# **Supporting Information**

A Solid-State [2+2] Photodimerization Involving Coordination of Ag(I) Ions to 2-Pyridyl Groups

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#### 1. Materials, Synthesis and Purification

#### Materials

Silver *p*-toluenesulfonate ( $\geq$  99%) and ethanol (95%) used in the syntheses were purchased from Sigma-Aldrich and used as received. The reactant *trans*-1-(4-acetoxyphenyl)-2-(2-pyridyl)ethylene **1** was prepared *via* a previous published report [1].

## Synthesis of [Ag(*p*-tol)(1)<sub>2</sub>]•(H<sub>2</sub>O)

The formation of  $[Ag(p-tol)(1)_2] \cdot (H_2O)$  was achieved by dissolving 50 mg of 1 in 2 mL of warm ethanol and then added to a 20-mL scintillation vial containing 2 mL of a deionized water solution of 29.2 mg of silver *p*-toluenesulfonate (2:1 molar ratio). The vial was then covered in aluminum foil and the cap was securely attached.

## Synthesis and purification of photoproduct 2

Photoreactions were conducted using UV-radiation from a 450 W medium-pressure mercury lamp in an ACE Glass photochemistry cabinet. The silver salt was placed between a pair of Pyrex glass plates for irradiation. The formation of the photoproduct **2** was achieved in a quantitative yield from  $[Ag(p-tol)(1)_2] \cdot (H_2O)$  within 100 hours of irritation as determined by <sup>1</sup>H NMR spectroscopy. The cyclobutane **2** was isolated and purified by dissolving the photoreacted material in a 20 ml solution of water and methylene chloride (1:1 ratio). The organic layer was separated using a separatory funnel where two additional washing of 10 ml of methylene chloride was performed.

#### 2. Powder X-ray Diffraction

PXRD data was collected on a Bruker D8 Advance X-ray diffractometer using CuK $\alpha_1$  radiation ( $\lambda = 1.5418$  Å) typically in the range of 5–35° two-theta (scan type: coupled TwoTheta/Theta; scan mode: continuous PSD fast; step size: 0.019°). The equipment was operated at 40 kV and 30 mA, and data was collected at room temperature every 10 hours of UV exposure.



**Figure S1.** Powder X-ray diffraction data at 10 h intervals during the [2+2] cycloaddition reaction.

## **3. NMR Spectral Analysis**

The <sup>1</sup>H NMR spectra were recorded on a Bruker spectrometer (Fourier-300) operating at 300 MHz, unless mentioned otherwise. Two-dimensional NMR analysis was performed for both  $[Ag(p-tol)(1)_2] \cdot (H_2O)$  and the photoreacted material  $[Ag(p-tol)(2)] \cdot (H_2O)$ . This type of analysis was necessary for the olefin, as the spectral region of aromatic and olefinic protons displayed a significant overlap. The NMR chemical shifts were determined from the chemical shifts of DMSO-*d*<sub>6</sub> (<sup>1</sup>H, 2.50 ppm; <sup>13</sup>C, 39.51 ppm). The 1D spectral data were processed with TOPSPIN (Version 3.1) suite of software programs. The percent conversion of the photoreaction was monitored using <sup>1</sup>H NMR spectroscopy every 10 hours of UV exposure.

A battery of 2D homonuclear and <sup>1</sup>H-<sup>13</sup>C heteronuclear experiments [<sup>1</sup>H, <sup>13</sup>C, 2D correlated spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), and heteronuclear multiple bond correlation (HMBC)] were performed to determine the resonance assignments. All the 2D NMR experiments were performed on a 600 MHz Bruker (AVANCE III) spectrometer with a 1.7 mm micro gradient-capable probe. Gradient-assisted versions of the pulse sequences and inverse detection were used for these 2D experiments. A recycle delay (D1) of 4.0s was used in all the 2D experiments. Typical parameters for the NMR experiments were as follows: <sup>1</sup>H [time domain data points (TD), 32k; NS, 32], <sup>13</sup>C (TD, 64k; NS, 10k), 2D COSY (TD, 2k; TD1, 150; NS, 16; DS, 32), <sup>13</sup>C-<sup>1</sup>H HSQC (TD, 2k; TD1, 256; NS, 16; DS, 128) and <sup>13</sup>C-<sup>1</sup>H HMBC (TD, 4k; TD1, 256; NS, 32; DS, 64). TD, NS, and DS refer to time domain data points, number of scans, and dummy scans, respectively. All 2D NMR data were processed with the zero-filling to 2,048 points and 1,024 points in acquisition and second dimension, respectively.



**Figure S2.** Structures of  $[Ag(p-tol)(1)_2] \cdot (H_2O)$  and photoproduct  $[Ag(p-tol)(2)] \cdot (H_2O)$  (water molecule omitted for clarity) and the atom labels as used in the NMR spectra. Note that the anion is  $[C_7H_7SO_3]^-$  in both cases.



**Figure S3.** <sup>1</sup>H NMR spectra showing the aromatic, olefinic and cyclobutyl region of (A)  $[Ag(p-tol)(1)_2] \cdot (H_2O)$  and (B) cyclobutane photoproduct  $[Ag(p-tol)(2)] \cdot (H_2O)$ . Note that the resonances H<sub>g</sub> is overlapping with the resonances of H<sub>i</sub>. 2D NMR data provided the evidence for the resonance assignment of H<sub>f</sub> and H<sub>g</sub>. A large spin-spin coupling constant of 16.1 Hz (Insert, A) is characteristic of *anti*-configuration between H<sub>f</sub> and H<sub>g</sub>. A doublet-of-a-doublet pattern with differential spin-spin coupling constants (11.0, 7.5 Hz) observed for H<sub>f</sub> and H<sub>g</sub> of the photoproduct  $[Ag(p-tol)(2)] \cdot (H_2O)$  are consistent with the X-ray crystal structure in which the protons in the opposite nodes of the cyclobutane ring are chemically and magnetically equivalent but with the neighboring protons in *syn*- and *anti*-configurations (Insert, B).



**Figure S4.** <sup>1</sup>H NMR spectra showing the methyl region of (A)  $[Ag(p-tol)(1)_2] \cdot (H_2O)$  and (B) cyclobutane photoproduct  $[Ag(p-tol)(2)] \cdot (H_2O)$ . The resonance assignments were determined using the 2D <sup>1</sup>H-<sup>1</sup>H homonuclear and <sup>1</sup>H-<sup>13</sup>C heteronuclear data.



**Figure S5.** <sup>1</sup>H NMR spectrum of  $[Ag(p-tol)(1)_2] \cdot (H_2O)$  at 10 h intervals of UV exposure and [2+2] cycloaddition reaction (300 MHz, DMSO-*d*<sub>6</sub>). Note the disappearance of doublets centered around 7.30 ppm and 7.66 ppm (f, g), which correspond to the olefinic protons and the emergence of the resonances due to cyclobutane protons around 4.65 ppm and 4.85 ppm. The spectra were collected on the Fourier-300 spectrometer operating at 300 MHz.



**Figure S6-A.** <sup>1</sup>H-<sup>1</sup>H COSY cross-section showing the aromatic and olefinic regions of the olefin of  $[Ag(p-tol)(1)_2] \cdot (H_2O)$  in presence of the anion,  $[C_7H_7SO_3]^-$ . The resonance assignments were annotated accordingly. Note that H<sub>g</sub> can be identified through the H<sub>f</sub>-H<sub>g</sub> and H<sub>i</sub>-H<sub>j</sub> COSY peaks, although it is overlapping with H<sub>i</sub> in the <sup>1</sup>H spectrum. It is also confirmed by the <sup>1</sup>H-<sup>13</sup>C HSQC and HMBC data (data not shown).



**Figure S6-B.** <sup>1</sup>H-<sup>1</sup>H COSY cross-section showing the methyl region of the olefin of  $[Ag(p-tol)(1)_2] \cdot (H_2O)$  in presence of the anion,  $[C_7H_7SO_3]^-$ . The resonance assignments were marked accordingly and were also confirmed by the <sup>1</sup>H-<sup>13</sup>C HSQC and HMBC data (data not shown).



**Figure S6-C.** <sup>1</sup>H-<sup>13</sup>C HSQC cross-section showing the aromatic and olefinic regions of the olefin of  $[Ag(p-tol)(1)_2] \cdot (H_2O)$  in presence of the anion,  $[C_7H_7SO_3]^-$ . Note that H<sub>g</sub> is resolved in the <sup>13</sup>C-dimension.



**Figure S7-A.** <sup>1</sup>H-<sup>1</sup>H COSY cross-section showing the aromatic and cyclobutyl regions of the photoproduct  $[Ag(p-tol)(2)] \cdot (H_2O)$  in presence of the anion,  $[C_7H_7SO_3]^-$ . The resonance assignments were labeled accordingly. Note that the resonances due to the olefinic protons are absent (cf. Figure S6-A). The assignments were also confirmed by the <sup>1</sup>H-<sup>13</sup>C HSQC and HMBC data.



**Figure S7-B.** <sup>1</sup>H-<sup>1</sup>H COSY cross-section showing the COSY correlation peak identifying the anion from,  $[C_7H_7SO_3]^-$ , from the resonances of the photoproduct  $[Ag(p-tol)(2)] \cdot (H_2O)$ . The relevant resonance assignments were marked. The assignments were also confirmed by the <sup>1</sup>H-<sup>13</sup>C HSQC and HMBC data.



**Figure S7-C.** <sup>1</sup>H-<sup>13</sup>C HMBC cross-section of the photoproduct  $[Ag(p-tol)(2)] \cdot (H_2O)$  in presence of the anion,  $[C_7H_7SO_3]^-$ . The cross peaks marked with boxes inside the spectrum are <sup>1</sup>H-<sup>13</sup>C single-bond correlation artefacts.

## References

[1] H.-J. Choi, I.-G. Song, Y.-H. Sim, H.-K. Bae, J.-W. Kim, L.S. Park. Mol. ( ryst. Liq. Cryst. 531, 4 (2010).