Supporting Information

Thiaporphyrin-Mediated Photocatalysis Using Red Light

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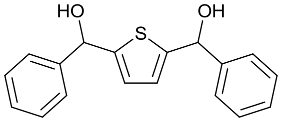
1. General methods

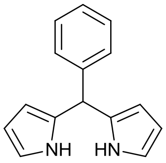
Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker DMX 300 MHz (^{1}H) spectrometer. Most of spectra were obtained in $CDCl_3$ and the chemical shifts (ppm) are relative to the $C\underline{H}Cl_3$ peak as an internal reference (7.27 ppm for ^{1}H). Agilent Technologies 6520 Accurate-Mass Q-TOF LC/MS instrument was used for HR-MS analyses. Agilent Technologies 6890N Gas Chromatography system coupled with 5973 Mass Selective Detector was used for GC-MS analysis. UV/Vis spectra were recorded using Cary 50 Bio and Cary 5000 spectrophotometers. Anhydrous solvents were prepared by standard methods (Na/benzophenone for THF and CaH_2 for DCM and Hexanes). TMEDA and pyrrole were dried with CaH_2 and distilled. "DriSolv" EMD Millipore grade DMF was used. All α-haloketones as well as DIPEA were purchased (Aldrich and VWR) and used as received. Visible light irradiation was completed with an Osram Sylvania FHS 300W 82V GX5.3 halogen bulb with a Kodak EKTAGRAPHIC III AM projector. A longpass 640 ± 5 nm wavelength filter purchased from Optosigma was used to filter the light.

2. Catalysts and reagent syntheses



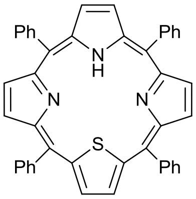
1

2,5-Bis(phenylhydroxymethyl)thiophene (1) – To a solution of TMEDA (6 mL, 40 mmol) in hexanes (100 mL) was added *n*-BuLi (20 mL of a 2.5 M solution in hexanes, 50 mmol) dropwise under a nitrogen atmosphere. Thiophene (1.6 mL, 20 mmol) was added and the resulting solution was refluxed for 1 h. The dilithiated species was transferred to an ice cold solution of benzaldehyde (4.9 g, 46 mmol) in 30 mL of THF by cannula. After the addition was complete, the reaction mixture was warmed to ambient temperature. A cold, saturated NH_4Cl solution (150 mL) was added followed by extractions with Et_2O (3 x 100 mL). The organic layers were combined, washed with water (3 x 100 mL) and brine (150 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was recrystallized from chloroform to give pure **1**, as a white solid (3.1 g, 52%). Spectral data are in agreement with literature data.[1]
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.46 – 7.29 (m, 10H), 6.72 (s, 2H), 5.99 (s, 2H), 2.35 (s, 2H).



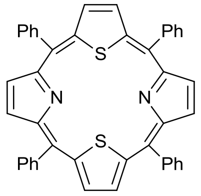
2

5-phenyldipyrromethane (2) – A solution of benzaldehyde (5.1 g, 48 mmol) in pyrrole (84 mL, 1.2 mol) was degassed by bubbling N_2 through it for 5 minutes. TFA (0.37 mL, 4.8 mmol, 0.1 equiv.) was then added and stirred for 5 minutes. The reaction mixture was quenched with 0.1 M NaOH (50 mL) and the product was extracted with ethyl acetate (3 x 100 mL). The combined organic layer was washed with water (3 x 50 mL), dried over Na_2SO_4 and concentrated under reduced pressure. A bulb-to-bulb distillation of the crude product was done to afford a yellow oil. The distillate was recrystallized from EtOH/water to afford **2**, as a yellow solid (5.6 g, 52%); NMR spectral data are in agreement with literature data.[2]
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (br s, 2H), 7.40-7.17 (m, 5H), 6.71 (q, *J* = 2.5 Hz, 2H), 6.22-6.07 (m, 2H), 5.93 (s, 2H), 5.50 (s, 1H)



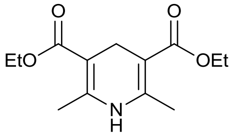
S1TPP

***meso*-5,10,15,20-Tetraphenyl-21-monothiaporphyrin (S1TPP)** – To a solution of 2,5-bis(phenylhydroxymethyl)thiophene (0.92 g, 3.1 mmol) in DCM (175 mL) was added 5-phenyldipyrromethane (0.86g, 3.9mmol, 1.25 equiv.). The solution was purged with N_2 for 15 minutes and then $BF_3{\cdot}OEt_2$ (0.22g, 1.6 mmol, 0.5 equiv.) was added at rt and stirred for 1 h. DDQ (0.77 g, 3.4 mmol, 1.1 equiv.) was added to the reaction mixture and stirred for 1 h. The reaction mixture was passed through a short alumina plug using DCM as the eluent and then concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (2:1:1 toluene: chloroform: hexanes) to give pure S1TPP (140 mg, 9%). The NMR spectral data are in agreement with literature data.[3]
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.75 (s, 2H), 8.94 (d, *J* = 1.8 Hz, 2H), 8.69 (d, *J* = 4.6 Hz, 2H), 8.61 (d, *J* = 4.6 Hz, 2H), 8.24 (m, 8H), 7.79 (m, 12H), 0.08 (brs, 1H); HR-MS (ESI) calcd. for $C_{44}H_{30}N_3S$ 632.2155 [M+H$^+$], found 632.2145.



S2TPP

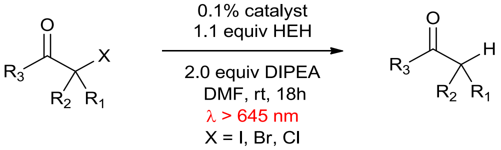
5,10,15,20-Tetraphenyl-21,23-dithiaporphyrin (S2TPP) – Pyrrole (0.26 mL, 3.7 mmol, 1.2 equiv) was added to a solution of 2,5-bis(phenylhydroxymethyl)thiophene (0.92 g, 3.1 mmol) in DCM (175 mL). The solution was purged with nitrogen for 15 minutes and then $BF_3{\cdot}OEt_2$ (0.5 equiv) was added at rt and stirred for 1 h. DDQ (0.77 g, 3.4 mmol, 1.1 equiv) was added to the reaction mixture and stirred for 1 h. The reaction mixture was passed through a short alumina plug using DCM as the eluent and then concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (2:1:1, toluene: chloroform: hexanes) to give pure S2TPP (150 mg, 8%). Spectral data are in agreement with literature data.[1]
^{1}H NMR (300 MHz, $CDCl_3$) δ 9.70 (s, 4H), 8.70 (s, 4H), 8.26 (m, 8H), 7.93 (m, 12H); HR-MS (ESI) calcd. for $C_{44}H_{29}N_2S_2$ 649.1767 [M+H$^+$], found 649.1775.



HEH

Hantzsch Ester (HEH) – In 20 mL of degassed water, paraformaldehyde (0.3 g, 10 mmol), ethyl acetoacetate (5.1 mL, 40 mmol) and ammonium acetate (1.54 g, 20 mmol) were combined. The mixture was stirred under reflux for 2 h in N_2 atmosphere and cooled down. The crude product was collected by vacuum filtration and recrystallized from EtOH to give pure bright yellow crystals (2.1 g, 83 %). Spectral data are in agreement with literature data.[4]
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.10 (s, 1H), 4.19 (m, 4H), 3.28 (s, 2H), 2.20 (s, 6H), 1.30 (t, J = 7.2 Hz, 6H)

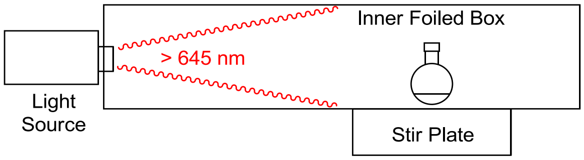
3. General procedure and experimental data for dehalogenation of α-haloketones



Scheme S1. General reaction conditions

To a solution of α-haloketone (1 mmol) in DMF (5 mL), HEH (278.8 mg, 1.1 equiv), DIPEA (0.35 mL, 2 equiv), and S1TPP, S2TPP, or Ru(bpy)$_3$Cl$_2$ (0.1 mol%) were added under stirring in a 10-mL round bottom flask. The reaction vessel was kept in the dark until irradiation with red light. After 18 h of irradiation, the reaction mixture was diluted with water (8 mL) and extracted with Et$_2$O (3 x 8 mL). The combined organic layer was washed with brine (20 mL), dried over Na$_2$SO$_4$ and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography to give pure product.

Dehalogenation reaction setup

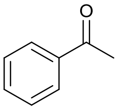


Reaction vessel kept 30 cm away from light source

Figure S1. Reaction Setup Diagram

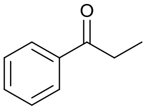
The reaction vessel was placed 30 cm away from the light source on a stir plate. An inner foiled box was used to cover the vessel to isolate from external light.

Acetophenone



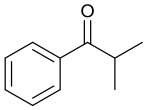
The title compound was synthesized according to the general procedure for dehalogenation, from 2-bromoacetophenone (199 mg, 1 mmol), in 90 % yield with S1TPP, 60 % yield with S2TPP, and 18 % yield with Ru(bpy)$_3$Cl$_2$. The NMR spectral data are in agreement with literature data.[5] As well, the compound was synthesized from 2-iodoacetophenone and 2-chloroacetophenone in quantitative and 12 % yield respectively with S1TPP.
^{1}H NMR (300 MHz, CDCl$_3$) δ 7.99 (m, 2H), 7.53 (m, 3H), 2.62 (s, 3H).

Propiophenone



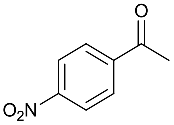
The title compound was synthesized according to the general procedure for dehalogenation, from 2-bromoacetophenone (213 mg, 1 mmol), in 78% yield with S1TPP and 60% yield with S2TPP. The NMR spectral data are in agreement with literature data.[5]
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (m, 2H) 7.50 (m, 3H), 3.02 (q, *J* = 7.2 Hz, 2H), 1.24 (t, *J* = 7.2 Hz, 3H)

Isobutyrophenone



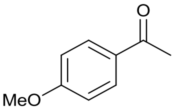
The title compound was synthesized according to the general procedure for dehalogenation, from 2-bromoisobutyrophenone (227 mg, 1 mmol), in 78% yield with S1TPP and 40% yield with S2TPP. The NMR spectral data are in agreement with literature data.[5]
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (m, 2H), 7.51, (m, 3H), 3.57 (hept, *J* = 6.9 Hz, 1H), 1.27, (d, *J* = 6.8 Hz, 6H).

1-(4-Nitrophenyl)ethanone



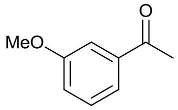
The title compound was synthesized according to the general procedure for dehalogenation, from 2-bromo-4'-nitroacetophenone (244 mg, 1 mmol), in 86% yield with S1TPP. The NMR spectral data are in agreement with literature data.[6]
^{1}H NMR (300 MHz, $CDCl_3$), δ 8.33 (m, 2H), 8.12 (m, 2H), 2.69 (s, 3H).

1-(4-Methoxyphenyl)ethanone



The title compound was synthesized according to the general procedure for dehalogenation, from 2-bromo-4'-methoxyacetophenone (229 mg, 1 mmol), in 85% yield with S1TPP. The NMR spectral data are in agreement with literature data.[7]
^{1}H NMR (300 MHz, $CDCl_3$), δ 7.95 (m, 2H), 6.94 (m, 2H), 3.88 (s, 3H), 2.57 (s, 3H).

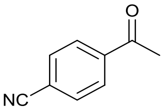
1-(3-Methoxyphenyl)ethanone



The title compound was synthesized according to the general procedure for dehalogenation, from 2-bromo-3'-methoxyacetophenone (229 mg, 1 mmol), in 92% yield with S1TPP. The NMR spectral data are in agreement with literature data.[7]

^{1}H NMR (300 MHz, $CDCl_3$), δ 7.52 (m, 2H), 7.38 (t, J = 7.9 Hz, 1H), 7.12 (ddd, J = 8.2, 2.7, 1.0 Hz, 1H), 3.87 (s, 3H), 2.61 (s, 3H)

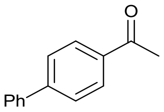
1-(4-Cyanophenyl)ethanone



The title compound was synthesized according to the general procedure for dehalogenation, from 2-bromo-4'-cyanoacetophenone (224 mg, 1 mmol), in 80% yield with S1TPP. The NMR spectral data are in agreement with literature data.[6]

^{1}H NMR (300 MHz, $CDCl_3$), δ 8.05 (m, 2H), 7.79 (m, 2H), 2.66 (s, 3H)

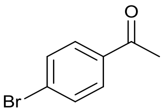
1-(4-Diphenyl)ethanone



The title compound was synthesized according to the general procedure for dehalogenation, from 2-bromo-4'-phenylacetophenone (275 mg, 1 mmol), in 98% yield with S1TPP. The NMR spectral data are in agreement with literature data.[8]

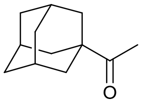
^{1}H NMR (300 MHz, $CDCl_3$), δ 8.03 (m, 2H), 7.63 (m, 4H), 7.48 (m, 2H), 2.64 (s, 3H)

1-(4-Bromophenyl)ethanone



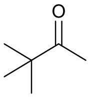
The title compound was synthesized according to the general procedure for dehalogenation, from 2,4’-dibromoacetophenone (278 mg, 1 mmol), in 76% yield with S1TPP. The NMR spectral data are in agreement with literature data.[5]
^{1}H NMR (300 MHz, $CDCl_3$), δ 7.83 (m, 2H), 7.62 (m, 2H), 2.60 (s, 3H)

1-Adamantyl methyl ketone



The title compound was synthesized according to the general procedure for dehalogenation, from 1-adamanthylbromomethylketone (257 mg, 1 mmol), in 36% yield with S1TPP. The NMR spectral data are in agreement with literature data.[9]
^{1}H NMR (300 MHz, $CDCl_3$), δ 2.10 (s, 3H), 2.06 (m, 3H), 1.82 (d, *J* = 2.9 Hz, 6H), 1.73 (dd, *J* = 20.1, 9.3 Hz)

3,3-Dimethyl-2-butanone



The title compound was synthesized according to the general procedure for dehalogenation, from 1-bromopinacolone (179 mg, 1 mmol), in 16% GC yield with S1TPP.

UV-Vis Absorption Spectra of S1TPP and S2TPP in DMF

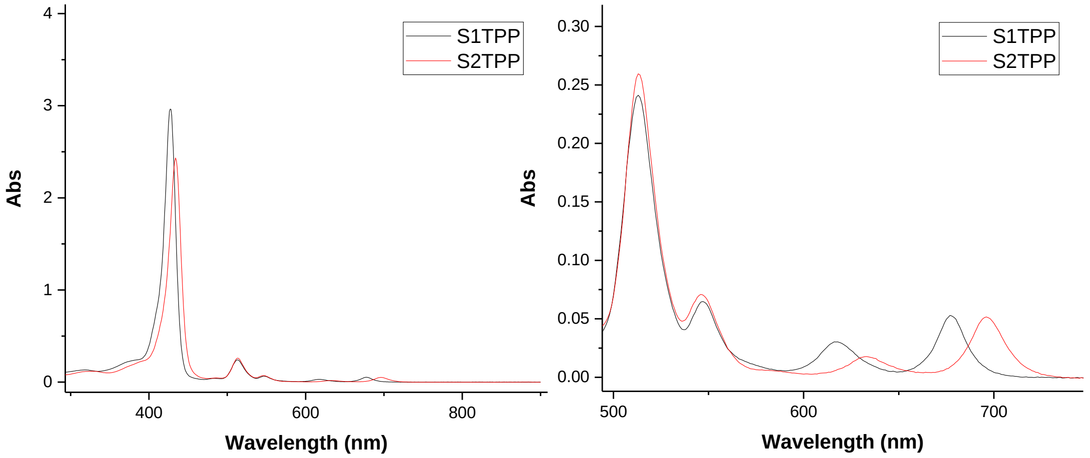


Figure S2. Left: Full UV-Vis Absorption Spectra of S1TPP and S2TPP at 8 x 10^{-6} M

Right: Expansion of UV-Vis Absorption Spectra at 500 – 750 nm at 8 x 10^{-6} M

Longpass Filter (645 nm) UV-Vis Spectrum

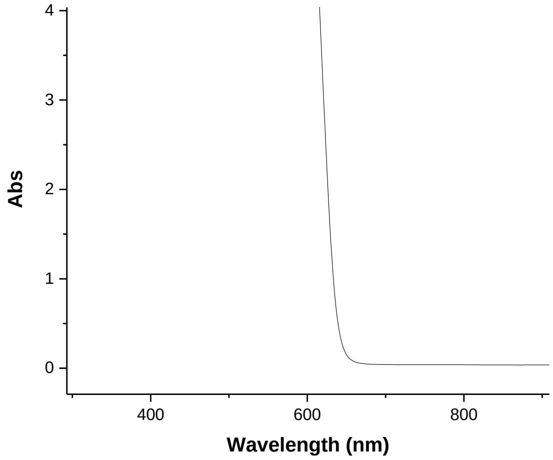


Figure S3. UV-Vis Absorption Spectrum of Longpass Filter

[1]. C. R. Stilts, M. I. Nelen, D. G. Hilmey, S. R. Davies, S. O. Gollnick, A. R. Oseroff, S. L. Gibson, R. Hilf, M. R. Detty, *J. Med. Chem*. **2000**, *43*, 2403-2410.

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[8]. L. S. Sobjerg, D. Gauthier, A. T. Lindhardt, M. Bunge, K. Finster, R. L. Meyer, T. Skrydstrup, *Green Chem.* **2009**, *11*, 2041-2046.

[9]. J. C. Walton, D. W. Manley, *Org. Lett.* **2014**, *16* (20), 5394–5397.

[10]. Abbreviations: Tetrahydrofuran (THF), dichloromethane (DCM), trifluoroacetic acid (TFA), dimethylformamide (DMF), *N,N,N'N'*-tetramethylethylenediamine (TMEDA), *N,N*-diisopropylethylamine (DIPEA), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ)