Electronic Supplementary Information

Assembly of silver-oxo complexes based on N-diphenylphosphanylmethyl-3-aminopyridine and their structures, photocatalysis and photocurrent responses

Lin-Yan Xu, Wei Yang, Chao-Fan Liu, Zhi-Gang Ren* and Jian-Ping Lang*

*Correspondence authors at: College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, People’s Republic of China.

Tel: +86-512-65882865; fax: +86-512-65880328.

E-mail address: jplang@suda.edu.cn (J.P. Lang).
Table of contents

**Fig. S1** The $^1$H NMR spectrum of 3-dppmapy.................................................................S3  
**Fig. S2** The $^{31}$P{$^1$H} NMR spectrum of 3-dppmapy....................................................S3  
**Fig. S3** Observed PXRD patterns of compounds 1-6 and the simulated PXRD patterns of compounds 1-6.................................................................................................................S4  
**Fig. S4** Thermogravimetric analysis (TGA) curves of compounds 1-6.................................S5  
**Fig. S5** The solid-state UV spectra absorption curves of 3-dppmapy and compounds 1-6.....S5  
**Fig. S6** UV-vis spectra of the mixture of aqueous solution of organic dyes (EBT (a), AB (b), NO (c)) and compound 6 under UV irradiation at different time intervals.................................S5  
**Fig. S7** UV-vis spectra of the mixture of aqueous solution of EBT and compound 6 after stirring for 1.5 h without UV irradiation at different time intervals..................................................S6  
**Fig. S8** UV-vis spectra of the aqueous solution of organic dyes (EBT (a), AB (b), NO (c)) under UV irradiation at different time intervals..........................................................S6  
**Fig. S9** UV-vis spectra of the mixture of aqueous solution of 3-dppmapy and organic dyes (EBT (a), AB (b), NO (c)) under UV irradiation at different time intervals.................................S6  
**Fig. S10** Observed PXRD patterns of 6 before (red) and after (black) the photodegradation of EBT, AB and NO..........................................................S6  
**Fig. S11** (a) Proposed mechanism for the catalytic photodegradation of EBT in water; (b) UV-vis spectra of the mixture of aqueous solution of EBT, t-BuOH and compound 6 after irradiation under UV light for 0-2 h..............................................................S7  
**Fig. S12** Fluorescence spectra during the irradiation of compound 6 mixed with a solution of terephthalic acid (5 × 10$^{-4}$ mol L$^{-1}$) and NaOH (2 × 10$^{-3}$ mol L$^{-1}$) (excitation at 315 nm) at different time intervals.........................................................................................S7  
**Fig. S13** The cyclic voltammetry of compound 6 with or without light...............................S8  
**Fig. S14** Observed PXRD patterns of 6 before (red) and after (black) the photocurrent responses tests.................................................................................................S8  
**Table S1** Selected bond angles (°) for compounds 1-6.............................................................S8  
**General procedures for the collection of the photoproducts after the photodegradation of dyes after the UV irradiation.................................................................S9  
**Table S2** Yields of NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$ left in the residual colorless solutions after the UV irradiation.................................................................S9  
**Density functional theory (DFT) calculation for HOMO-LUMO analysis of 6.----------S10  
**Fig. S15** Frontier molecular orbitals (HOMO and LUMO) of 6 calculated with DFT on the B3LYP level.................................................................S10
Fig. S1  The $^1$H NMR spectrum of 3-dppmapy.

Fig. S2  The $^{31}$P{$^1$H} NMR spectrum of 3-dppmapy.
Fig. S3 Observed PXRD patterns of compounds 1-6 (black) and the simulated PXRD patterns of compounds 1-6 (red).
**Fig. S4** Thermogravimetric analysis (TGA) curves of compounds 1-6.

![Thermogravimetric analysis (TGA) curves of compounds 1-6.](image)

**Fig. S5** The solid-state UV spectrum absorption curves of 3-dppmapy and compounds 1-6.

![The solid-state UV spectrum absorption curves of 3-dppmapy and compounds 1-6.](image)

(a) ![Graph](image) (b) ![Graph](image) (c) ![Graph](image)

**Fig. S6** UV-vis spectra of the mixture of aqueous solution of organic dyes (EBT (a), AB (b), NO (c)) and compound 6 under UV irradiation at different time intervals.

![UV-vis spectra of the mixture of aqueous solution of organic dyes](image)

**Fig. S7** UV-vis spectra of the mixture of aqueous solution of EBT and compound 6 after stirring for 1.5 h without UV irradiation at different time intervals.

![UV-vis spectra of the mixture of aqueous solution of EBT and compound 6](image)
Fig. S8  UV-vis spectra of the aqueous solution of organic dyes (EBT (a), AB (b), NO (c)) under UV irradiation at different time intervals.

Fig. S9  UV-vis spectra of the mixture of aqueous solution of 3-dppmapy and organic dyes (EBT (a), AB (b), NO (c)) under UV irradiation at different time intervals.

Fig. S10  Observed PXRD patterns of 6 before (red) and after (black) the photodegradation of EBT, AB and NO.
**Fig. S11**  (a) Proposed mechanism for the catalytic photodegradation of EBT in water; (b) UV-vis spectra of the mixture of aqueous solution of EBT, t-BuOH and compound 6 after irradiation under UV light for 0-2h.

**Fig. S12**  Fluorescence spectra during the irradiation of compound 6 mixed with a solution of terephthalic acid ($5 \times 10^{-4}$ mol L$^{-1}$) and NaOH ($2 \times 10^{-3}$ mol L$^{-1}$) (excitation at 315 nm) at different time intervals.
Fig. S13  The cyclic voltammetry of compound 6 with or without light.

Fig. S14  Observed PXRD patterns of 6 before (red) and after (black) the photocurrent responses tests.

Table S1  Selected bond angles (°) for compounds 1-6.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(2)#1-Ag(1)-O(1)</td>
<td>113.51(12)</td>
<td>154.0(2)</td>
<td>154.02(11)</td>
<td>139.37(14)</td>
<td>135.84(7)</td>
<td>147.74(10)</td>
</tr>
<tr>
<td>N(2)#1-Ag(1)-P(1)</td>
<td>131.83(8)</td>
<td>--</td>
<td>--</td>
<td>100.7(2)</td>
<td>96.67(9)</td>
<td>85.49(12)</td>
</tr>
<tr>
<td>N(2)#1-Ag(1)-O(1)#2</td>
<td>--</td>
<td>--</td>
<td>98.89(19)</td>
<td>90.76(9)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>O(1)-Ag(1)-P(1)</td>
<td>113.68(9)</td>
<td>--</td>
<td>102.86(16)</td>
<td>119.82(18)</td>
<td>124.77(6)</td>
<td>126.77(8)</td>
</tr>
</tbody>
</table>

Symmetry transformations used to generate equivalent atoms: (1) #1 -x+1, -y, -z+1; (2) #1 -x+1, -y+1, -z+1; (3) #1 x, -y+1, z+1/2; #2 -x+1, -y+1, -z+1; #3 x, -y+1, z-1/2; (4) #1 x, -y+1, z-1/2; #2 -x+1, y, -z+1/2; #3 x, -y+1, z+1/2; (5) #1 -x+1, -y+2, -z+1; #2 -x+1, -y+1, -z+1; (6) #1 x-1, y, z; #2 x+1, y, z.
General procedures for the collection of photoproducts after the photodegradation of dyes in water.

Under the UV irradiation, the dyes solutions (0.1 mg/L, 10 mL) were completely degraded after 1.5 h (for EBT, 0.1 mg/L, 10 mL), 6 h (for AB, 0.5 mg/L, 10 mL) and 6 h (for NO, 0.5 mg/L, 10 mL) respectively in the presence of 6. The final solution was colourless. We assumed that all the dyes were converted into CO2 and H2O during the photodegradation reaction. The proposed CO2 evolved from the reaction was collected by hanging a small bottle of saturated Ba(OH)2 solution inside the reaction tube loaded with a suspension of 6 and organic dyes (EBT, AB and NO) under O2 atmosphere. After the irradiation, white BaCO3 precipitate was observed, which was collected, dried and weighed to calculate the yield of CO2. At the end of the reaction, the residue colorless mixtures were filtered and diluted to 20 mL for EBT, 100 mL for AB and 100 mL for NO, respectively. After the above measurements, the mass balance of the N, S and N were also determined by Ion Chromatography (ICS-1100). A summary of the pertinent data are listed in Table S2.

Table S2  Yields of NH₄⁺, SO₄²⁻ and NO₃⁻ left in the residual colorless solutions after the UV irradiation.

<table>
<thead>
<tr>
<th>Anions</th>
<th>EBT (ppm)</th>
<th>AB (ppm)</th>
<th>NO (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH₄⁺</td>
<td>11.6</td>
<td>43.7</td>
<td>43.7</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>21.0</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>39.8</td>
<td>150</td>
<td>150</td>
</tr>
</tbody>
</table>

$c_{\text{cal}}$: The calculated concentration of anions (NH₄⁺, SO₄²⁻ and NO₃⁻) left in the residual colorless solutions. 
$c_{\text{exp}}$: The experimental concentration of anions (NH₄⁺, SO₄²⁻ and NO₃⁻) by using IC method. 
Average of two runs.
The HOMO-LUMO gaps of 6 calculated with Gaussian 09 program by using the Cartesian coordinates at their solid-state structures. LanL2DZ relativistic effective core potential was used for Ag atom and the 6-31G(d,p) basis set was used for the other atom (P, C, N, O and H). Calculations with B3LYP functional were estimated. Test calculations with Stuttgart-Dresden (SDD) ECPs basis set for Ag atoms in M06 calculations give close result to that obtained by LanL2DZ basis set.

**Fig. S15.** Frontier molecular orbitals (HOMO and LUMO) of 6 calculated with DFT on the B3LYP level.