Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

Photoswiching tetranuclear rhenium(I) tricarbonyl diimine complexes with a stilbene-like bridging ligand

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Experimental Section

Equipment and Procedures. NMR spectra were obtained using a Brucker AM 360 spectrometer. Infared spectra were measured on a Nicolet 20SXC Fourier Transform Infrared spectrophotometer. Infrared spectra were measured on a Nicolet 20SXC Fourier transform infrared spectrophotometer. UV-Vis spectra were obtained using a Varian Cary 300 UV-Vis spectrophotometer. Emission spectra were recorded in deoxygenated CH_3CN solution at 293 K with a Fluorolog III fluorescence spectrophotometer equipped with a red sensitive Hamamatsu R928 photomultiplier tube. Luminescence quantum yields were calculated relative to $[Re(bpy)(CO)_3(4\text{-}Etpy)]PF_6$ in deoxygenated acetonitrile ($\Phi = 0.027$).[1] Luminescence quantum yields were taken as the average of three separate determinations and were reproducible to within 10%. Photolysis experiments were carried out with a 200-W medium-pressure Hg arc lamp with Ealing Corp. interference filters (10-nm band pass) to isolate the excitation wavelength. The quantum efficiencies of photoisomerization (Φ_{iso}) in CH_3CN at 293 K were determined based on the first 5% of the absorbance change. High-resolution mass spectra were acquired on a Waters LCT time-of-flight mass spectrometer equipped with an electrospray ionization probe.

Materials and Synthesis. All chemicals are commercially available unless noted otherwise. All reactions and manipulations were carried out under N_2 with the use of standard inert-atmosphere and Schlenk techniques. Solvents used for synthesis were dried by standard procedures and stored under N_2. Solvents used in luminescent and electrochemical studies were spectroscopic and anhydrous grade, respectively. The compounds 1,2,4,5-tetrakis((*E*)-2-(pyridin-4-yl)vinyl)benzene (**L**)[2] and $(NN)Re(CO)_3(CH_3CN)(PF_6)$[3] were prepared according to published procedures.

Complex 1. Yield: 45%. IR (υ_{CO}, CH_3CN): 2035, 1931. ^{1}H NMR (360 MHz, DMSO-d_6): 9.35 (d, 8 H, J = 5.3 Hz, $H_{6,6'}$-bpy), 8.72 (d, 8H, *J* = 8.0 Hz, $H_{3,3'}$-bpy), 8.42 (t, 8H, *J* = 7.8 Hz, $H_{4,4'}$-bpy), 8.30 (d, 8H, *J* = 5.9 Hz, H_α-py) 8.04 (s, 2 H, ph), 7.95 (t, 8H, *J* = 7.8 Hz, $H_{5,5'}$-bpy), 7.88 (d, 4H, *J* = 15.8 Hz, py-C*H*=CH-ph), 7.58 (d, 8H, *J* = 6.2 Hz, H_β-py), 7.20 (d, 4H, *J* = 15.8 Hz, py-CH=C*H*-ph). ^{13}C NMR (90 MHz, DMSO-d_6): 195.5, 192.1, 155.1, 154.0, 151.7, 147.4, 141.4, 135.5, 132.6, 129.0, 128.0, 124.8, 124.6, 123.8. HRESIMS: m/z = 2633.1555 (Calcd. m/z = 2633.1453 for $[M\text{-}PF_6]^+$). Anal. Calcd. for $C_{86}H_{58}N_{12}O_{12}Re_4P_4F_{24}$: C, 37.21; H, 2.11; N, 6.05. Found: C, 37.05; H, 2.19; N, 5.88.

Complex 2. Yield: 62%. IR (υ_{CO}, CH_3CN): 2034, 1932. ^{1}H NMR (360 MHz, DMSO-d_6): 9.34 (d, 4H, *J* = 5.4 Hz, H_6-bpy), 8.62 (d, 4H, *J* = 8.4 Hz, $H_{3'}$-bpy), 8.49

(d, 4H, *J* = 8.0 Hz, H_3-bpy), 8.38 (t, 4H, *J* = 7.9 Hz, $H_{4'}$-bpy), 8.27 (t, 4H, *J* = 8.0 Hz, H_4-bpy), 8.02 (d, 8H, *J* = 6.0 Hz, H_α-py), 7.99 (d, 4H, *J* = 8.4 Hz, $H_{5'}$-bpy), 7.90 (t, 4H, *J* = 7.0 Hz, H_5-bpy), 7.90 (s, 2H, -ph), 7.87 (d, 4H, *J* = 16.0 Hz, py-C*H*=CH-ph), 7.54 (d, 8H, *J* = 6.0 Hz, H_β-py), 7.20 (d, 4H, *J* = 16.0 Hz, py-CH=C*H*-ph), 3.17 (s, 12H, -CH_3). ^{13}C NMR (90 MHz, DMSO-d$_6$): 196.3, 194.9, 191.9, 162.7, 155.8, 155.7, 153.7, 152.0, 147.3, 141.4, 141.3, 135.5, 132.7, 129.1, 128.8, 128.0, 125.2, 125.0, 123.9, 122.4, 30.4. HRESIMS: m/z = 2689.2012 (Calcd. m/z = 2689.2079 for $[M\text{-}PF_6]^+$). Anal. Calcd. for $C_{90}H_{66}N_{12}O_{12}Re_4P_4F_{24}$: C, 38.17; H, 2.35; N, 5.93. Found: C, 37.99; H, 2.45; N, 5.99.

Complex 3. Yield: 70%. IR (υ_{CO}, CH_3CN): 2032, 1927. ^{1}H NMR (360 MHz, DMSO-d_6): 9.16 (d, 8H, *J* = 5.7 Hz, $H_{6,6'}$-bpy), 8.59 (s, 8H, $H_{3,3'}$-bpy), 8.28 (d, 8H, *J* = 6.3 Hz, H_α-py), 7.98 (s, 2H, ph), 7.88 (d, 4H, *J* = 16.0 Hz, py-C*H*=CH-ph), 7.75 (d, 8H, *J* = 5.3 Hz, $H_{5,5'}$-bpy), 7.59 (d, 8H, *J* = 6.5 Hz, H_β-py), 7.19 (d, 4H, *J* = 16.0 Hz, py-CH=C*H*-ph), 2.55 (s, 24H, -CH_3). ^{13}C NMR (90 MHz, DMSO-d_6): 195.6, 192.4, 154.7, 153.7, 153.3, 151.7, 147.3, 135.5, 132.6, 129.5, 128.0, 125.3, 125.2, 123.9, 21.0. HRESIMS: m/z = 2745.2646 (Calcd. m/z = 2745.2705 for $[M\text{-}PF_6]^+$). Anal. Calcd. for $C_{94}H_{74}N_{12}O_{12}Re_4P_4F_{24}$: C, 39.21; H, 2.66; N, 5.95. Found: C, 39.09; H, 2.58; N, 5.82.

Complex 4. Yield: 67%. IR (υ_{CO}, CH_3CN): 2032, 1927. ^{1}H NMR (DMSO-d_6): 9.51 (s, 8H, $H_{2,9}$-phen), 8.41 (s, 8H, $H_{5,6}$-phen), 8.40 (d, 8H, *J* = 4.8 Hz, H_α-py), 7.81 (s, 2H, ph), 7.69 (d, 4H, *J* = 16.2 Hz, py-C*H*=CH-ph), 7.41 (d, 8H, *J* = 5.7 Hz, H_β-py), 7.03 (d, 4H, J = 16.1 Hz, py-CH=C*H*-ph), 2.84 (s, 24H, 4,7-Me), 2.71 (s, 24H, 3,8-Me). ^{13}C NMR (90 MHz, DMSO-d_6): 195.6, 192.5, 155.0, 151.8, 148.5, 147.2, 144.2, 135.9, 135.4, 132.3, 128.9, 128.0, 125.1, 124.3, 123.6, 17.3, 15.1. HRESIMS: m/z = 2953.4067 (Calcd. m/z = 2953.3957 for $[M\text{-}PF_6]^+$). Anal. Calcd. for $C_{110}H_{90}N_{12}Re_4O_{12}P_4F_{24}$: C, 42.66; H, 2.93; N, 5.43. Found: C, 42.81; H, 2.79; N, 5.55.

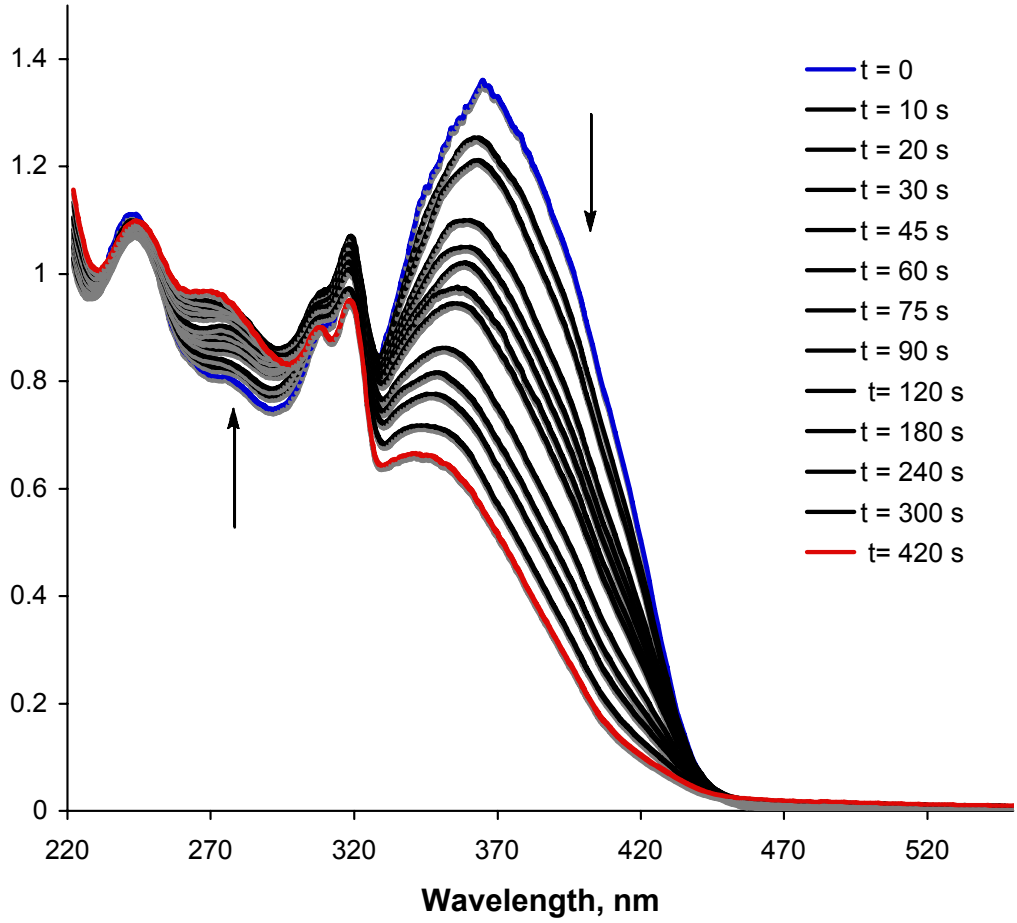

Fig. S1 Spectral changes of complex **1** (1.6×10^{-5} M) in a N_2 degassed acetonitrile solution upon irradiation at 405 nm at 293 K. The direction of arrows shows increasing photolysis time.

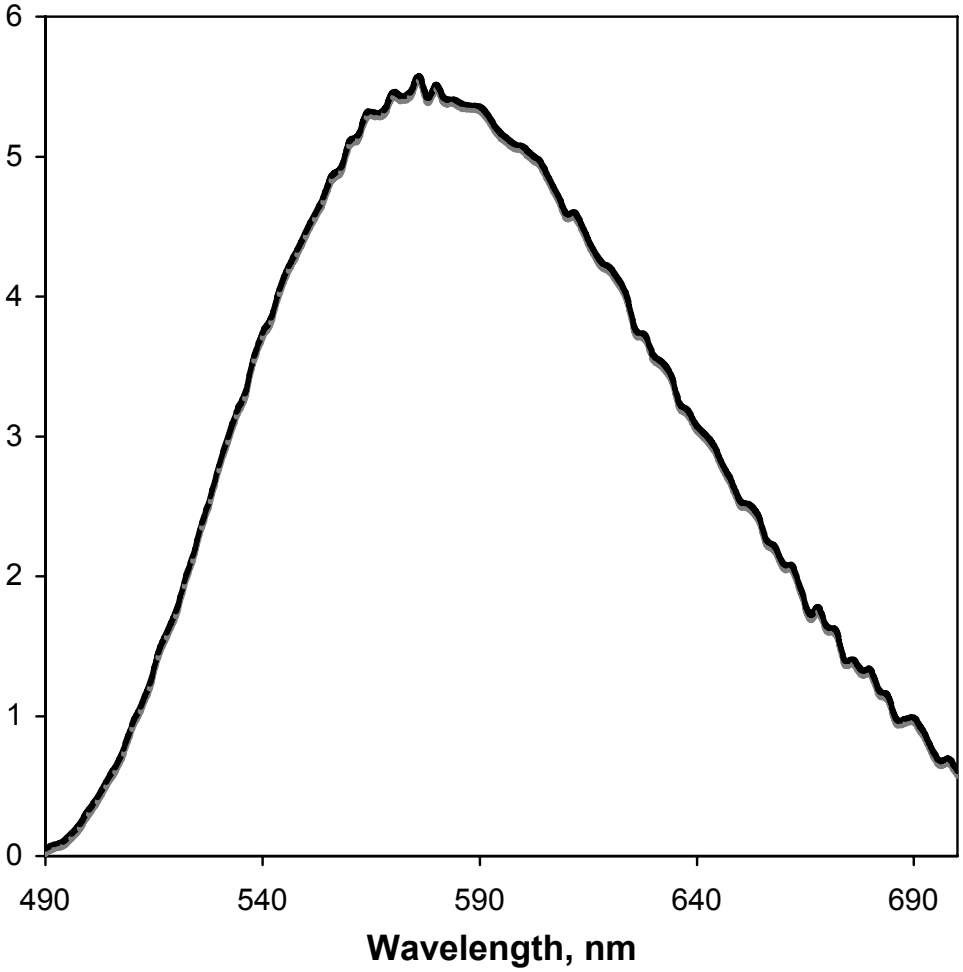

Fig. S2 Emission spectrum of complex **1** (1.6×10^{-5} M) in a N_2 degassed acetonitrile solution after irradiation at 405 nm for 420 s at 293 K. The excitation wavelength was 380 nm.

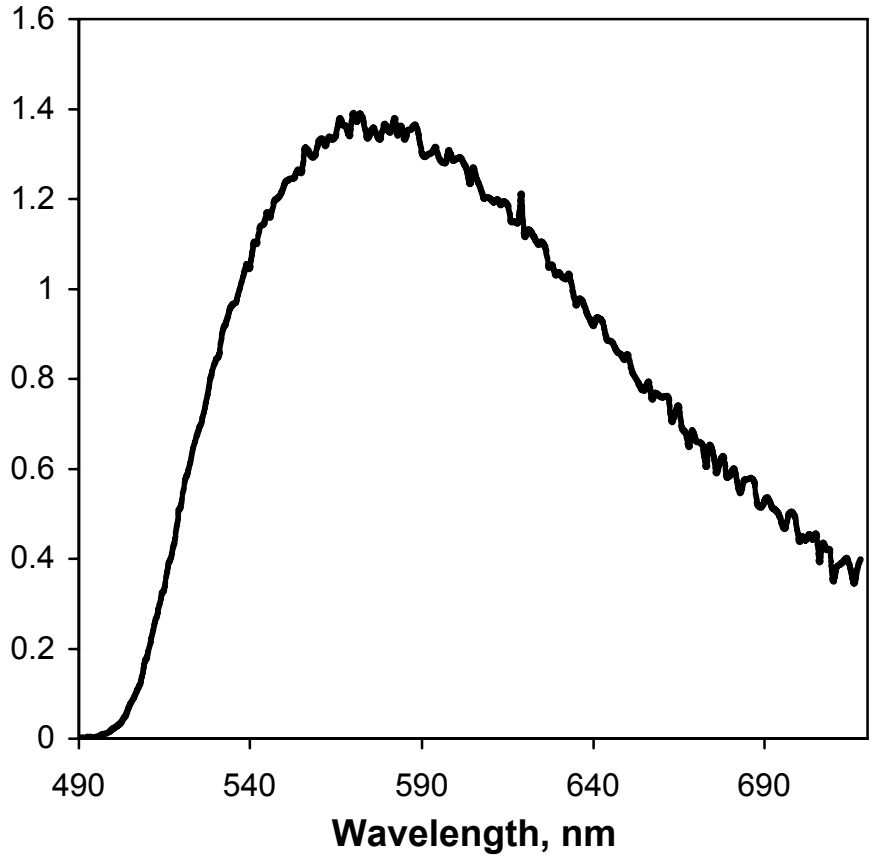

Fig. S3 Emission spectrum of complex **2** (3.1×10^{-5} M) in a N_2 degassed acetonitrile solution after irradiation at 405 nm for 300 s at 293 K. The excitation wavelength was 380 nm.

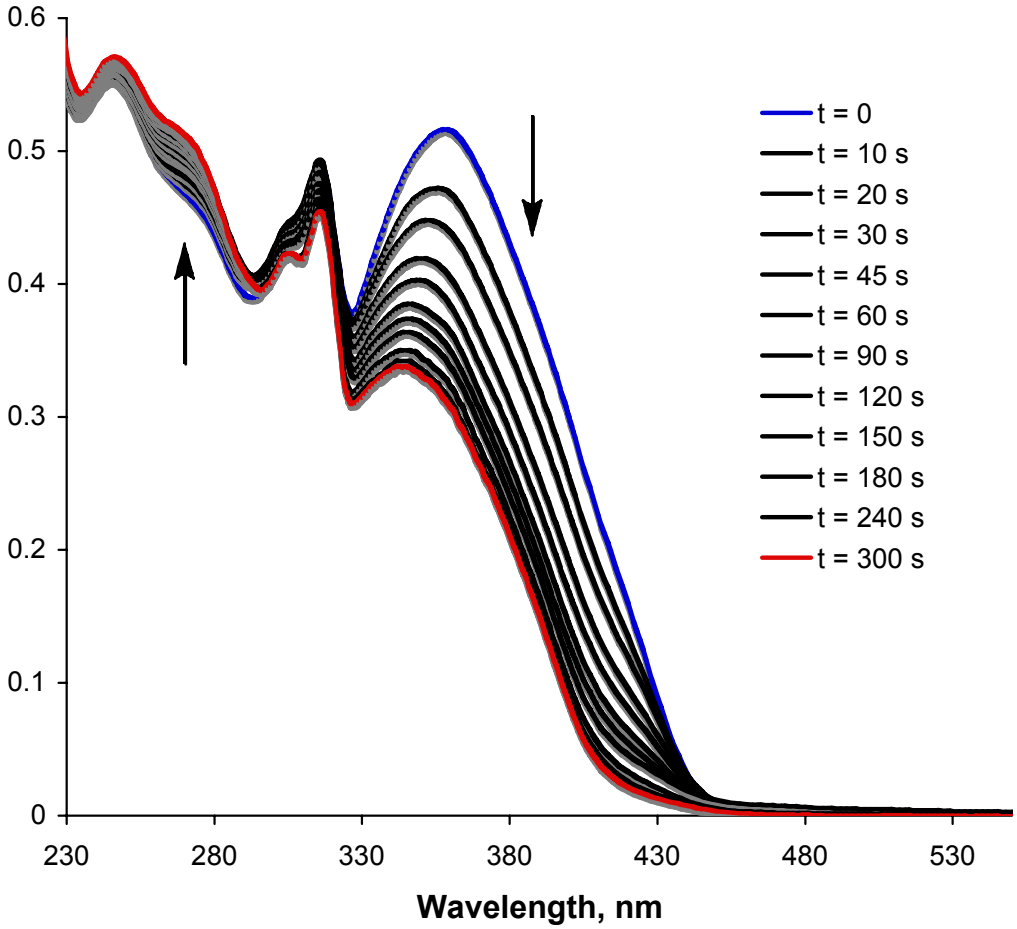

Fig. S4 Spectral changes of complex **3** (5.0×10^{-6} M) in a N_2 degassed acetonitrile solution upon irradiation at 405 nm at 293 K. The direction of arrows shows increasing photolysis time.

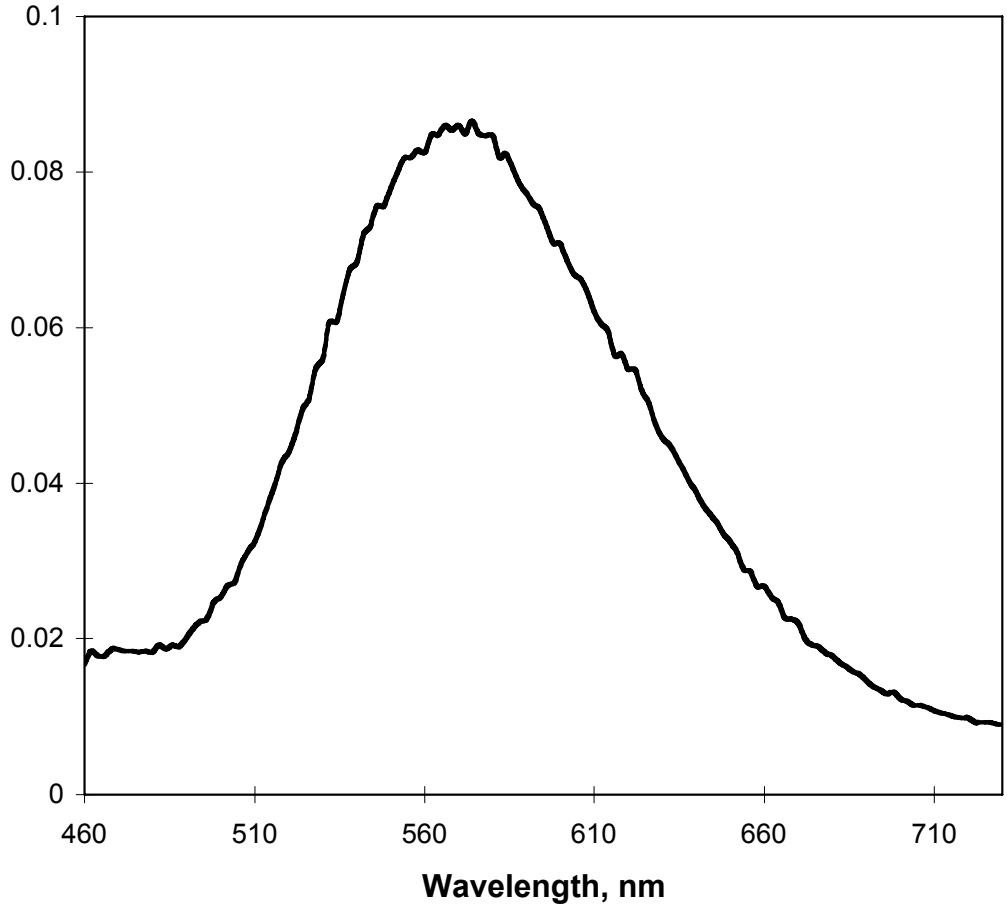

Fig. S5 Emission spectrum of complex **3** (5.0×10^{-6} M) in a N_2 degassed acetonitrile solution after irradiation at 405 nm for 300 s at 293 K. The excitation wavelength was 380 nm.

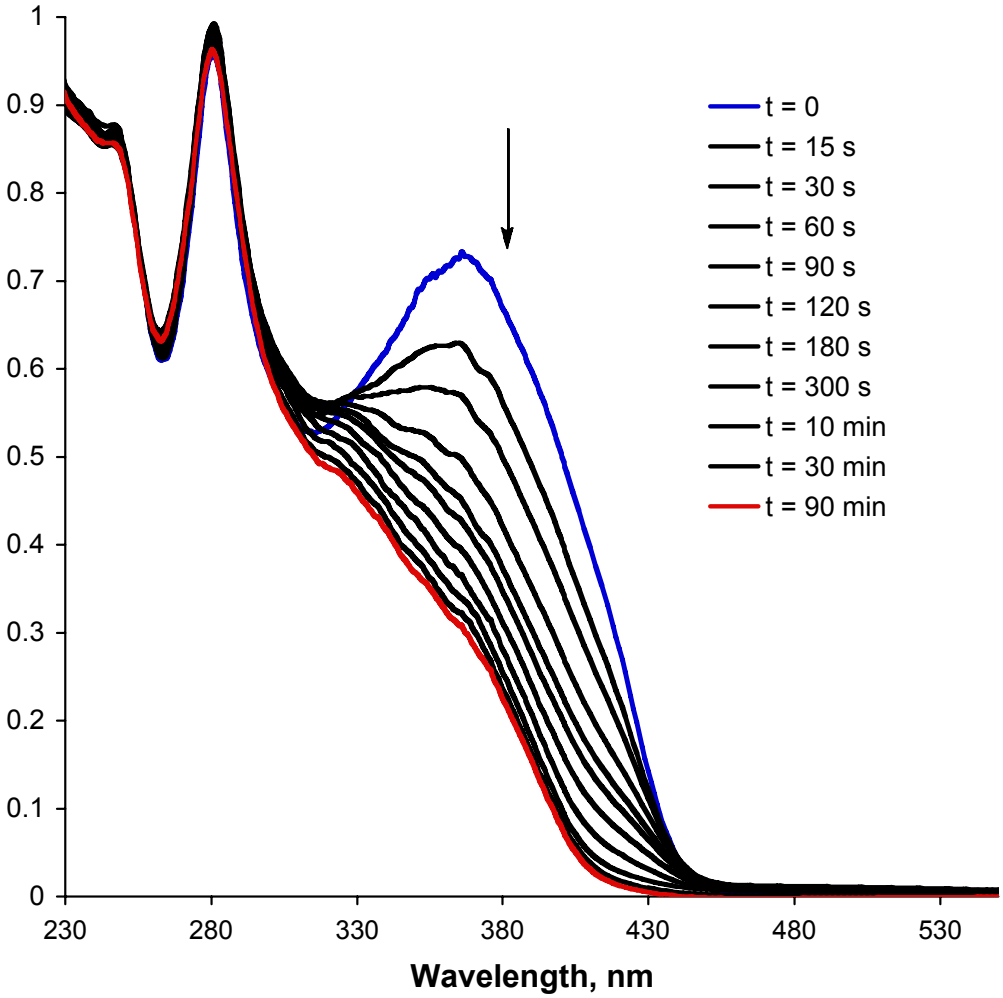

Fig. S6 Spectral changes of complex **4** (7.3×10^{-6} M) in a N_2 degassed acetonitrile solution upon irradiation at 405 nm at 293 K. The direction of arrows shows increasing photolysis time.

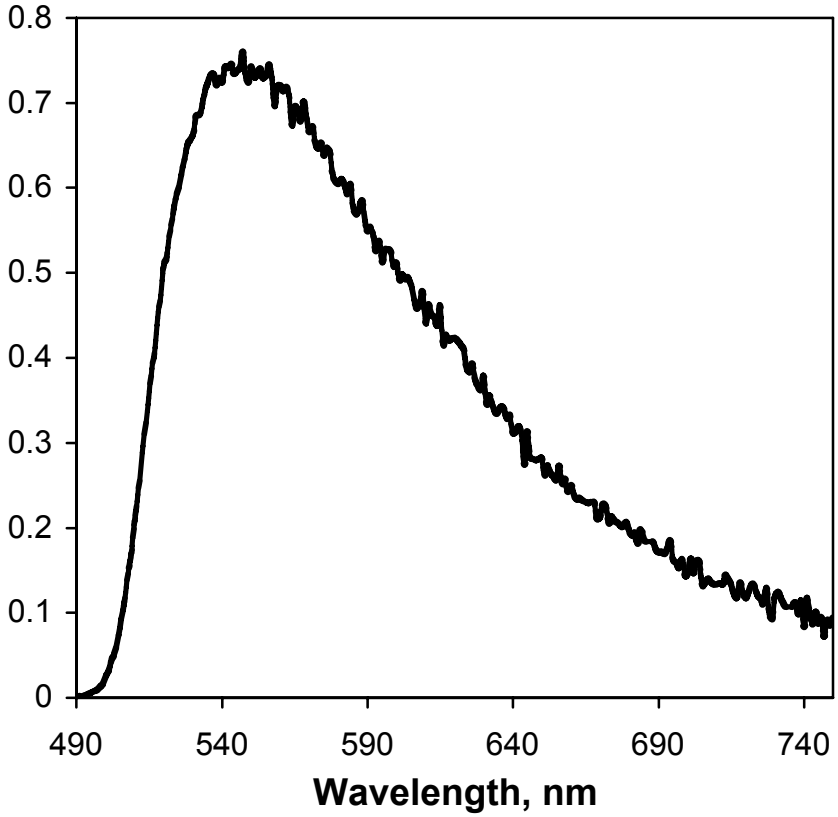

Fig. S7 Emission spectrum of complex **4** (7.3×10^{-6} M) in a N_2 degassed acetonitrile solution after irradiation at 405 nm for 90 min at 293 K. The excitation wavelength was 380 nm.

References:

1. G. Tapolsky, R. Duesing, T. J. Meyer, *Inorg. Chem.,* 1990, **29**, 2285-2294.
2. A. J. Amoroso, A. M. W. Cargill Thompson, J. P. Maher, J. A. McCleverty, M. D. Ward, *Inorg. Chem.,* 1995, **34**, 4828-4835.
3. (a) J. V. Caspar, T. J. Meyer, *J. Phys. Chem.,* 1983, **87**, 952-957. (b) S.-S. Sun, P. Zavilij, A. J. Lees, *Acta. Cryst*., 2001, **E57**, m119-m121.