

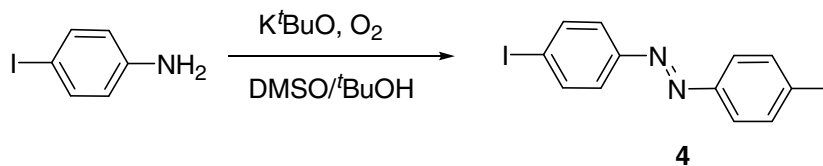
Supporting Information for Langmuir Monolayers of a Photo-isomerizable Macrocycle Surfactant

Eric Karp¹, Cory S. Pecinovsky², Michael J. McNevin², Douglas L. Gin^{1,2},
and Daniel K. Schwartz^{1*}

Experimental Section:

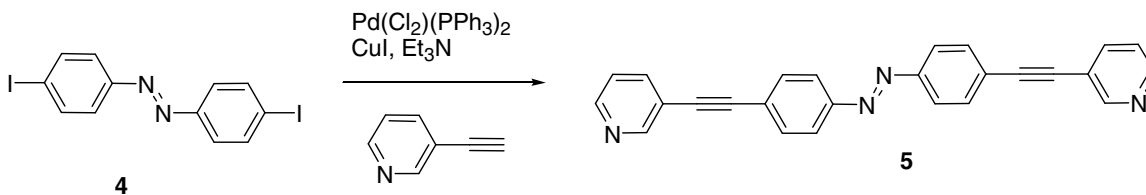
Materials and General Procedures. All solvents and reagents were purchased from the Aldrich Chemical Co. Triethylamine was distilled over sodium and used as required. Dichloromethane was distilled over CaH₂, and used as required.

Instrumentation. ¹H and ¹³C NMR spectra were obtained using a Varian Inova 400 (400 MHz for ¹H, 100 MHz for ¹³C), or a Varian Inova 300 (300 MHz ¹H) spectrometer. Chemical shifts are reported in ppm relative to residual non-deuterated solvent. UV-Visible absorption spectra were obtained at 21 ± 1 °C using an Agilent 8453 spectrometer. Infrared spectra were recorded using a Mattson Satellite FTIR spectrometer. The FT-IR samples were prepared as thin films on Ge crystals. The Shark series (OTLH-0280-UV) 375 nm UV-LED from Opto Technology, Inc. was used to irradiate samples, driven at 200 mA. Visible light was provided by the 470 nm UV-LED (OTLH-0010-BU), driven at 300 mA. Minimization of **1b** was performed with Cache Ab Initio (version 6.1.12.33), using the semi-empirical PM5 method.



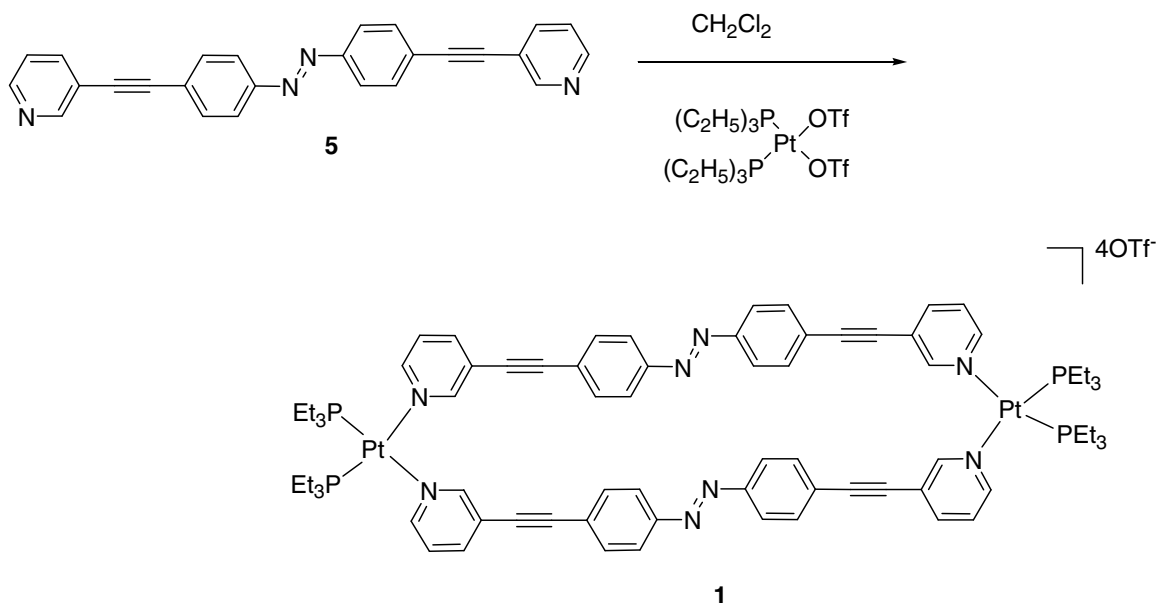
Scheme S1. Synthesis of azobenzene **4**

Bis-(4-iodo)-azobenze (4): 4-iodoaniline (3.1 g, 14 mmol) and ^tBuO⁻K⁺ (3.5 g, 36 mmol) were added to a 1000 mL flask containing a magnetic stir bar, followed by 500 mL of an 80/20 mixture of DMSO/^tBuOH. O₂ was bubbled for 2 h with stirring, during which time an orange precipitate formed. The mixture was filtered through a fritted funnel, and washed successively with methanol (50 mL), water (50 mL), and methanol (50mL). The orange powder was dried under vacuum to yield 1.5 g (48 %). Spectral data agreed with literature values.¹



Scheme S2. Synthesis of azobenzene bipyridine **5**

Bis-(4-pyridin-3-ylethynyl)-azobenzene (5): Into a flask charged with **4** (1.05 g, 2.4 mmol) was added 3-ethynylpyridine (0.52 g, 4.8 mmol), copper (I) iodide (23 mg, 0.12 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (84 mg, 0.12 mmol), triphenylphosphine (50 mg, 0.2 mmol) and triethylamine (25 mL). The mixture was heated to 60 °C and stirred for 16 h under argon. After cooling, the solvent was evaporated and the mixture was chromatographed over silica gel using CH_2Cl_2 with gradient elution of EtOAc (increasing concentration from 0% to 50% by volume). Yield of orange powder: 350 mg (40%; low due to poor solubility). $^1\text{H NMR}$ (400 MHz): δ 8.78 (d, 2H), 8.57-8.55 (dd, 2H), 7.94-7.92 (m, 4H), 7.84-7.81 (m, 2H), 7.69-7.67 (m, 4H), 7.31-7.28 (m, 2H). $^{13}\text{C NMR}$ (125 MHz): δ 152.5, 152.3, 149.1, 132.8, 125.7, 123.4, 120.3, 92.5, 88.8. IR (cm^{-1}) 453, 564, 701, 724, 800, 852, 1020, 1108, 1153, 1186, 1284, 1405, 1492, 1557, 1594. HRMS $[\text{M}+\text{H}]^+$ calcd: 385.1447 found: 385.1435.



Scheme S3. Synthesis of macrocycle **1**

Azobenzene macrocycle (1): Into a flask was added equimolar amounts of **5** and $\text{Pt}(\text{PEt}_3)_2(\text{OTf})_2$ with 5 mL dichloromethane. The solution started turbid due to the poor solubility of **5** but turned clear red over the course of 6 h. At this point, diethyl ether can be added to precipitate **1** and the orange precipitate washed with cold dichloromethane to produce pure product in nearly quantitative yield. X-ray quality crystals can be grown by the slow vapor diffusion of diethyl ether into nitromethane.³ $^1\text{H NMR}$ (400 MHz): δ 9.77, 9.75 (s,s 4H), 9.22, 9.20 (s,s 4H), 8.27-8.25 (m, 4H), 7.85-7.71 (m, 20H), 2.82-2.14

(m, 24H) 1.45-1.37 (m, 36H). ^{13}C NMR (125 MHz): δ 152.6, 152.3, 149.2, 138.8, 132.8, 125.7, 123.4, 123.3, 120.3, 92.5, 88.8. ^{31}P (162 MHz) δ 10.1 (Pt satellite), 0.4, 0.3, -9.3 (Pt satellite). IR (cm^{-1}) 700, 852, 1019, 1152, 1402, 1491, 1593, 2322, 2329, 2343, 2357.

The NMR data clearly show the presence of two sets of resonances, presumably one for each of two conformers as seen previously.⁴ The two conformers are found in nearly equal amounts and are likely close in energy. The boat conformer crystallizes preferentially. This creates some difficulty in interpreting the NMR data of the “open” form, given the complex mixture in that state. From the NMR data, it appears as if there is a mixture of *cis-cis*, *cis-trans*, and *trans-trans* isomers of the boat and chair conformers (Figure S1). What is clear from the NMR data, is that the macrocycle remains intact during the isomerization process, since no free pyridine was observed.

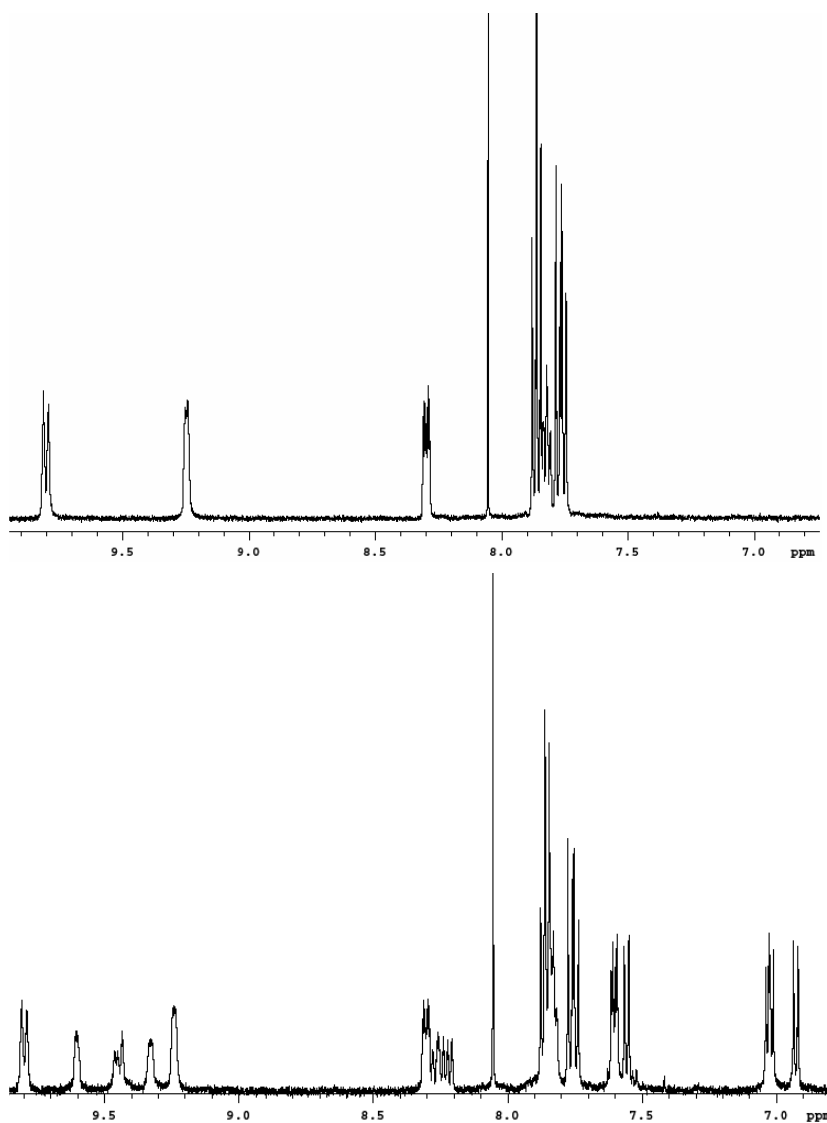
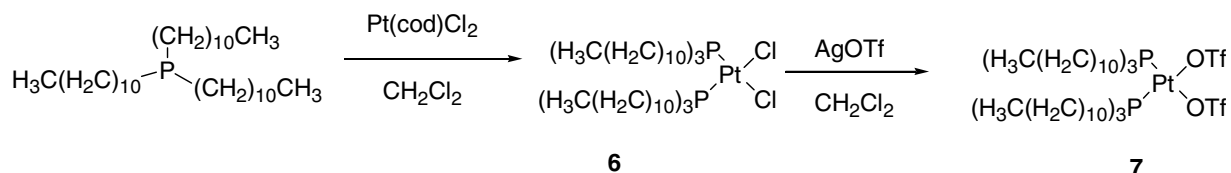


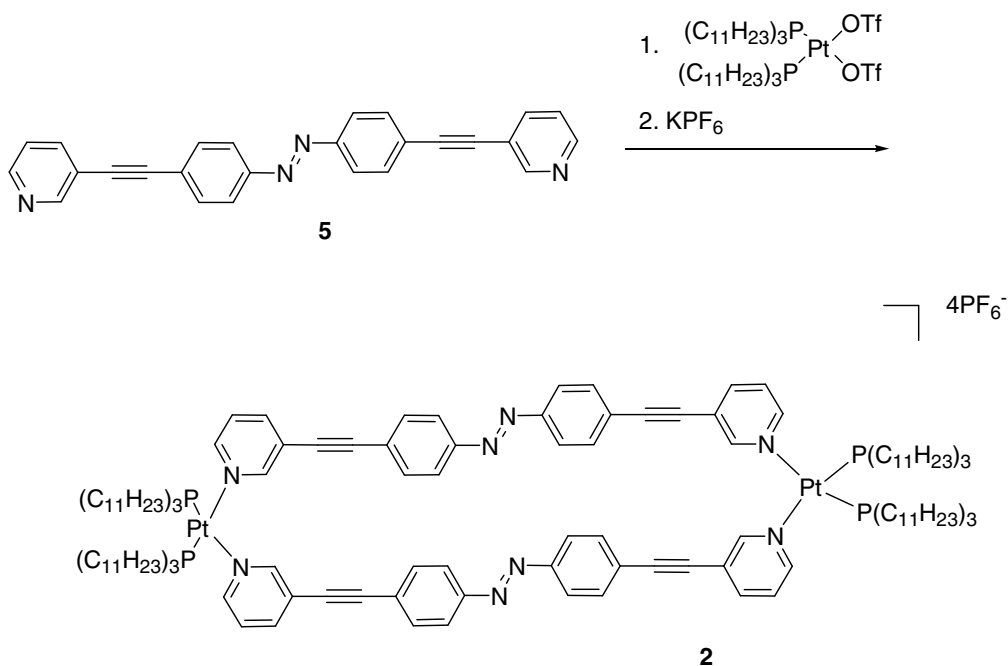
Figure S1. NMR before (top) and after (bottom) irradiation of **1** with 375 nm light.



Scheme S4. Synthesis of triundecylphosphineplatinum(II) compounds

Dichlorobis(triundecylphosphine)platinum(II) (6): To a flask containing triundecylphosphine⁵ (0.66 g, 1.4 mmol) under argon was added dichloro(1,5-cyclooctadiene)platinum(II) (0.20 g, 0.59 mmol) and 10 mL dichloromethane. After 2 h, the solvent was removed under vacuum. The product **6** was purified by successive recrystallizations from ethanol as a white, waxy solid. Yield: 410 mg (40%). ¹H NMR (300 MHz): δ 1.95 (brd, 12H), 1.52 (brd, 12H), 1.38 (brd, 12H), 1.25 (brd, 84H), 0.87 (t, 18H). ¹³C NMR (125 MHz): δ 31.2, 31.3, 29.9, 29.8, 29.6, 24.7, 22.9, 14.3. ³¹P NMR (162 MHz): δ 12.9 (Pt satellite), 2.0, -8.8 (Pt satellite). IR (cm⁻¹) 721, 1467, 2850, 2920, 2956. HRMS [M-Cl]⁺ calcd: 1221.9588 found: 1221.9531

Ditrifluoromethanesulfonate(triundecylphosphine)platinum(II) (7): To a flask containing **6** (0.32 g, 0.25 mmol) was added silver triflate (0.14 g, 0.53 mmol) and dichloromethane (20 mL). The two were allowed to stir in the dark for 16 h. The silver chloride was filtered off, and the solvent evaporated under vacuum to yield a viscous oil. The oil could be purified by making a suspension in nitromethane (20 mL), centrifugation, and evaporation of the solvent under vacuum. This oil then solidified upon standing. Yield: 0.27 g (75%). ¹H NMR (400 MHz) δ 1.90 (brd, 12H), 1.56 (brd, 12H), 1.45 (brd, 12H), 1.26 (brd, 84H), 0.87 (t, 9H). ¹³C NMR (125 MHz): δ 32.1, 31.0, 29.8, 29.7, 29.6, 29.4, 24.3, 22.9, 14.3. ³¹P NMR (162 MHz): δ 13.5 (Pt satellite), 2.1, -6.2 (Pt satellite). IR (cm⁻¹) 2955, 2925, 2854, 1295, 1225, 1024, 638, 569, 519. HRMS [M-OTf]⁺ calcd: 1334.9279 found: 1334.9266



Scheme S5. Synthesis of amphiphilic macrocycle **2**

Amphiphilic Azobenzene Macrocycle (2): To a flask containing **7** (48 mg, 0.032 mmol) and **5** (10 mg, 0.026 mmol) dichloromethane (5 mL) was added as the solvent. The solution started turbid but gradually turned clear over the course of 6 h. A saturated solution of KPF_6 was prepared in water (20 mL), and was added to the reaction mixture and transferred to a separatory funnel. The organic fraction was separated and the solvent evaporated. Isopropyl ether was added (10 mL) and the product **2** precipitated out in the freezer as a red solid. Yield: 55%. ^1H NMR (400 MHz) δ 9.42 (s, 2H), 9.38 (s, 2H), 8.87 (brd, 4H), 7.84-7.82 (m, 4H), 7.78-7.71 (q, 8H), 7.65 (s, 8H), 7.54-7.50 (m, 4H), 1.90 (brd, 24H), 1.78 (brd, 24H), 1.60 (brd, 24H), 1.25 (brd, 84H), 0.88-0.84 (t, 36H). ^{13}C NMR (125 MHz): δ 153.0, 149.5, 141.5, 133.0, 127.0, 122.5, 32.1, 31.3, 29.9, 29.8, 29.5, 29.0, 23.8, 22.9, 14.3. ^{31}P NMR (162 MHz): δ -1.2 (Pt satellite), -10.9, -11.0, -21.0 (Pt satellite). IR (cm^{-1}) 2955, 2926, 2854, 2224, 1600, 1570, 1465, 1419, 845, 557.

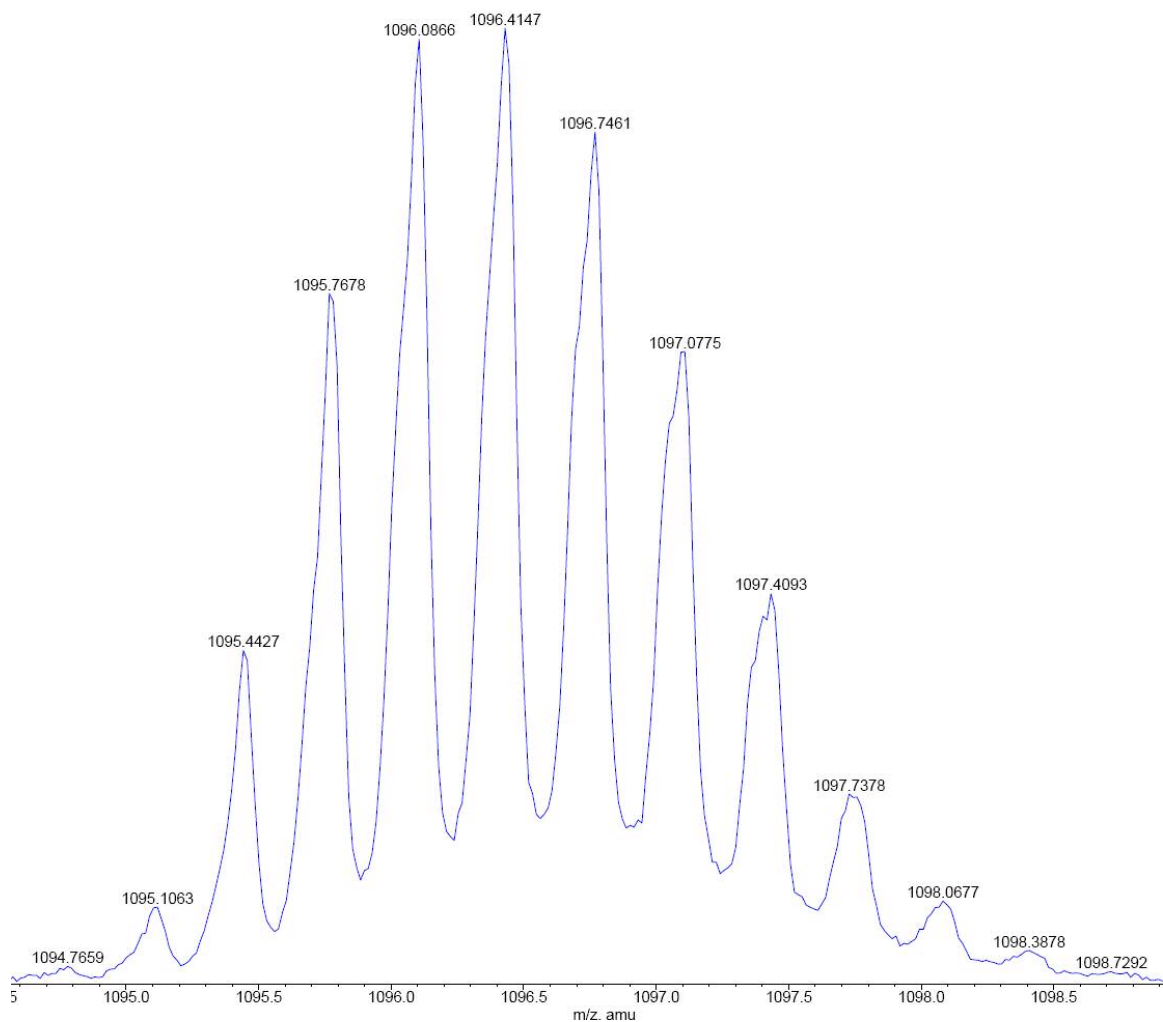


Fig. S1. Mass spectrum obtained from the +3 ion of **2**

UV-Vis Spectra

An Agilent® 8453 spectrometer was used to obtain the UV-vis spectra of the LB film on the quartz substrate. The quartz slides were held in the beam path of the UV-vis spectrometer, with a small slide holder purchased from THOR Labs®. The integration time was set at 20 seconds, in order to improve the signal to noise ratio. After a spectrum was obtained, the LB films was irradiated by a UV LED array, at a distance of about 5 cm, for 20 minutes. Another UV-vis spectrum was then taken to determine the extent of the isomerization that had occurred.

Isomerization experiments of molecule **2** were also performed in bulk solution. A quartz cuvette filled with acetone (3 mL) was used to blank the Agilent® 8453. 0.5 mg of **2** was added, mixed to homogeneity, and an initial spectrum was obtained. The UV light was turned on, placed approximately 5 cm from the cuvette, and spectra were obtained in 30 s intervals until the absorbance band at 375 nm decreased to a consistent value.

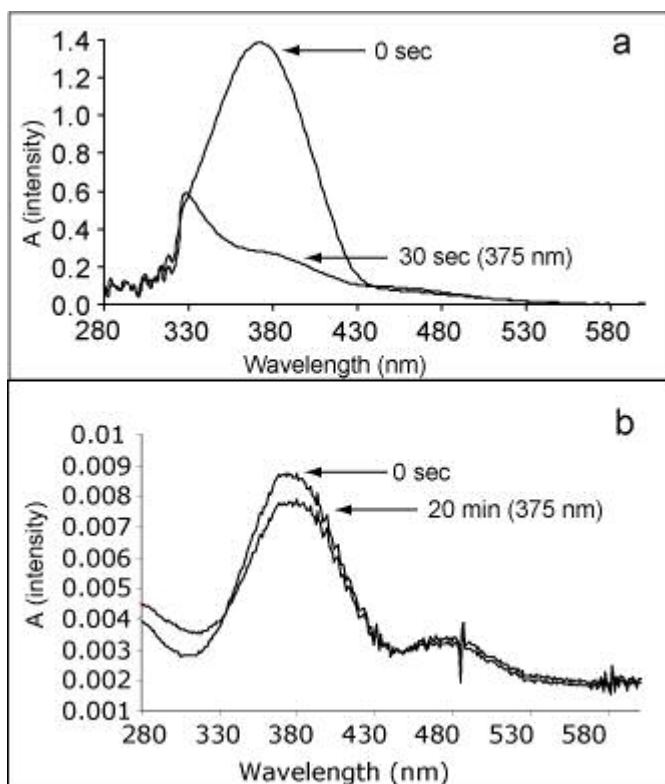


Fig. S2. UV-vis spectra of **2** taken in (a) dilute acetone soln (b) transferred onto a quartz substrate as a monolayer. Samples were irradiated with 375 nm light until a steady state was reached.

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- (1) Li, Y. Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1998**, *110*, 8092-8.
- (2) Stang, P. J.; Cao, D. H. *J. Am. Chem. Soc.*, **1994**, *116*, 4981.
- (3) CCDC 646228 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- (4) Chi, K.; Addicott, C.; Arif, A. M.; Das, N.; Stang, P. J. *J. Org. Chem.* **2003**, *68*, 9798-9801.
- (5) Franks, S.; Hartley, F. R.; McCaffrey, D. J. A. *J. Chem. Soc. Perkin Trans. 1* **1979**, *12*, 3029-33.