Supporting Information

Accelerating the initial rate of hydrolysis of methyl parathion with laser excitation using monolayer protected 10 nm Au nanoparticles capped with a Cu(bpy) catalyst.

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Synthesis. All reactions were conducted under N_2 using standard Schlenk line and catheter-tubing techniques unless otherwise stated. All ^{1}H and ^{13}C NMR were recorded on a Bruker 400 MHz NMR spectrometer and referenced to internal tetramethylsilane. Mass spectra were recorded on a Jeol AccuTOF JMS-T100LC mass spectrometer in DART or ESI mode, or were performed by HT Labs, San Diego, CA. Isotopic distributions and simulations were performed using IsoCalc(TM) v. 3.0 (part of the Jeol MassCenter Main Version 1.3.2e sofware suite) IR spectra were recorded on a Nicolet Magna 550 FT-IR spectrophotometer. UV/Vis spectra were recorded on a Hewlett Packard 8453 diode array UV/Vis spectrophotometer. Elemental analysis was performed by Atlantic Microlab, Norcross, GA.

Solvents were purified as follows: methanol, distilled from CaO; CH_2Cl_2 distilled from CaH_2; diethyl ether, THF (Sigma-Aldrich), chloroform (Fisher), ethanol (VWR), and $CDCl_3$, (Cambridge Isotope Laboratories). Silica gel (60-230 mesh, Sigma-Aldrich) and anhydrous Na_2SO_4 (Fisher) were used as received. Flash chromatography was performed using silica gel (60-230 mesh, 60Å). TLC was performed on SiO_2 plates with fluorescent indicator. Compounds were visualized under UV light, 1% $FeCl_2$ solution or phosphomolybdic acid.

Reagents were obtained as follows and used without further purification: pyridine, thionyl chloride, triethylamine, copper(II) chloride dihydrate (Sigma-Aldrich), hydrochloric acid, sodium hydroxide (Fisher).

S-(6-aminohexyl)ethanethioate,[1] and 2,2'-bipyridinyl-5-carbonyl chloride[2] were synthesized according to the literature procedures. The reaction scheme for compounds **1-4** is shown in Figure S1.

***S*-(6-(2,2'-bipyridinyl-5-carboxamido)hexyl)ethanethioate (1)**. A 250 mL round bottom flask was charged with 2,2'-bipyridinyl-5-carbonyl chloride (0.19 g, 0.98 mmol) and CH_2Cl_2 (12 mL). Then, a solution of *S*-(6-aminohexyl)ethanethioate, Et_3N (3.0 mL), and pyridine (3.0 mL) in CH_2Cl_2 (20 mL) was added dropwise. The mixture was refluxed for 16 hours, allowed to cool and filtered through celite. The celite plug was rinsed with CH_2Cl_2 (100 mL) and the organic phase was washed with water (7 x 100 mL). The aqueous layers were combined and extracted with CH_2Cl_2 (3 x 100 mL) and the organic phase was then dried over Na_2SO_4. The solvent was removed under oil-pump vacuum and the resulting residue was purified using flash chromatography (SiO_2/$CHCl_3$:MeOH:NH_4OH (75:23:2)) to give **1** as an orange solid. Yield: 0.16 g, 85%. IR (NaCl, thin film): ν(C=O) 1689 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.10 (s, 1H, CH), 8.74 (d, 1H, CH), 8.50 (dd, 2H, 2 x CH), 8.25 (d, 1H, CH), 7.93 (t, 1H), 7.43 (t, 1H, CH), 6.41 (br, s, NH), 3.50 (m, 2H, CH_2), 2.88 (m, 2H, CH_2), 2.33 (s, 3H, $OCCH_3$), 1.25 – 1.66 (m, 8H, 4 x CH_2). HR-ESI-MS (*m*/*z*): 358.33 (100%). Calcd. for $[C_{19}H_{24}N_3O_2S]^+$ + H: 358.16.

***N*-(6-mercaptohexyl)-2,2'-bipyridinyl-5-carboxamide (2)**. A 10 mL vial was charged with **1** (0.100 g, 0.279 mmol) and EtOH (1.2 mL). Then NaOH (7.2 M, 0.8 mL) was added dropwise and the resulting solution was refluxed for 2 hours. The solution was allowed to cool to room temperature and neutralized with HCl (2 M, 0.200 mL). Diethyl ether (1.2 mL) and water (1.2 mL) were added, and the organic layer was washed with H_2O (1.2 mL), dried over Na_2SO_4 and the solvent removed under oil-pump vacuum to give **2** as a white solid. Yield: 0.0402 g, 46%. IR (NaCl, thin film): ν(S-H) 2546 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 9.05 (s, 1H, CH), 8.71 (d, 1H, CH), 8.43 (dd, 2H, 2 x CH), 8.19 (d, 1H, CH), 7.85 (t, 1H), 7.36 (t, 1H, CH), 6.35 (br, s, NH), 3.50 (m, 2H, CH_2), 2.52 (m, 2H, CH_2), 1.25 – 1.64 (m, 8H, 4 x CH_2). ^{13}C NMR ($CDCl_3$): δ 165.57, 158.23, 155.03, 149.28, 147.63, 137.20, 135.84, 129.97, 124.40, 121.74, 120.77, 40.12, 33.82, 29.56, 27.98, 26.46, 24.53. HR-ESI-MS (*m*/*z*): 316.14 (100%). Calcd. for $[C_{17}H_{21}N_3OS]^+$ + H: 316.15.

Cu[(*N*-(6-mercaptohexyl)-2,2'-bipyridinyl-5-carboxamide)]Cl_2 (3). A 10 mL tube was charged with **2** (0.161 g, 0.512 mmol) and MeOH (5 mL) and was stirred for 5 min. Then, a solution of $CuCl_2 \bullet 2H_2O$ (0.087 g, 0.510 mmol) in MeOH (5 mL) was added dropwise and the brown-green solution was stirred for another 30 min. Stirring was discontinued, and after 2 hours the resulting precipitate was collected by filtration, washed with MeOH (ca. 5 mL) and dried under oil-pump vacuum to give **3** as a blue-green solid. Yield: 0.160 g, 69%. Anal. Calcd for $C_{17}H_{21}Cl_2CuN_3O$: C, 45.39; H, 4.70; N, 9.34. Found: C, 45.23; H, 4.69; N, 8.93.

Cu[*S*-(6-(2,2'-bipyridinyl-5-carboxamido)hexyl)ethanethioate]Cl_2 (4). A 10 mL tube was charged with **1** (0.031 g, 0.088 mmol) and MeOH (7 mL) and was stirred for 5 min. Then, a solution of $CuCl_2 \bullet 2H_2O$ (0.015 g, 0.088 mmol) in MeOH (5 mL) was added dropwise and the green solution was stirred for another 30 min. Stirring was discontinued, and after 2 hours the resulting precipitate was collected by filtration, washed with MeOH (ca. 5 mL) and dried under oil-pump vacuum to give **4** as a blue-green solid. Yield: 0.003 g, 10%. Anal. Calcd for $C_{19}H_{23}Cl_2CuN_3O_2S$: C, 46.39; H, 4.71; N, 8.54. Found: C, 45.21; H, 4.61; N, 8.47. HR-ESI-MS (*m*/*z*): 533.12 (100%), 535.12 (70%), 534.13 (30%), 536.17 (25%), 537.16 (20%), 538.133 (15%)/455.09 (100%), 457.09 (83%), 456.15 (18%), 458.11 (11%), 459.14 (10.5%). Calcd. for: $[Cu\{S$-(6-(2,2'-bipyridinyl-5-carboxamido)hexyl)ethanethioate$\}(OH)(OH_2)]^+$ + DMSO: 533.11 (100.0%), 535.11 (60%), 534.11 (60%), 536.11 (15%), 537.11 (10%), 538.11 (5.0%). Calcd. for: $[Cu\{S$-(6-(2,2'-bipyridinyl-5-carboxamido)hexyl)ethanethioate$\}(OH)(OH_2)]^+$: 455.09 (100.0%), 457.09 (55%), 456.10 (25%), 458.10 (15%), 459.10 (7.5%).[3]

Kinetics and laser excitation. UV-visible measurements were made with a Agilent 8453 diode array spectrometer and referenced against a solvent blank using a 50-µl micro-cell cuvette (part number 5062-2496, Agilent Technologies). For the laser photolysis studies, the samples were irradiated with an Aries 100 532 nm green laser with an average sustained power of 117.4 mW tested by the manufacturer. The bulk temperature was measured as a function of laser illumination time using a USB TC-08 thermocouple (Pico Technology) mount inside the micro-cell cuvette. No changes larger than 0.5 C in bulk temperature were measured with laser illumination.

References

1. A. Hallet, P. Christian, J. E. Jones, S. J. A. Pope, *Chem. Commun.*, 2009, 4278.
2. A. Kiehne, T. Weilandt and A. Lützen, Eur. *J. Org. Chem.*, 2008, 2056.
3. Percent abundances are reported for all isotopic distributions of separate species observed in the ESI-mass spectra. Identification of aquo-hydroxy copper species, presumably due to trace water in the solvent (DMSO), were based on the best-fit to calculated/simulated values. It should be noted however that alternative species of the type $[Cu(L)Cl]^+$ and $[Cu(L)DMSO]^+$ gave almost identical fits. A more detailed analysis of the ESI-MS data will be published elsewhere.

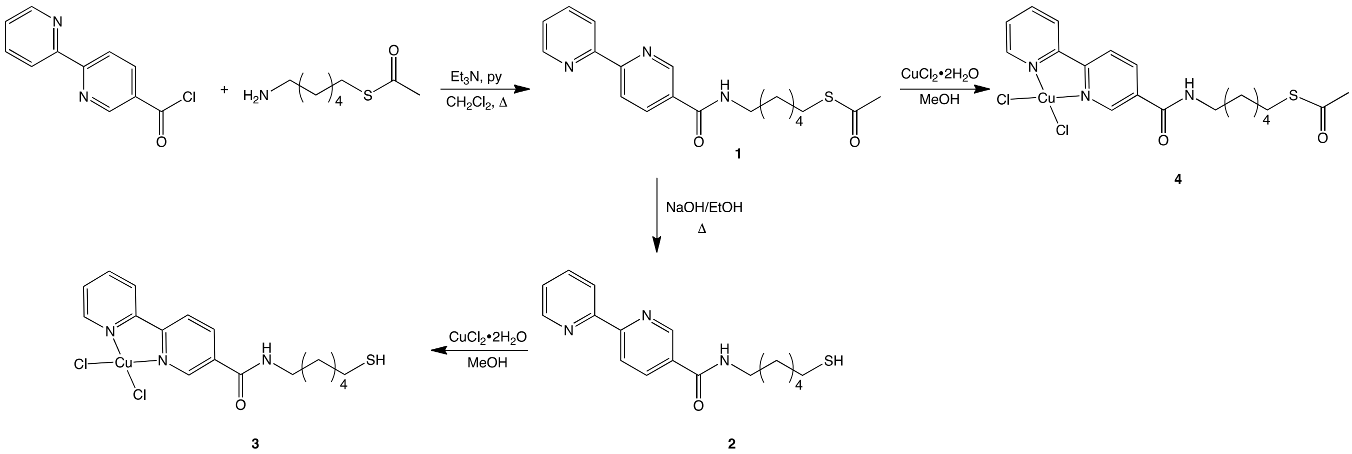

Figure S1. Synthesis of compounds 1-3.