Electronic Supplementary Material (ESI) for Chemical Science.

Electronic Supplementary Information

Expanding Azobenzene Photoswitching into Near-Infrared via Endothermic Triplet Energy Transfer

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Materials

All the solvents were purchased from Sigma-Aldrich (Merck KGaA, Germany) and used as provided. PdP and PtP were purchased from Frontier Scientific Inc. (USA) and H_2P was purchased from Porphychem SAS (France). Syntheses of PdNP[1] TFA[2] and FPA[3] are previously published. Bis(methylthio)methane was purchased from Tokyo Chemical Industry (Japan).

Photophysical characterization of the sensitizers

Absorption spectra of the sensitizers were measured with UV-3600 spectrophotometer (Shimadzu Corporation, Japan). Phosphorescence spectra and phosphorescence decays were measured with FLS1000 spectrofluorometer (Edinburgh Instruments Ltd, UK). Absorption spectra (see Fig. S1 and S2) were measured from sensitizers dissolved in DMSO. Phosphorescence samples were prepared in a 1 cm^2 SOG9 cuvette (Starna Scientific Ltd, UK) sealed with a screw cap and a silicon/PTFE septum. 1 μM concentration of sensitizer was dissolved in DMSO to which 0.48 M concentration of Bis(methylthio)methane was added. The sample was then purged of oxygen by bubbling vigorously with nitrogen for 1 hour. The phosphorescence spectra (Fig. S3 and S4) were measured by exciting the sensitizers at their Q band maxima with a Xe lamp. Their triplet energies were then determined by the maxima wavelengths. The phosphorescence decays (Fig. S5 and S6) were measured by exciting the samples at their Q band maxima (PdP and PtP) and B band maximum (PdNP) under 100 Hz pulsed excitation and detected at the phosphorescence maxima. The phosphorescence lifetimes of PdP and PdNP were determined by tail fitting ($\chi < 1.2$) and the lifetime of PtP was determined by reconvolution fit ($\chi < 1.2$) of the decay and the instrument response function.

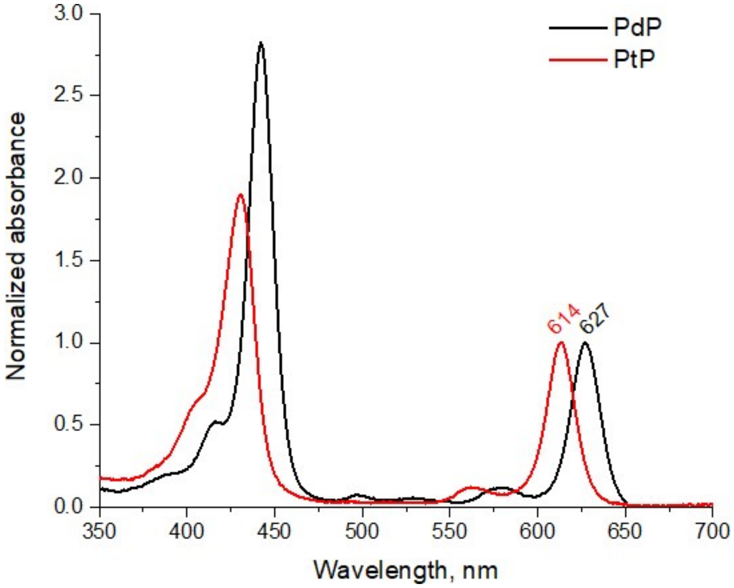


Figure S1. Normalized (by Q band absorbance) absorption spectra of PdP and PtP in DMSO.

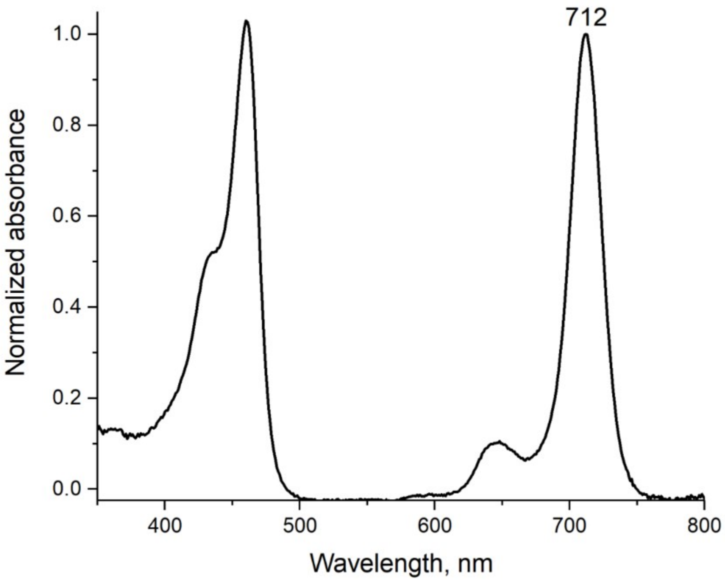


Figure S2. Normalized (by Q band absorbance) absorption spectra of PdNP in DMSO.

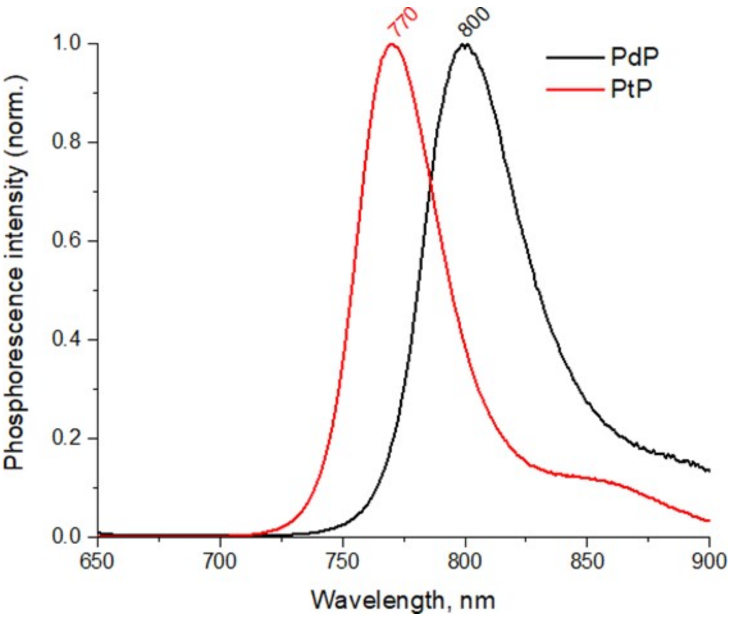


Figure S3. Normalized phosphorescence spectra of PdP and PtP in DMSO. The wavelengths of the maxima are labeled.

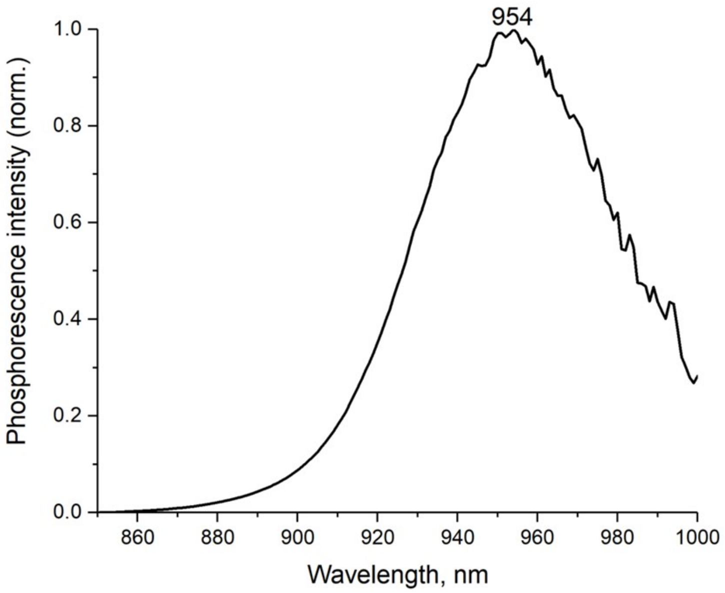


Figure S4. Normalized phosphorescence spectra of PdNP in DMSO. The wavelength of the maximum is labeled.

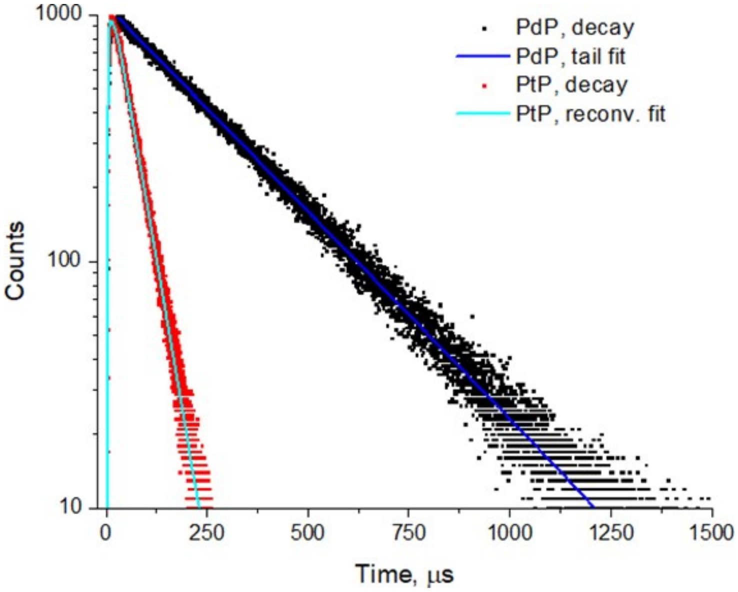


Figure S5. Phosphorescence decays of PdP and PtP in DMSO. The resulting tail fit yields 259.2 µs for PdP phosphorescence lifetime and the reconvolution fit yields 46.2 µs for PtP phosphorescence lifetime.

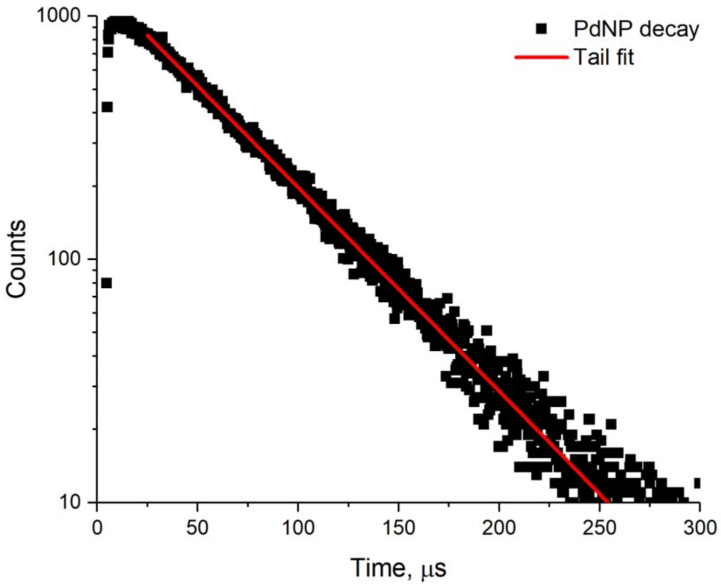


Figure S6. Phosphorescence decays of PdNP in DMSO. The resulting tail fit yields 52.1 μs for PdNP phosphorescence lifetime.

Phosphorescence quenching experiments

Quenching samples were prepared as described above with 1 μM concentration of sensitizer. Azobenzenes were added as chloroform solution to the sample and purged for 1 hour after each addition before measuring the phosphorescence decays. The quenching of azobenzenes in *Z*-conformation was performed by illuminating the sample by either a 530 nm LED (Thorlabs inc. USA) through a 495 nm longpass filter (Edmund Optics Inc, USA) in case of TFA or 365 nm UV lamp (Analytik Jena, Germany) in case of FPA. The resulting phosphorescence decays were then either tail-fitted or reconvoluted with instrument response function (if lifetime was less than 50 μs, per manufacturer instructions) to extract the phosphorescence lifetimes. All decays were monoexponential ($\chi < 1.2$). The phosphorescence decays of each quenching pair is shown in Figures S7-S10. A linear equation was fitted ($R^2 > 0.99$) on Origin 2017 on the Stern-Volmer plots. The monoexponential decays and linearity of the plots Stern-Volmer plots indicates that nearly pure (>90 %) *Z* or *E* isomer was present in the samples. The diffusion rate constant in DMSO was evaluated by performing phosphorescence quenching of PdP with 9,10-bis(phenylethynyl)anthracene that has triplet energy of 1.12-1.30 eV[4]. The large exothermic energy gap (≥ 0.25 eV or 10 k_BT) between the triplet donor and acceptor thus ensures truly diffusion-controlled rate for triplet energy transfer, i.e. $k_{TET} = k_{diff} \approx 1.1 \times 10^9\ M^{-1}s^{-1}$ in DMSO.

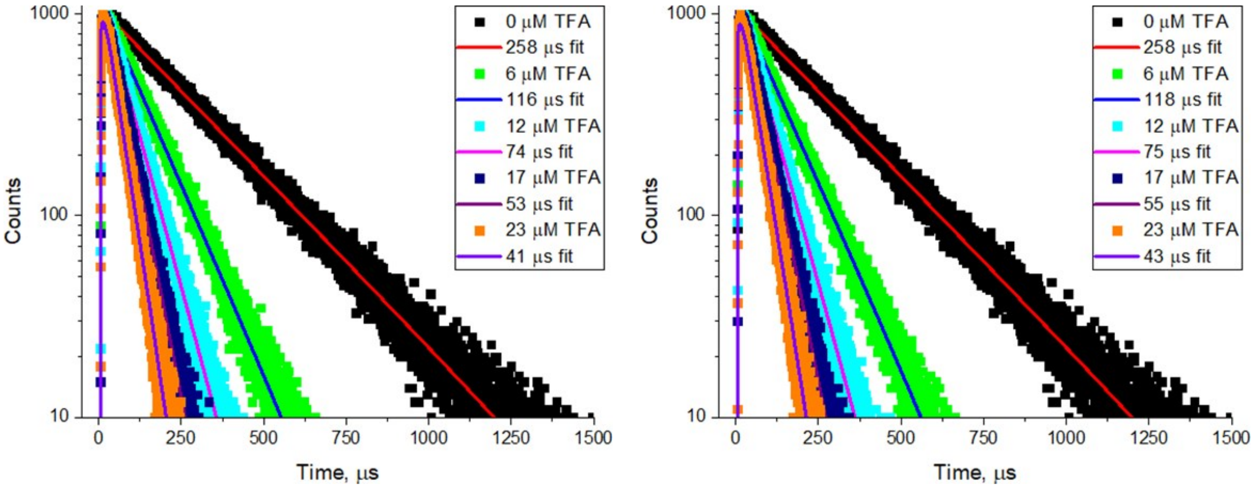


Figure S7. Phosphorescence decays of PdP in presence of *E*-TFA (left) and *Z*-TFA (right).

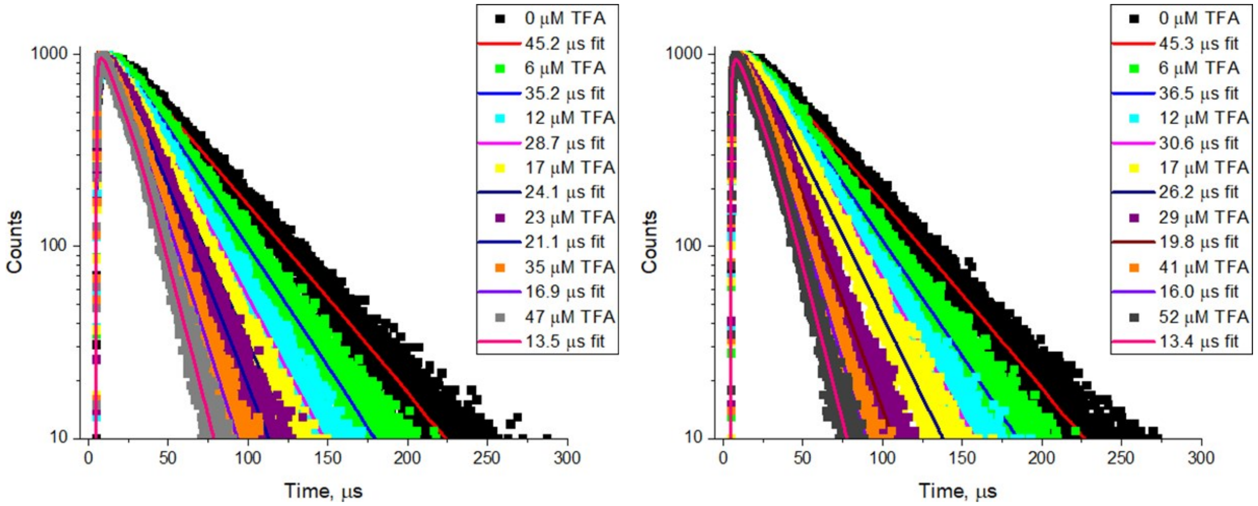


Figure S8. Phosphorescence decays of PtP in presence of *E*-TFA (left) and *Z*-TFA (right).

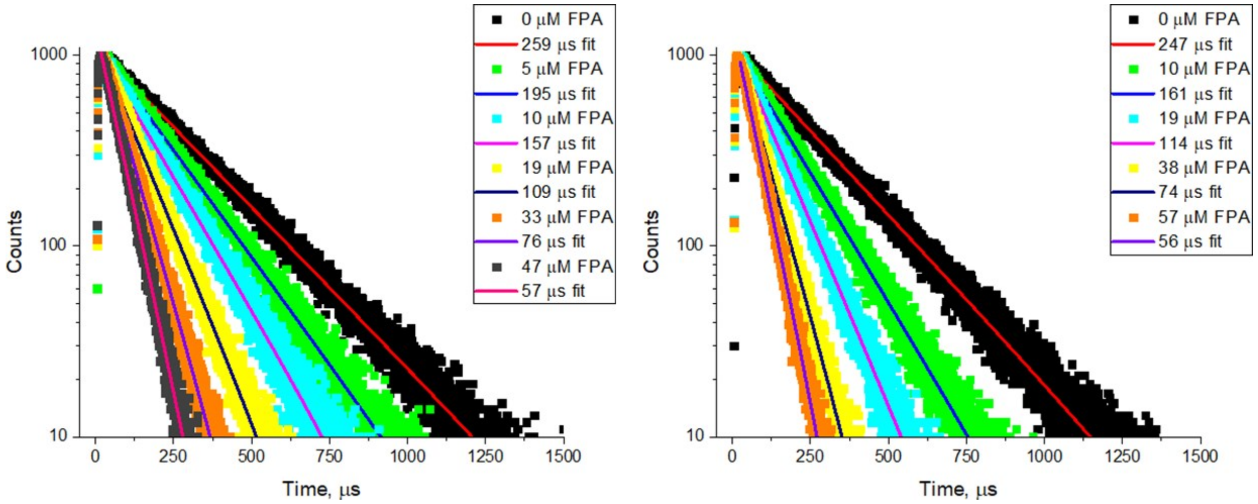


Figure S9. Phosphorescence decays of PdP in presence of *E*-FPA (left) and *Z*-FPA (right).

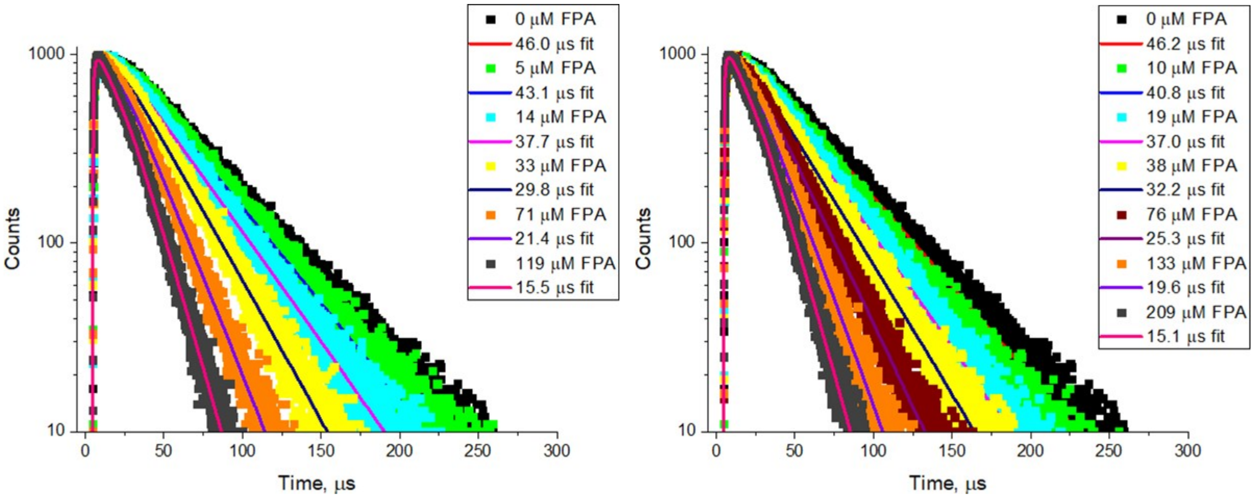


Figure S10. Phosphorescence decays of PtP in presence of *E*-FPA (left) and *Z*-FPA (right).

Isomerization experiments

Photoisomerization studies were performed also in DMSO to which 0.48 M concentration of Bis(methylthio)methane was added. The samples were also prepared in screw cap cuvettes (vide supra) and purged vigorously with nitrogen for 1 h prior to measuring. The azobenzene concentration was 150 µM and sensitizer concentration was 1.8 µM.

The photoisomerization measurements were performed on a Cary 60 spectrophotometer (Agilent Technologies Inc, USA) equipped with an Ocean Optics (USA) qpod 2e Peltier-thermostated cell holder at 20 ℃. Excitation source was a Prior Lumen 1600 (Prior Scientific Inc, USA) with multiple choices for narrow-band LEDs at different wavelengths.[2] PdP and PtP were excited with the 635 nm LED at 200 mW power. The excitation beam passed through a 10 nm bandpass filter with 640 nm center wavelength (Edmund Optics Inc, USA). PdNP was excited with either 740 nm (80 mW) or 770 nm (110 mW) LEDs. The excitation beam passed through a NIR long-pass filter (transmittance spectrum of the filter is shown in Figure S11). The samples were mixed at 1000 rpm during measurements.

The isomerization studies were performed with the following procedure: The azobenzene absorption was monitored at 340 nm (TFA) or 470 nm (FPA) initially in dark for 30 seconds. Then the excitation light (525 nm for TFA or 405 nm for FPA) was switched on for either 5 minutes (TFA) or 30 seconds (FPA) to effect *E*-to-*Z* isomerization. When sensitizers were present in the system, 635 nm (for PdP and PtP) or 740 nm or 770 nm (for PdNP) LED was turned on to initiate *Z-to-*E isomerization and turned off after the absorbance had plateaued (no change in the absorbance was observed for 30 seconds).

The isomerization rates under excitation of sensitizers were determined from exponential equations fitted on Origin 2017 on the photoisomerization curves as $r_{Z\rightarrow E} = 1/t$. The curves and corresponding fits are shown in Figures S12-14. Photoisomerization curve of 3.6 µM concentration of PdNP and TFA under 770 nm excitation is shown in Fig. S15. Photoisomerization curve of FPA without sensitizer under direct 640 nm excitation is shown in Fig. S16. No isomerization of TFA under 640 nm was observed.

The thermal isomerization rate of pure FPA in room temperature was already published[2]. For TFA the thermal isomerization lifetime was measured in three elevated temperatures (60, 80 and 100°C) and extrapolated to 20°C using the Arrhenius equation (Fig. S17) with the same Matlab script as in our earlier work[2].

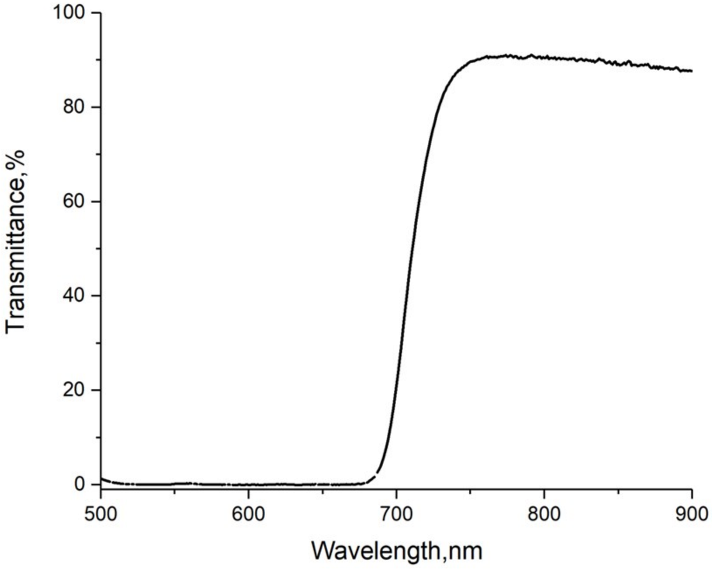
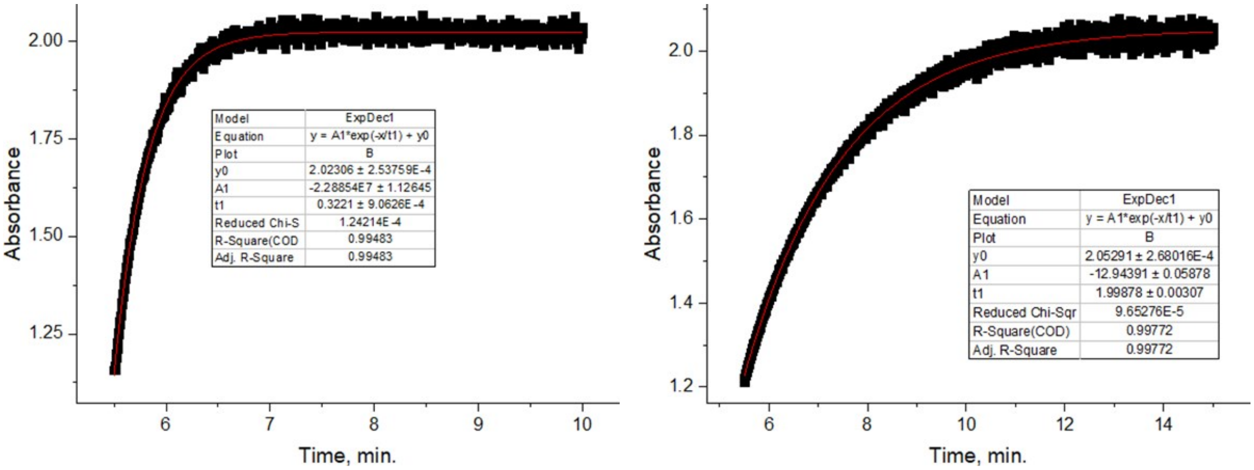


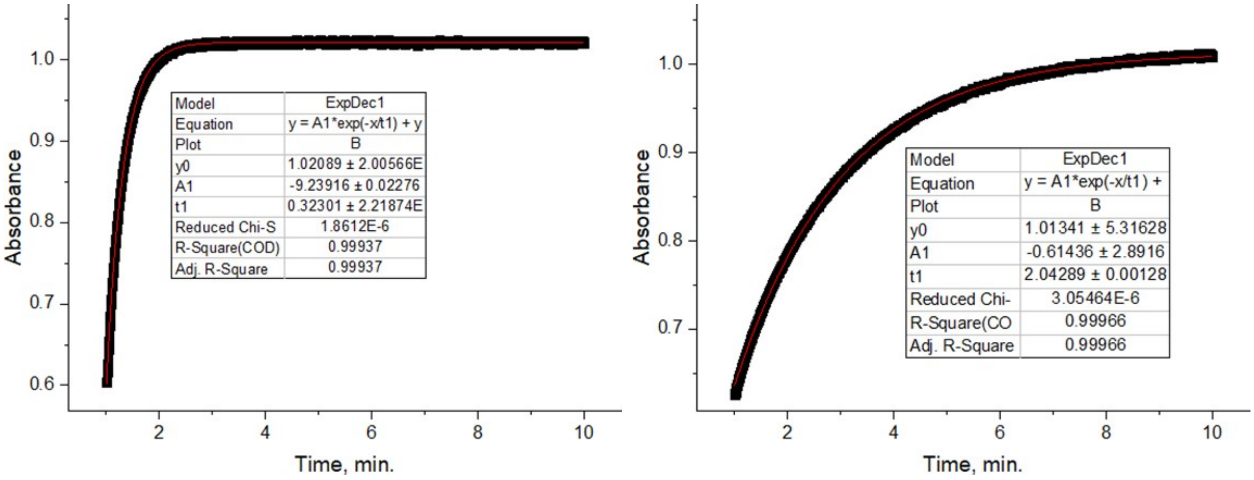
Figure S11. Transmittance curve of the NIR long pass filter.



Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	B
y0	2.02306 ± 2.53759E-4
A1	-2.28854E7 ± 1.12645
t1	0.3221 ± 9.0626E-4
Reduced Chi-S	1.24214E-4
R-Square(COD	0.99483
Adj. R-Square	0.99483

Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	B
y0	2.05291 ± 2.68016E-4
A1	-12.94391 ± 0.05878
t1	1.99878 ± 0.00307
Reduced Chi-Sqr	9.65276E-5
R-Square(COD)	0.99772
Adj. R-Square	0.99772

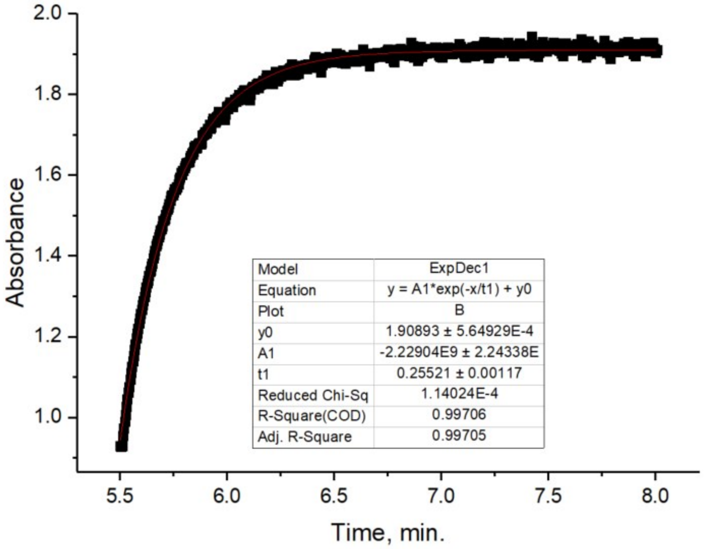
Figure S12. Photoisomerization curves of TFA and PdP (left) and PtP (right) with fitted equations. Absorbance was monitored at 340 nm.



Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y
Plot	B
y0	1.02089 ± 2.00566E
A1	-9.23916 ± 0.02276
t1	0.32301 ± 2.21874E
Reduced Chi-S	1.8612E-6
R-Square(COD)	0.99937
Adj. R-Square	0.99937

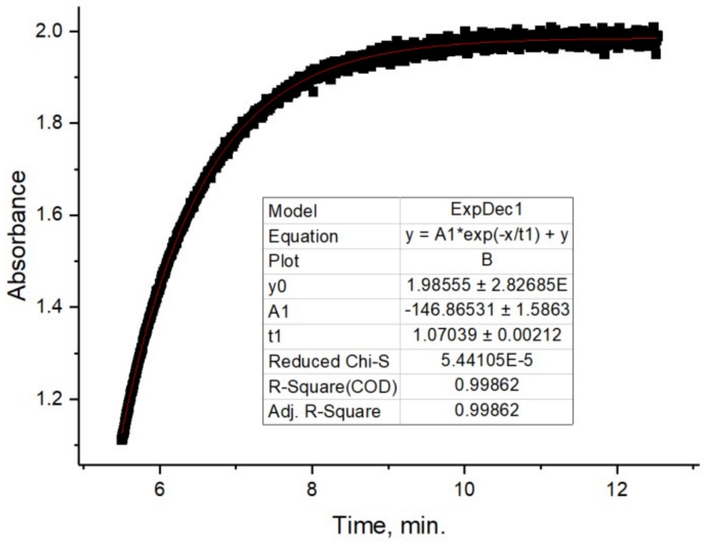
Model	ExpDec1
Equation	y = A1*exp(-x/t1) +
Plot	B
y0	1.01341 ± 5.31628
A1	-0.61436 ± 2.8916
t1	2.04289 ± 0.00128
Reduced Chi-	3.05464E-6
R-Square(CO	0.99966
Adj. R-Square	0.99966

Figure S13. Photoisomerization curves of FPA and PdP (left) and PtP (right) with fitted equations. Absorbance was monitored at 470 nm.



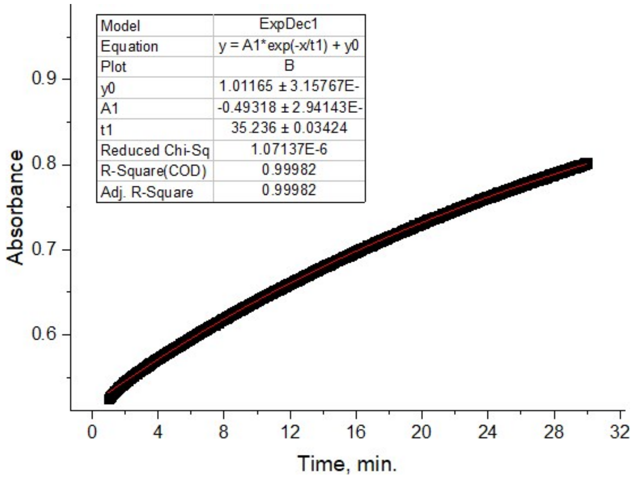
Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	B
y0	1.90893 ± 5.64929E-4
A1	-2.22904E9 ± 2.24338E
t1	0.25521 ± 0.00117
Reduced Chi-Sq	1.14024E-4
R-Square(COD)	0.99706
Adj. R-Square	0.99705

Figure S14. Photoisomerization curve of TFA and PdNP (1.8 μM) under 740 nm excitation with fitted equations. Absorbance was monitored at 340 nm.



Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y
Plot	B
y0	1.98555 ± 2.82685E
A1	-146.86531 ± 1.5863
t1	1.07039 ± 0.00212
Reduced Chi-S	5.44105E-5
R-Square(COD)	0.99862
Adj. R-Square	0.99862

Figure S15. Photoisomerization curve of TFA and PdNP (3.6 μM) under 770 nm excitation with fitted equation. Absorbance was monitored at 340 nm.



Model	ExpDec1
Equation	y = A1*exp(-x/t1) + y0
Plot	B
y0	1.01165 ± 3.15767E-
A1	-0.49318 ± 2.94143E-
t1	35.236 ± 0.03424
Reduced Chi-Sq	1.07137E-6
R-Square(COD)	0.99982
Adj. R-Square	0.99982

Figure S16. Photoisomerization curve of FPA without sensitizers under 640 nm excitation with fitted equation. Resulting $r_{Z\to E} =$ 0.03 min^{-1}. Absorbance was monitored at 470 nm.

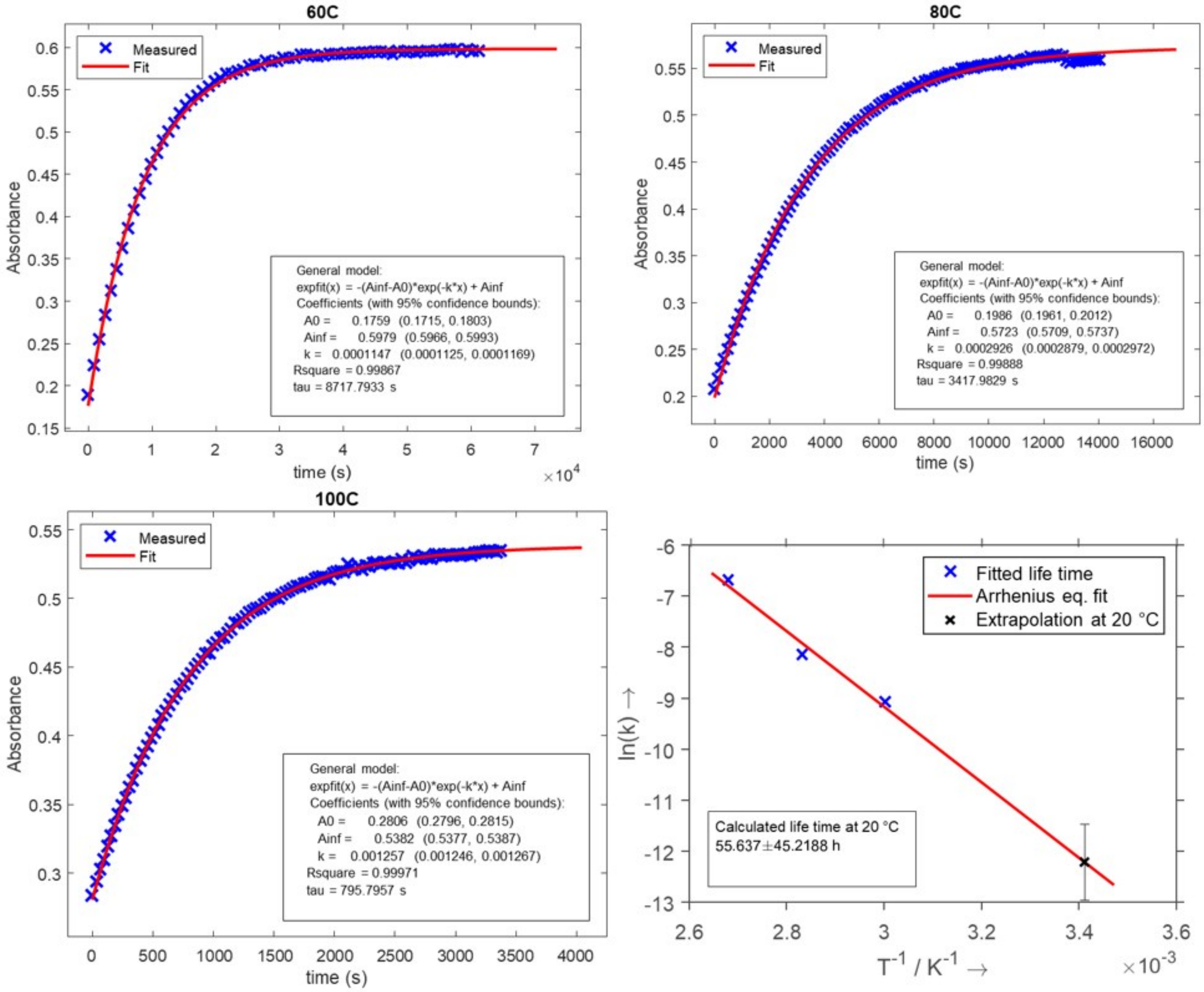


Figure S17. Thermal isomerization curves of TFA in 60, 80 and 100°C with fitted equations and an Arrhenius fit with extrapolation to 20°C. Absorbance was monitored at 340 nm.

Catalyzing effect of porphyrins on FPA

The explanation to this effect is given in the main text. The isomerization curves of FPA in dark and under 640 nm excitation after initial *E*-to-*Z* isomerization with 405 nm excitation are shown in Figure S12. The rates of isomerization were determined as detailed above. This catalysis effect was not observed with TFA.

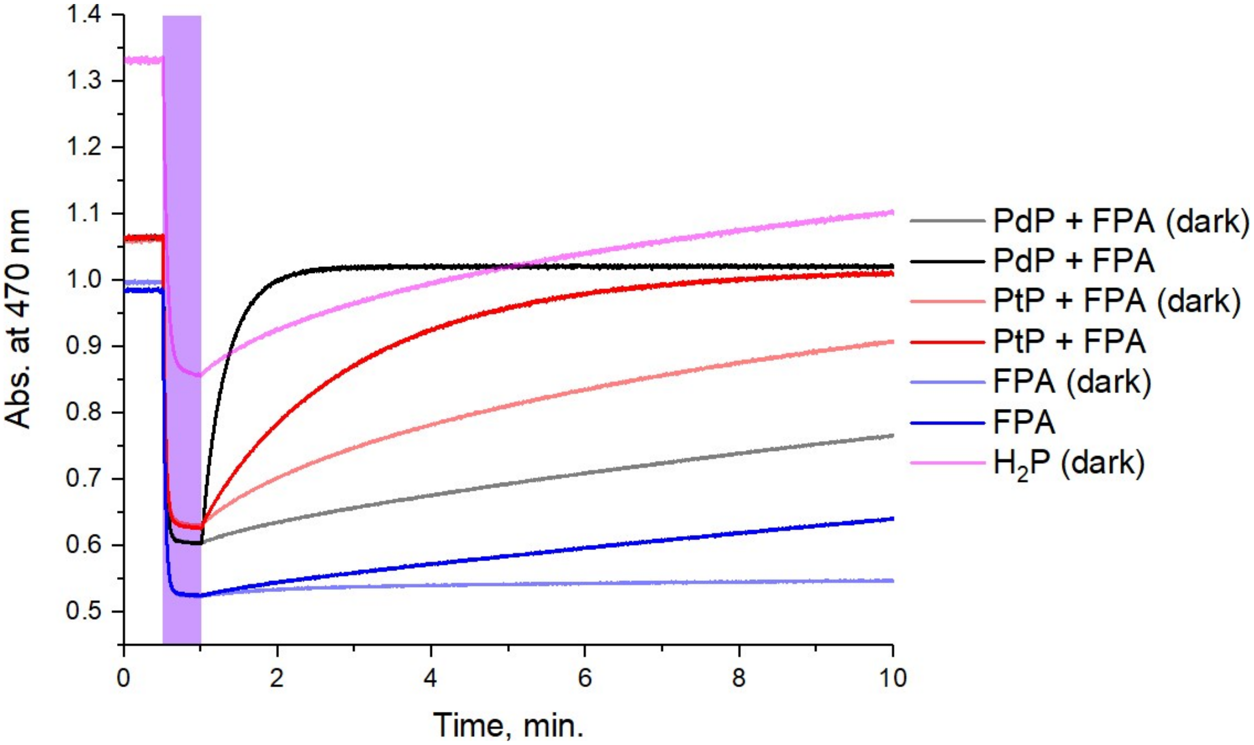


Figure S18. Comparison of isomerization of FPA with and without porphyrin sensitizers.

Sensitized isomerization in presence of oxygen

The isomerization curve of TFA/PdP in presence of oxygen (sample preparation as described above, however sample was bubbled with air instead of nitrogen) is also shown in Fig. S19. It is evident that oxygen slows the kinetics of the system (due to the capability of oxygen to quench triplet states) and causes photobleaching to some extent (the curve does not recover to as high level as in the deoxygenated case). However, this is only a demonstration that triplet sensitization is capable of driving isomerization even in ambient conditions. More efficient oxygen scavenging, photorobust dyes, or prevention of oxygen diffusion is required for applications.

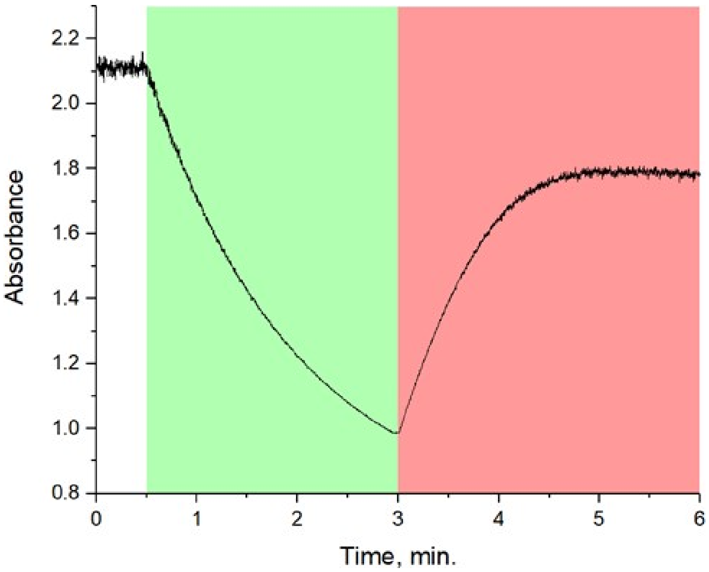


Figure S19. Isomerization of TFA/PdP under varied light doses (left) and in presence of oxygen (right).

References

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(4) Bae, Y. J.; Christensen, J. A.; Kang, G.; Zhou, J.; Young, R. M.; Wu, Y.-L.; Van Duyne, R. P.; Schatz, G. C.; Wasielewski, M. R. Substituent Effects on Energetics and Crystal Morphology Modulate Singlet Fission in 9,10-Bis(Phenylethynyl)Anthracenes. *J. Chem. Phys.* **2019**, *151* (4), 44501. https://doi.org/10.1063/1.5110411.