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. 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 an PANalytical Aeris diffractometer (Cu-Kα). 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(μ₃-η³-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 CHCl₃. 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, 3.60; 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-η²-NO₃)₂(μ-η,η²-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, 3.40; 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), 856(w), 735(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 Kα (λ = 1.54178 Å, for 1·2CH₂Cl₂) and Mo Kα (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$_2$Cl$_2$ molecule in 12CH$_2$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$^{32}$. Compounds 1 and 2 were ground and pressed uniformly on a cleaned indium tin oxide (ITO) glass (10 Ω/square) with an effective area of 0.2 cm$^2$ (0.4 cm × 0.5 cm). A 150 W Xenon lamp equipped with a UV filter (<400nm) 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$_2$SO$_4$ 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$^{33}$. 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)$^{34}$. Calculations with the B3LYP functional were estimated$^{35}$. 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.

<table>
<thead>
<tr>
<th>Compound</th>
<th>1·2CH₂Cl₂</th>
<th>2</th>
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<tr>
<td>empirical formula</td>
<td>C₅₈H₅₂Ag₄N₆O₁₂P₄, 2CH₂Cl₂</td>
<td>C₅₈H₅₂Ag₄N₆O₁₂P₄</td>
</tr>
<tr>
<td>formula weight</td>
<td>1750.26</td>
<td>1580.41</td>
</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>C₂/c</td>
<td>P₂₁/c</td>
</tr>
<tr>
<td>a (Å)</td>
<td>28.2415(8)</td>
<td>11.096(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>13.1850(3)</td>
<td>23.934(5)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>19.6699(5)</td>
<td>11.876(2)</td>
</tr>
<tr>
<td>β (°)</td>
<td>114.578(3)</td>
<td>108.96(3)</td>
</tr>
<tr>
<td>V(Å³)</td>
<td>6660.7(3)</td>
<td>2982.8(12)</td>
</tr>
<tr>
<td>ρ_calc (g cm⁻³)</td>
<td>1.745</td>
<td>1.760</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>μ (mm⁻¹)</td>
<td>12.215</td>
<td>1.468</td>
</tr>
<tr>
<td>F(000)</td>
<td>3480.0</td>
<td>1572.0</td>
</tr>
<tr>
<td>R₁</td>
<td>0.0800</td>
<td>0.0570</td>
</tr>
<tr>
<td>wR₂</td>
<td>0.2333</td>
<td>0.0989</td>
</tr>
<tr>
<td>GOF</td>
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<td>1.092</td>
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aR₁ = Σ||F₀|-|Fₛ||/Σ|F₀|.  
bwR₂ = Σw(F₀²-Fₛ²)²/Σw(F₀²)²)1/2.  
cGOF = (Σw((F₀²-Fₛ²)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 dpppda (18 mg) in 1 mL CH₃OH and 4 mL CH₂Cl₂ (60 minutes, for 1) or in 1 mL CH₃OH and 2 mL CHCl₃ (300 minutes, 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 form DFT calculations.

<table>
<thead>
<tr>
<th></th>
<th>HOMO-1 eV</th>
<th>HOMO eV</th>
<th>LUMO eV</th>
<th>LUMO+1 eV</th>
<th>∆E_{LUMO-HOMO} eV</th>
<th>λ nm</th>
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<tr>
<td>1</td>
<td>-5.57</td>
<td>-4.19</td>
<td>-3.27</td>
<td>-2.31</td>
<td>0.92</td>
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<tr>
<td>2</td>
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</table>

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$_2$Cl$_2$ solutions. Microwave Freq = 9.1486 GHz, Field Center = 326.000 mT, Width = 0.4000 mT, Sweep Time = 30.0 s.
Fig. S7  ESI-MS spectra of compounds 1 (a) and 2 (b) using CH$_3$OH as mobile phase.
Fig. S8 Cyclic voltammogram of 1 and 2 on ITO glasses (0.4 × 0.5 cm²) with and without Xe light (λ > 400 nm, 150W) irradiation in 0.1 mol/L Na₂SO₄ aqueous solution.

References


