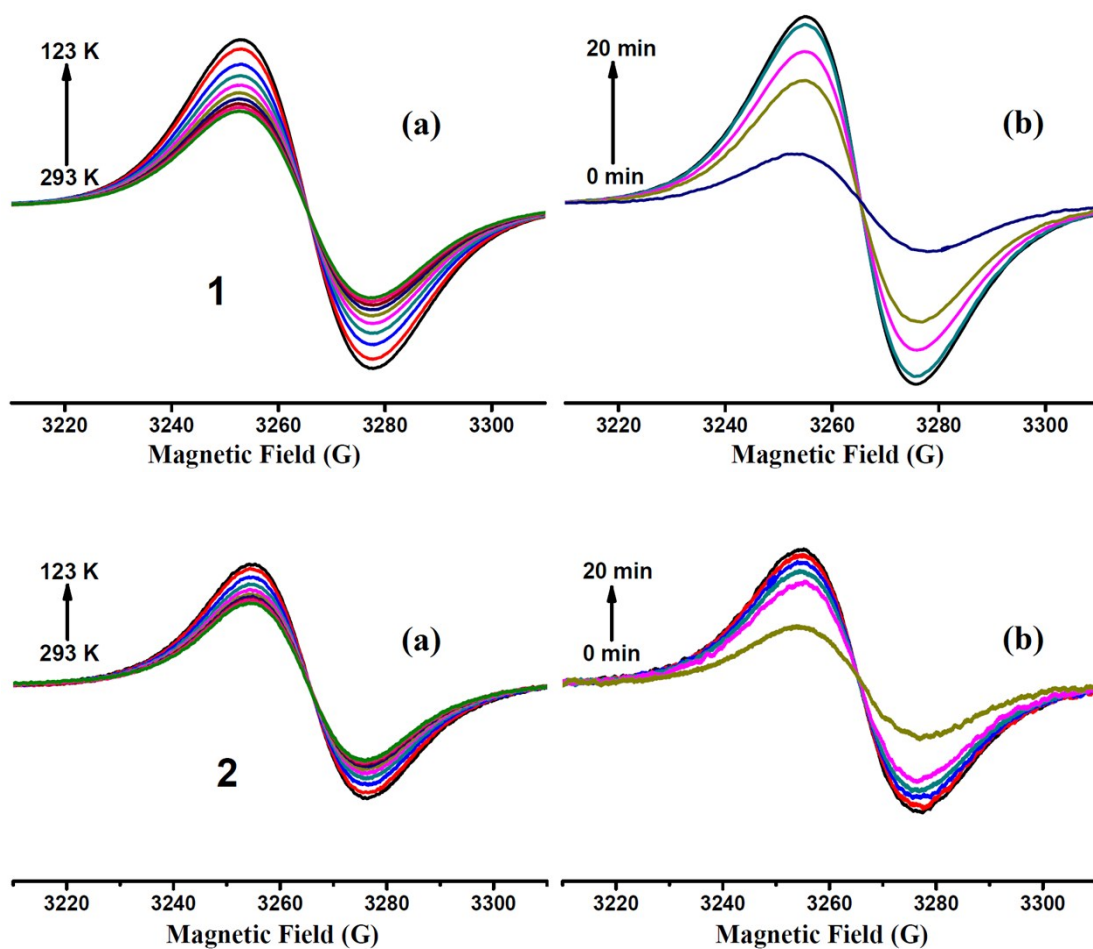


Fig. S5 ESR spectra of compounds **1** (upper) and **2** (lower) recorded in the solid state (a) on cooling from 293 K to 123 K with 20 K temperature intervals, and (b) at 293 K under irradiation by Xe a light (>400 nm) with 4 minute time intervals. Microwave Freq = 9.1516 GHz, Field Center = 326.000 mT, Width = 0.4000 mT, Sweep Time = 30.0 s.

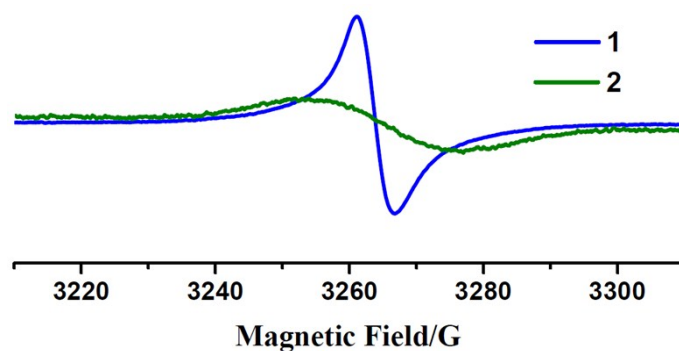
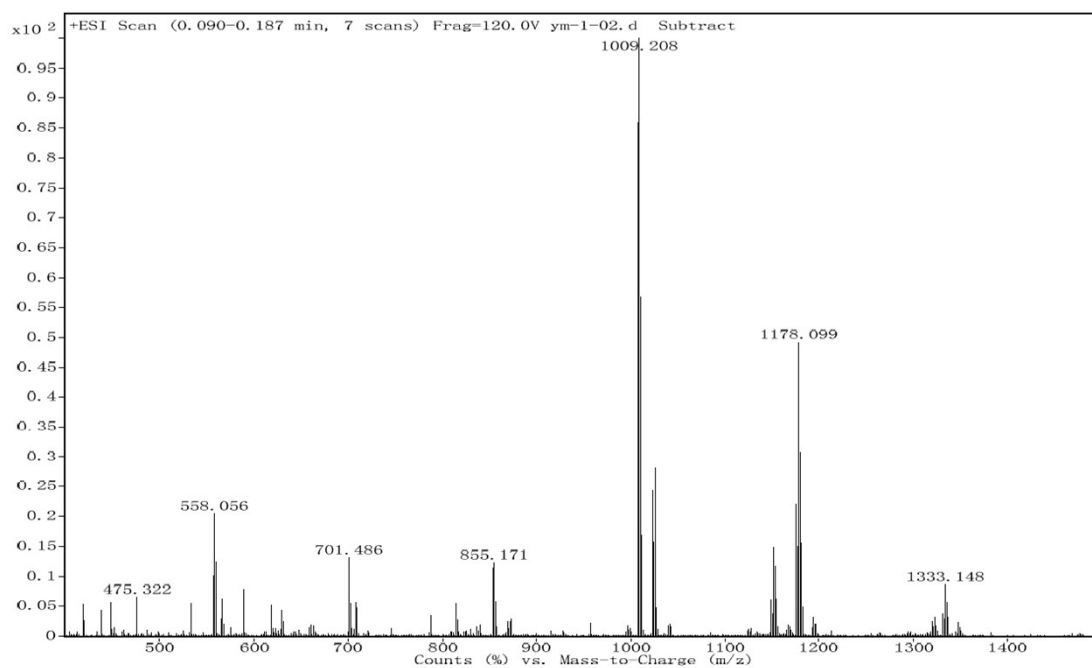
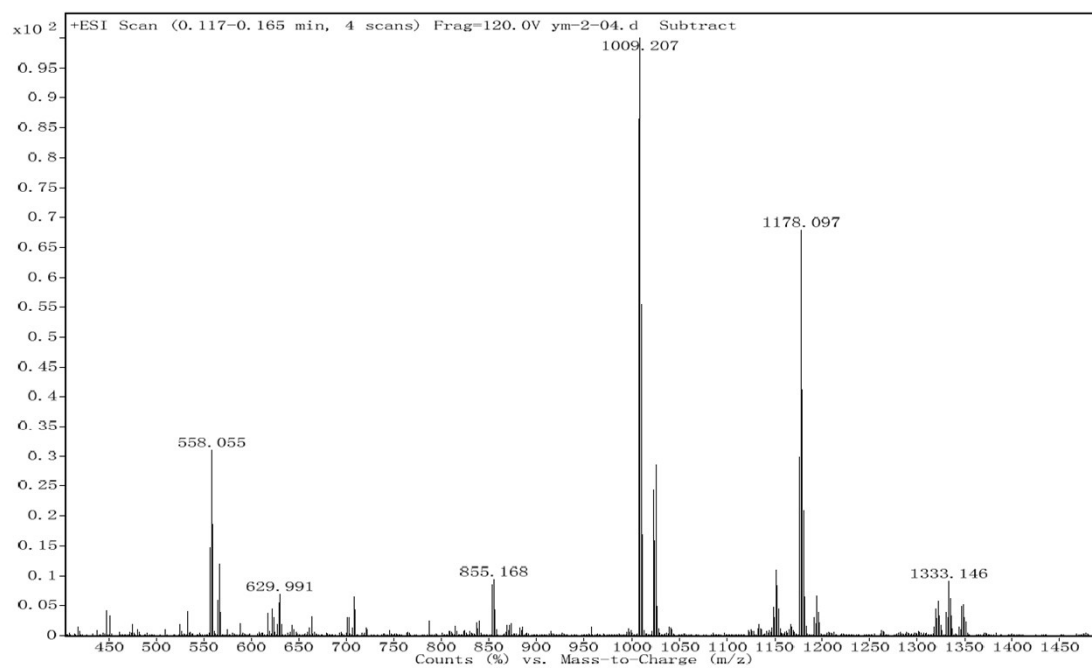


Fig. S6 ESR spectra of compounds **1** and **2** recorded in the CH_2Cl_2 solutions. Microwave Freq = 9.1486 GHz, Field Center = 326.000 mT, Width = 0.4000 mT, Sweep Time = 30.0 s.



(a)



(b)

Fig. S7 ESI-MS spectra of compounds **1** (a) and **2** (b) using CH₃OH as mobile phase.

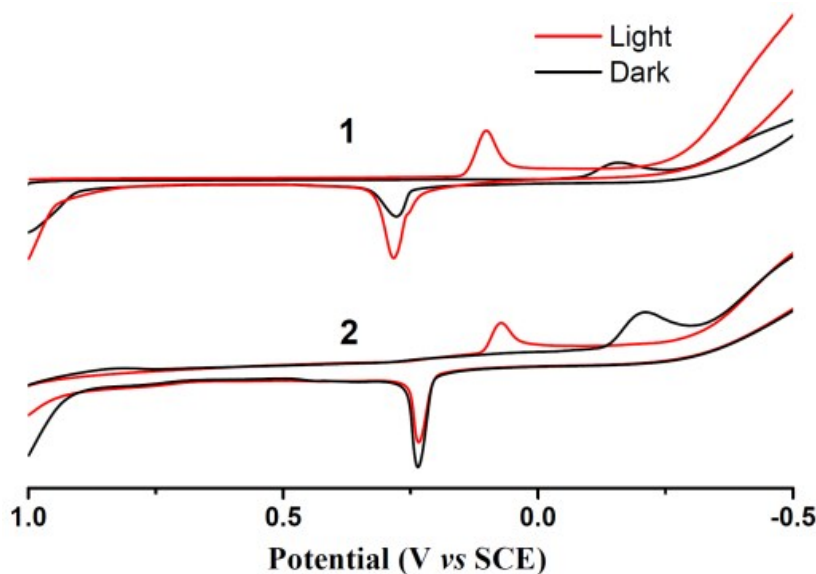


Fig. S8 Cyclic voltammogram of **1** and **2** on ITO glasses ($0.4 \times 0.5 \text{ cm}^2$) with and without Xe light ($\lambda > 400 \text{ nm}$, 150W) irradiation in 0.1 mol/L Na_2SO_4 aqueous solution.

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