Supporting Information

Chromoselective Synthesis of Sulfonyl Chlorides and Sulfonamides with Potassium Poly(heptazine imide) Photocatalyst

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# Supporting information

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Figure S1. Sulfonamide group in medicines.

**Chemicals**

All chemicals were used without purification. Acetonitrile (≥99.8%, Sigma Aldrich), benzyl chloride (99%, Sigma Aldrich), acetyl chloride (≥98%, Sigma Aldrich), chloroform-d (99.8 atom% D, Sigma Aldrich), dichloromethane (≥99.9%, Sigma Aldrich), dimethylsulfoxide-d₆ (99.5 atom % D, Sigma Aldrich), ethanol (99.8%, Sigma Aldrich), HCl (37 wt.%, Carl-Roth), HCl in 1,4-dioxane (4 mol·L⁻¹, TCI), N-chlorosuccinimide (≥98%, TCI), sodium sulphate (≥99%, Sigma Aldrich), S-phenylthioacetate (≥98%, Alfa Aesar), thionyl chloride (≥99%, Sigma Aldrich), thiophenol (97%, Sigma Aldrich), 4-nitrobenzene thiol (≥95%, TCI), 2-trifluoromethylthiophenole (≥95%, Maybridge), 4-trifluoromethylbenzylchloride (98%, Alfa Aesar), 4-methoxythiophenole (98%, Acros Organics), Ir(ppy)₃ (99%, Sigma Aldrich), Ru(bpy)₃Cl₂·6H₂O (99.95%, Sigma Aldrich), sulfuryl chloride(99%, Sigma Aldrich), 4-fluorothiophenol (97%, Alfa Aesar), 4-bromothiophenol (95%, Sigma Aldrich), 2-chlormothiophenol (99%, Sigma Aldrich), 2,2,6,6-Tetramethylpiperidine (98%, Alfa Aesar).
Characterization methods

$^1$H and $^{13}$C NMR spectra were recorded on an Agilent 400 MHz (at 400 MHz for Protons and 101 MHz for Carbon-13). NMR spectra were recorded in CDCl$_3$ or DMSO-d6. The chemical shifts are reported in ppm relative to the residual signal of CHCl$_3$ (7.26 ppm for $^1$H NMR, 77.16 ppm for $^{13}$C NMR) or DMSO (2.5 ppm in $^1$H NMR, 39.52 ppm for $^{13}$C NMR).

**GC-MS.** Agilent 6890 Network GC System coupled with Agilent 5975 Inert Mass Selective detector (electron ionization) were used for reaction mixture composition analysis and to obtain mass spectra of the products.

**Fourier transform infrared (FT-IR) spectra** were recorded on Thermo Scientific Nicolet iD5 spectrometer.

**Optical absorbance spectra** of powders were measured on a Shimadzu UV 2600 equipped with an integrating sphere in diffuse reflectance mode.

**Steady-state fluorescence** spectra were measured on Jasco FP-8300 fluorescence spectrometer. Internal Quantum Efficiency (IQE) of fluorescence was determined using integrating sphere.

**Powder X-Ray diffraction** patterns were measured on a Bruker D8 Advance diffractometer equipped with a scintillation counter detector with CuKα radiation ($\lambda = 0.15418$ nm) applying 2θ step size of 0.05° and counting time of 3 s per step.

**Nitrogen adsorption/desorption** measurements were performed after degassing the samples at 150 °C for 20 hours using a Quantachrome Quadrasorb SI-MP porosimeter at 77.4 K. The specific surface areas were calculated by applying the Brunauer-Emmett-Teller (BET) model to adsorption isotherms for $0.05 < p/p_0 < 0.3$ using the QuadraWin 5.11 software package.

**Elemental analysis** was accomplished as combustion analysis using a Vario Micro device. Method allows to identify the elemental ratios of C, N, H, and S atoms in a sample.

**Scanning electron microscopy (SEM)** images were obtained on JSM-7500F (JEOL) microscope. Energy disperse X-ray (EDX) analysis and morphology observation by scanning electron microscope (SEM) were performed using a Link ISIS-300 system (Oxford Microanalysis Group).

**X-ray photoelectron spectroscopy (XPS)** measurements were carried out in an ultrahigh vacuum (UHV) spectrometer equipped with a VSW Class WA hemispherical electron analyzer. A dual anode Al Kα X-ray source (1486.6 eV) was used as incident radiation. Survey and high resolution spectra were recorded in constant pass energy mode (44 and 22 eV, respectively). During the UPS (He I excitation energy $h\nu=21.23$ eV) measurements a bias of 15.32 V was applied to the sample, in order to avoid interference of the spectrometer threshold in the UP spectra. The values of the valence band maximum (VBM) are determined by fitting a straight line into the leading edge.

**TEM measurements** were acquired using a double-corrected JEOL JEM-ARM200F, equipped with a cold field emission gun and a Gatan GIF Quantum.
**Electrochemical Impedance Spectroscopy.**

*Mott-Schottky analysis* was carried out with Arbin electrochemical testing station. Measurements were performed in three electrode cell equipped with the Ar inlet using Biologic potentiostat to control the potential of the working electrode (WE) and EC-Lab v. 10.40 software for data logging. Samples were tested in a potential range from -1 to 1 V vs Ag/AgCl, -0.1 V potential step, and selected frequencies 10; 7.5; 5 kHz. Ag/AgCl (3M KCl) was used as a reference electrode (RE), Pt wire as a counter electrode. Measurements were performed at room temperature (20-25°C). A solution of Na₂SO₄ in water (0.5 mol L⁻¹) was used as electrolyte. The solution was purged with Ar before the measurements. The electrodes were prepared by deposition of known amount of the powder on an FTO glass slide, so that the area of the coating is around 1 cm². 2-3 mg of the powder and 20 µL of Nafion in 0.2 mL water were sonicated for 1 h. The suspension was deposited on the FTO slide and dried in air, then heated at 120 °C to remove Nafion leftovers. The measured potentials vs. Ag/AgCl were converted to the normal hydrogen electrode (NHE) scale according to the Nernst equation.

**Cyclic voltammetry**

Electrochemical measurements were performed in three electrode cell equipped with the Ar inlet and magnetic stir bar using Biologic potentiostat to control the potential of the working electrode (WE) and EC-Lab v. 10.40 software for data logging. Glassy carbon (diameter 3 mm) was used as a WE, Ag wire in AgNO₃ (0.01M) with tetrabutylammonium perchlorate (0.1M) in MeCN as a reference electrode (RE), Pt wire as a counter electrode. Measurements were performed at room temperature (20-25°C). A solution of tetrabutylammonium perchlorate (0.1M) in MeCN was used as electrolyte. The electrochemical cell was placed in the grounded Faraday’s cage in order to reduce noise.

**Time resolved fluorescence measurements**

TR-PL spectra were recorded on fluorescence lifetime spectrometer (Fluo Time 250, PicoQuant) equipped with PDL 800-D picosecond pulsed diode laser drive. The decay curves were fitted using a nonlinear method with a multicomponent decay law given by

\[ I(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2) + a_3 \exp(-t/\tau_3). \]

The solid-state TR PL spectra were obtained with λexc = 375, 470 and 640 nm, respectively. The following settings were used for the spectra acquisition: Laser Frequency 40 MHz, Emission Monochromator Bandwidth 2 nm, Delta (step between λem) 10 nm. Long pass filters of 495 and 665 nm were used for λexc = 470 and 640 nm, respectively.

**Electron paramagnetic resonance (EPR)**

EPR measurements were performed on Bruker EMXnano benchtop X-Band EPR spectrometer. The following settings were used for the spectra acquisition unless other is specified: Receiver Gain 60 dB, Modulation Amplitude 1.000 G, Microwave Attenuation 10 dB.
**Singlet-oxygen fluorescence** measurements were conducted on a Floruolog 3 (Horiba Scientific) equipped with an InGaAs symphony as the detection unit. The mass concentrations was about 0.01 g L\(^{-1}\) for K-PHI and Na-PHI in MeCN, such that the optical density at 360 nm was 0.13 for both. To ensure maximum fluorescence intensity, the suspensions were purged with O\(_2\) prior measurements for 30 minutes.

**Transient absorption spectroscopy (TAS)**

Ultrafast pump-probe transient absorption spectroscopy (TAS) was performed using a Clark MXR CPA 2101 Ti:sapphire as the laser source (775 nm, 1 kHz, 150 fs pulse width). To acquire the time-resolved transient absorption spectra on a sub-ps and ns resolution, an Ultrafast Systems HELIOS or EOS fs/ns transient absorption spectrometer was used with time delays from 0 to 5500 ps and 1 ns to 50 µs, respectively. For sub-ps, white light for the probing pulse in the visible region of the optical spectrum (~420-750 nm) was generated by focusing part of the fundamental 775 nm output onto a 2 mm sapphire disk. For (near) IR (800-1350 nm) white light, a 10 mm sapphire was used. For ns timescale experiments, white light for probing was generated by a photonic crystal fiber supercontinuum laser with a 1064 nm fundamental. The excitation wavelength was generated via the second harmonic of the fundamental CPA laser wavelength and the energy per pulse reduced to 2 µJ using neutral density filter. All spectra were recorded in 2 mm quartz (OS) cuvettes at ambient conditions with continuous stirring during the measurements. Prior the measurement the suspensions were either purged with argon or O\(_2\) for 30 min. The mass concentration for the suspensions used in TAS experiments was 0.1 g L\(^{-1}\).
**Light sources**

Irradiance of the LED modules was measured using PM400 Optical Power and Energy Meter equipped with integrating sphere S142C.

![Emission spectra of white, blue and green LEDs.](image)

**Figure S2.** Emission spectra of white, blue and green LEDs.

**Table S1.** Optical power of LEDs*

| Entry | Light identification | Wavelength, nm | Irradiance, mW cm\(^{-2}\) |
|-------|----------------------|----------------|-----------------------------|
| 1     | UV                   | 365            | 17.1                        |
| 2     | Violet               | 410            | 64.7                        |
| 3     | Blue                 | 465            | 46.2                        |
| 4     | Blue (50% power)     | 465            | 22.6                        |
| 5     | White                | 410-800        | 139.3                       |
| 6     | Green                | 525            | 20.5                        |
| 7     | Red                  | 625            | 29.9                        |

* Optical power was measured at the distance of 10 cm.
Photocatalysts preparation

mpg-CN preparation

mpg-CN was prepared according to the procedure described in literature.\(^1\) Cyanamide (3.0 g) and Ludox HS-40 (7.5 g) were mixed in a 10 mL glass vial. The mixture was stirred at room temperature for 30 min until cyanamide has completely dissolved. The resultant solution was stirred at +60°C for 16 h until water has completely evaporated. The magnetic stirrer bar was removed and white solid was transferred to the porcelain crucible and heated under N\(_2\) flow in the oven. The temperature was increased from room temperature to 550°C within 4 h and maintained at 550°C for 4 h. The crucible was spontaneously cooled to room temperature. The solid from the crucible was briefly grinded in the mortar and transferred to the polypropylene bottle. A solution of (NH\(_4\))HF\(_2\) (0.24 g·mL\(^{-1}\), 50 mL) was added and suspension was stirred at room temperature for 24 h. The solid was filtered, thoroughly washed with water, once with ethanol and dried in vacuum (55°C, 20 mbar) overnight.

\(g\)-CN preparation

\(g\)-CN was prepared according to the following procedure. Dicyandiamide (15 g) was heated to 600°C with a ramp 2.4°C min\(^{-1}\) under N\(_2\) flow. After cooling to room temperature, solid was finely ground in mortar.

K-PHI preparation

K-PHI was prepared according to the literature procedure.\(^2\) A mixture of lithium chloride (3.71 g), potassium chloride (4.54 g) and 5-aminotetrazole (1.65 g) was ground in ball mill for 5 min at the shaking rate 25 s\(^{-1}\). Reaction mixtures were transferred into porcelain crucibles and covered with lids. Crucibles were placed in the oven and heated under constant nitrogen flow (15 L·min\(^{-1}\)) and atmospheric pressure at a following temperature regime: heating from room temperature to 550 °C for 4 hours, annealing at 550 °C for 4 hours. After completion of the heating program, the crucibles were allowed to cool slowly to room temperature under nitrogen flow. The crude products were removed from the crucibles, washed with deionized water (100 mL) for 3 hours in order to remove salts, then filtered, extensively washed with deionized water and dried in a vacuum oven (20 mbar) at 50 °C for 15 h.
Figure S3. K-PHI characterization. a) PXRD pattern of K-PHI; b) XPS C 1s and K 2p spectra of K-PHI; c) XPS N 1s spectrum of K-PHI; d) XPS O 1s spectrum of K-PHI; e) UPS spectrum of K-PHI; f) UV-vis absorption spectrum of K-PHI with Tauc plot as inset assuming that K-PHI is a direct semiconductor; g) PL spectrum of K-PHI obtained upon excitation with 350 nm; h) N₂ sorption isotherm measured at 77 K. BET surface area; i) FTIR spectrum of K-PHI; j) Dynamic light scattering (DLS) analysis of K-PHI suspension in water; k) representative SEM image of K-PHI photocatalyst. Scale bar 200 nm; l) AC-HRTEM image of K-PHI photocatalyst. Scale bar 20 nm. Reproduced with permission from *Nat Commun* 10, 945 (2019).
**H-PHI preparation**

H-PHI was prepared according to the following procedure. A suspension of K-PHI (408 mg) in HCl (18 mL, 0.1 M) was stirred at room temperature for 24 h. The suspension was subjected to centrifugation (13000 rpm, 10 min). Supernatant layer was decanted and deionized water (2 mL) was added to the solid. The solid was dispersed by vortex mixer and centrifuged (13000 rpm, 10 min) again. Supernatant layer was decanted and washing procedure was repeated in total 7 times until suspension pH 7. The solid was dried in vacuum overnight.

**Na-PHI preparation**

Na-PHI was prepared according to the literature procedure. Melamine (1 g) was grinded with NaCl (10 g). Reaction mixture was transferred into a porcelain crucible and covered with lid. Crucible was placed in the oven and heated under constant nitrogen flow (15 L·min\(^{-1}\)) to 600 °C with a heating rate of 2.3 °C min\(^{-1}\), held at 600 °C for 4 hours, then allowed to cool down. The crude product was removed from the crucible, washed with deionized water (100 mL), isolated by filtration, then thoroughly washed with deionized water on the filter (100 mL) and dried in a vacuum oven at 50°C for 15 h.

**RFT preparation**

RFT was prepared according to the following procedure. Riboflavin (0.5 g, 1 mmol) was suspended in a mixture of acetic acid (20 mL) and acetic anhydride (20 mL). To the mixture HClO\(_4\) (70%, 0.1 mL, 1 mmol) was added dropwise and the resulting mixture was stirred at 40 °C for 1 h. After cooling, water (40 mL) was added and mixture was extracted with CH\(_2\)Cl\(_2\) (4 times 50 mL). Organic layer was washed with water (twice 40 mL) and NaHCO\(_3\) (solution 40 mL), dried with Na\(_2\)SO\(_4\) and concentrated.

**Procedure of K-PHI regeneration**

K-PHI after the reaction was separated by centrifugation, washed with acetonitrile (2 times, 2 mL each) and with water (2 times, 2 mL each). KOH solution (9 mL, 0.1 M) was added to the catalyst and suspension was stirred for 2 h. The catalyst was separated by centrifugation, washed with water (3 times, 3 mL each), once with methanol and dried in vacuum overnight.
Band gap characterization

**Figure S4.** DRUV-vis spectra and Tauc plot of K-PHI

**Figure S5.** DRUV-vis spectra and Tauc plot of Na-PHI
Figure S6. DRUV-vis spectra and Tauc plot of H-PHI

Mott Schottky analysis of K-PHI, Na-PHI, H-PHI

Figure S7. Mott-Schottky plots of Na-PHI, H-PHI, and K-PHI recorded at 5 kHz
Table S2. Catalysts used for sulfonyl chlorides synthesis in Table 1

| Photocatalyst | VB (M*/M⁻), V vs. NHE | CB (M*/M⁺), V vs. NHE |
|---------------|------------------------|------------------------|
| K-PHI         | 2.36                   | −0.35⁻                  |
| Na-PHI        | 2.30                   | −0.46⁻                  |
| H-PHI         | 2.30                   | −0.52⁻                  |
| Mpg-CN⁶       | 1.4                    | −1.3                   |
| g-CN⁶         | 1.4                    | −1.3                   |
| RFT⁷          | 1.91                   |                         |
| Ru(bpy)₃Cl₂⁸ | 1.01                   | −0.57                  |
| Ir(ppy)₃⁸    | 0.55                   | −1.49                  |

[a] Oxidation power of semiconductors is defined by the VB potential, reduction power – by the CB potential. For molecular photocatalysts, redox potential of the reaction M*/M⁻ is used as the equivalent of oxidation power and M*/M⁺ – of the reduction power, where M* is an excited state of sensitizer, M⁻ and M⁺ are reduced and oxidized forms of a sensitizer.  

[b] Calculated from Mott-Schottky plots (Figure S7).
**Synthesis methods**

*Synthesis of S-benzylisothiourea hydrochloride and S-(4-trifluoromethylbenzyl)isothiourea hydrochloride*

In a round bottom flask with a reflux condenser benzylchloride (8 mmol), thiourea (8 mmol) and ethanol (5 mL) were placed. The mixture was refluxed for 2 h and cooled to room temperature. The resulting solution was concentrated under reduced pressure. The formed precipitate was washed with EtOAc (5 mL), filtered, dried and analyzed by NMR.

**S-benzylisothiourea hydrochloride**

Yield: 93%. $^1$H NMR (400 MHz, DMSO) δ 9.19 (s, 4H), 7.46 - 7.28 (m, 5H), 4.49 (s, 2H). $^{13}$C NMR (101 MHz, DMSO) δ 169.01, 135.09, 129.03, 128.87, 128.06, 34.15. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -61.00.

**S-(4-trifluoromethylbenzyl)isothiourea hydrochloride**

Yield: 86%. $^1$H NMR (400 MHz, DMSO) δ 9.17 (s, 4H), 7.77 (d, $J = 8.2$ Hz, 2H), 7.65 (d, $J = 8.1$ Hz, 2H), 4.58 (s, 2H). $^{13}$C NMR (101 MHz, DMSO) δ 168.62, 140.57, 129.79, 128.57, 125.73, 125.69, 122.81, 33.32.

*Synthesis of 4-methoxybenzene thioacetate and 2-trifluoromethylbenzene thioacetate*

In a round bottom flask aryl thiol (0.7 mmol) and trimethylamine (1.4 mmol, 2 equiv.) were dissolved in dichloromethane (15 mL). Solution was cooled with ace bath to 0 °C and acetyl chloride (1.05 mmol, 1.5 equiv.) in dichloromethane (5 mL) was added dropwise (exothermic reaction). Reaction was kept with stirring overnight at room temperature. Then solution was washed with water (3 times 5 mL), dried over NaSO$_4$, concentrated and analyzed by NMR.

**4-methoxybenzene thioacetate**

Yield: 93%. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (d, $J = 8.9$ Hz, 2H), 6.94 (d, $J = 8.9$ Hz, 2H), 3.83 (s, 2H), 2.40 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 195.40, 160.74, 136.18, 118.72, 114.96, 55.44, 30.06.

**2-trifluoromethylbenzene thioacetate.**
Yield: 93%. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.79 (d, $J = 7.8$ Hz, 1H), 7.66 – 7.50 (m, 3H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 192.68, 139.04, 132.40, 130.05, 127.24, 127.19, 121.94, 30.39. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -60.44.

**Sulfonyl chlorides synthesis**

In a glass vial a substrate (0.04 mmol) was dissolved in acetonitrile (0.5 mL). HCl (0.1 mL, 36 wt. %, 1.2 mmol), water (0.1 mL) and K-PHI (4 mg) were added. The reaction mixture was stirred under light irradiation ($\lambda_{\text{max}} = 461$ nm, at 10 cm distance) at room temperature for 24 h under $O_2$ atmosphere. After the irradiation CHCl$_3$ (3 mL) and water (0.3 mL) were added to the reaction mixture. The layers were separated, organic layer was dried over NaSO$_4$ and concentrated under reduced pressure. Residue was analyzed by NMR.

* In the catalytic cyclic experiments, K-PHI was washed with acetonitrile (2 times, 2 mL each), water (2 times, 2 mL each), dried in vacuum overnight and used again.

**Benzenesulfonyl chloride**

![](benzenesulfonyl chloride.png)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, 2H), 7.74 (t, 1H), 7.62 (t, 2H).

**2-trifluoromethylbenzenesulfonyl chloride**

![](2-trifluoromethylbenzenesulfonyl chloride.png)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.35 (d, $J = 8.7$ Hz, 1H), 7.97 (d, $J = 7.4$ Hz, 1H), 7.92 – 7.79 (m, 2H).

**4-nitrobenzenesulfonyl chloride**

![](4-nitrobenzenesulfonyl chloride.png)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.46 (d, $J = 9.1$ Hz, 2H), 8.24 (d, $J = 9.6$ Hz, 2H).

**4-methoxybenzenesulfonyl chloride**

![](4-methoxybenzenesulfonyl chloride.png)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J = 9.0$ Hz, 2H), 7.05 (d, $J = 9.0$ Hz, 2H), 3.93 (s, 3H).
**Phenylmethanesulfonyl chloride**

\[
\begin{align*}
\text{O} & \begin{array}{c}
\text{S} \\
\text{O} \\
\text{Cl}
\end{array} \\
\text{C}
\end{align*}
\]

\[^{1}\text{H NMR}\ (400 \text{ MHz}, \text{CDCl}_3) \delta 7.55 - 7.42 \text{ (m, 5H)}, 4.87 \text{ (s, 2H)}.\]

**4-trifluoromethylbenzylsulfonyl chloride**

\[
\begin{align*}
\text{O} & \begin{array}{c}
\text{S} \\
\text{O} \\
\text{Cl}
\end{array} \\
\text{C} & \begin{array}{c}
\text{F}_3
\end{array}
\end{align*}
\]

\[^{1}\text{H NMR}\ (400 \text{ MHz}, \text{CDCl}_3) \delta 7.72 \text{ (d, } J = 8.2 \text{ Hz, 2H}), 7.62 \text{ (d, } J = 8.2 \text{ Hz, 2H)}, 4.92 \text{ (s, 2H)}.\]

**4-bromobenzenesulfonyl chloride**

\[
\begin{align*}
\text{O} & \begin{array}{c}
\text{S} \\
\text{Cl}
\end{array} \\
\text{C} & \begin{array}{c}
\text{Br}
\end{array}
\end{align*}
\]

\[65\% \ ^{1}\text{H NMR}\ (400 \text{ MHz}, \text{CDCl}_3) \delta 7.91 \text{ (d, } J = 8.7 \text{ Hz, 1H)}, 7.78 \text{ (d, } J = 8.8 \text{ Hz, 1H)}.\]

**4-fluorobenzenesulfonyl chloride**

\[
\begin{align*}
\text{O} & \begin{array}{c}
\text{S} \\
\text{Cl}
\end{array} \\
\text{C} & \begin{array}{c}
\text{F}
\end{array}
\end{align*}
\]

\[97\% \ ^{1}\text{H NMR}\ (400 \text{ MHz}, \text{CDCl}_3) \delta 8.08 \text{ (dd, } J = 9.0, 4.8 \text{ Hz, 2H}), 7.30 \text{ (t, } J = 8.5 \text{ Hz, 2H)}.\]^\text{19}\text{F NMR}\ (376 \text{ MHz}, \text{CDCl}_3) \delta -99.55 \text{ (m)}.\]

**2-chlorobenzenesulfonyl chloride**

\[
\begin{align*}
\text{O} & \begin{array}{c}
\text{S} \\
\text{Cl}
\end{array} \\
\text{C} & \begin{array}{c}
\text{Cl}
\end{array}
\end{align*}
\]

\[95\% \ ^{1}\text{H NMR}\ (400 \text{ MHz}, \text{CDCl}_3) \delta 8.15 \text{ (d, } J = 7.7 \text{ Hz, 1H)}, 7.71 - 7.58 \text{ (m, 2H), 7.50 (ddd, } J = 8.4, 5.9, 2.8 \text{ Hz, 1H)}.\]

**Sulfonyl amides synthesis**

In a glass vial a substrate (0.04 mmol) was dissolved in acetonitrile (0.5 mL). NH\(_4\)Cl (10 mg, 0.19 mmol), water (0.2 mL) and K-PHI (4 mg) were added. The reaction mixture was stirred under blue LED (465 nm, 46 mW-cm\(^{-2}\)) irradiation at room temperature for 24 h under \(\text{O}_2\) atmosphere. After the irradiation CHCl\(_3\) (3 mL) and water (0.3 mL) were added to the reaction mixture. The layers were separated, organic layer was dried over NaSO\(_4\) and concentrated under reduced pressure. Residue was analyzed by \(^{1}\text{H NMR}.\)
Benzenesulfonamide

\[
\text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.93 \text{ (d, } J = 7.2 \text{ Hz, 1H), } 7.62 - 7.51 \text{ (m, 3H).}^{12}
\]

4-nitrobenzenesulfonamide

\[
\text{H NMR (400 MHz, CDCl}_3\text{) } \delta 8.34 \text{ (d, } J = 8.9 \text{ Hz, 2H), } 8.10 \text{ (d, } J = 8.9 \text{ Hz, 2H).}^{13}
\]

4-methoxybenzenesulfonamide

\[
\text{H NMR (400 MHz, CDCl}_3\text{) } \delta 7.86 \text{ (d, } J = 9.0 \text{ Hz, 2H), } 6.98 \text{ (d, } J = 8.9 \text{ Hz, 2H), } 3.83 \text{ (s, 3H).}^{14}
\]

4-bromobenzenesulfonamide

\[
\text{75% H NMR (400 MHz, CDCl}_3\text{) } \delta 7.80 \text{ (d, } J = 8.5 \text{ Hz, 2H), } 7.67 \text{ (d, } J = 8.6 \text{ Hz, 2H).}^{15}
\]

4-fluorobenzenesulfonamide

\[
\text{69% H NMR (400 MHz, CDCl}_3\text{) } \delta 7.95 \text{ (dd, } J = 8.8, 5.0 \text{ Hz, 1H), } 7.20 \text{ (t, } J = 8.5 \text{ Hz, 1H).}^{19}\text{F NMR (376 MHz, CDCl}_3\text{) } \delta -105.06 \text{ (m).}^{15}
\]

2-chlorobenzenesulfonamide

\[
\text{56% H NMR (400 MHz, CDCl}_3\text{) } \delta 8.16 \text{ (d, } J = 7.7 \text{ Hz, 1H), } 7.67 - 7.64 \text{ (m, 2H), } 7.50 \text{ (m, 1H).}^{11}
\]
**Synthesis of N-substituted sulfonyl amides**

In a glass vial a substrate (0.04 mmol) was dissolved in acetonitrile (0.5 mL). RHN₂Cl (0.25 mmol), water (0.2 mL) and K-PHI (4 mg) were added. The reaction mixture was stirred under blue LED (465 nm, 46 mW·cm⁻²) irradiation at room temperature for 24 h under O₂ atmosphere. After the irradiation CHCl₃ (3 mL) and water (0.3 mL) were added to the reaction mixture. The layers were separated, organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. Residue was analyzed by GC-MS.

GC-MS of the reaction mixture prepared with thiophenol (0.04 mmol) and butylamine hydrochloride (0.25 mmol):

![GC-MS of the reaction mixture prepared with thiophenol (0.04 mmol) and butylamine hydrochloride (0.25 mmol)](image1)

GC-MS of the reaction mixture prepared with 4-fluorothiophenol (0.04 mmol) and ethylamine hydrochloride (0.25 mmol):

![GC-MS of the reaction mixture prepared with 4-fluorothiophenol (0.04 mmol) and ethylamine hydrochloride (0.25 mmol)](image2)
**Synthesis of benzenesulfonyl chloride**

N-chlorosuccinimide (4.85 g, 4 equiv.) was dissolved in a mixture of hydrochloric acid (2 mL, 2 M) and acetonitrile (10 mL). The solution was cooled to 5°C and thiophenol (1 g, 9 mmol) in acetonitrile (5 mL) was added dropwise. The reaction mixture was stirred at 5°C for 10 min and was let warm up to room temperature for 30 min. Water (5 mL) was added to the reaction mixture and it was extracted with ether (3 times, 10 mL). Organic solution was dried over NaSO\(_4\) and concentrated. Precipitate was filtered off, washed with cold ether (2 mL). Filtrate was purified by column chromatography. Yield 86%.

\( ^{1}H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.06 (d, \( J = 8.1 \) Hz, 2H), 7.76 (t, \( J = 7.5 \) Hz, 1H), 7.64 (t, \( J = 7.9 \) Hz, 2H). \( ^{13}C\) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 135.39, 129.85, 127.15.

**Synthesis of phenylsulfonyl chloride under sunlight**

In a glass vial S-phenylthioacetate (0.04 mmol) was dissolved in acetonitrile (0.5 mL). HCl (0.1 mL, 36 wt. %, 1.2 mmol), water (0.1 mL) and K-PHI (5 mg) were added. The reaction mixture was stirred under direct sunlight irradiation (69 mW·cm\(^{-2}\) at reactor surface, 10 AM 04 June 2019 at 52°24’53.2”N 12°58’11.4”E) at ambient temperature for 5 h under O\(_2\) atmosphere. After the irradiation CHCl\(_3\) (3 mL) and water (0.3 mL) were added to the reaction mixture. The layers were separated, organic layer was dried over NaSO\(_4\) and concentrated under reduced pressure. Residue was analyzed by \( ^{1}H\) NMR.

**Benzenesulfenyl chloride synthesis**

In a round-bottom flask, thiophenol (110 mg, 1 mmol) was dissolved in dichloromethane (5 mL). The solution was purged with N\(_2\) and cooled under ice bath. Sulfuryl chloride (1.05 mmol) in dichloromethane (5 mL) was added dropwise within 2 min. The reaction was stirred under ice bath for 30 min and warmed to room temperature. The solution was used further.

\[ \text{SCl} \]

\( ^{1}H\) NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.67-7.65 (m, 3H), 7.41-7.39 (m, 3H). \( ^{13}C\) NMR (101 MHz, CDCl\(_3\)) \( \delta \) 135.53, 131.84, 130.21, 129.43.
**Scale synthesis of 4-bromobenzenesulfonyl chloride**

In a glass vial with the gas inlet and finger cooler, a *p*-bromothiphenol (0.55 mmol) was dissolved in acetonitrile (15 mL). HCl (2 mL, 36 wt. %, 20 mmol) and K-PHI (50 mg) were added. The reaction mixture was stirred under light irradiation (white LED, at 10 cm distance) under O₂ atmosphere and water-cooling (20 °C) for 24 h. After the irradiation, CHCl₃ (50 mL) and water (5 mL) were added to the reaction mixture. The layers were separated; organic layer was dried over NaSO₄ and concentrated under reduced pressure. Sulphonyl chloride (0.51 mmol) was obtained with 90% yield and 100% selectivity according to the GC-MS analysis.
Reaction conditions optimization

Table S3. Optimization of sulfonyl chloride synthesis conditions\(^{[a]}\)

| Entry | Substrate | K-PHI | HCl, 6 M | CH\(_3\)CN | Atmosphere | Light, nm | Yield, % |
|-------|-----------|-------|----------|------------|------------|-----------|----------|
| 1     | 5 mg      | 4 mg  | 0.2 mL   | 0.5 mL     | O\(_2\)     | 465       | 93       |
| 2     | 5 mg      | -     | 0.2 mL   | 0.5 mL     | O\(_2\)     | 465       | 0        |
| 3     | 5 mg      | 4 mg  | -        | 0.5 mL     | O\(_2\)     | 465       | 0        |
| 4     | 5 mg      | 4 mg  | 0.2 mL   | 0.5 mL     | Ar         | 465       | 0        |
| 5     | 5 mg      | 4 mg  | 0.2 mL   | 0.5 mL     | O\(_2\)     | dark      | 0        |
| 6     | 5 mg      | 4 mg  | HCl/diox | 0.5 mL     | O\(_2\)     | 465       | 0        |

\(^{[a]}\) S-Phenylthioacetate 0.035 mmol; K-PHI 4 mg; HCl (36 wt. %) 50 \(\mu\)L; H\(_2\)O 0.2 mL; MeCN 0.5 mL; T = 25 °C; electron scavenger – O\(_2\); LED module 465 nm;

Table S4. Sulfonyl chloride synthesis at different temperatures\(^{[a]}\)

| Entry | Substrate | K-PHI | Atmosphere | Temperature, °C | Yield, % |
|-------|-----------|-------|------------|-----------------|----------|
| 1     | 5 mg      | 4 mg  | O\(_2\)    | 30              | 90       |
| 2     | 5 mg      | 4 mg  | O\(_2\)    | 45              | 0        |
| 3     | 5 mg      | 4 mg  | O\(_2\)    | 60              | 0        |

\(^{[a]}\) S-Phenylthioacetate 0.035 mmol; K-PHI 4 mg; HCl (36 wt. %) 50 \(\mu\)L; H\(_2\)O 0.2 mL; MeCN 0.5 mL; T = 25 °C; electron scavenger – O\(_2\); LED module 465 nm;
| Substrate | Product | Yield (Conversion) % |
|-----------|---------|----------------------|
|           |         | 365 nm  | 410 nm  | 465 nm  | White LED | 535 nm  | 635 nm  |
| ![Chemical Structure](image1.png) | ![Chemical Structure](image2.png) | 31 | 70 | - | - | - | - |
| ![Chemical Structure](image3.png) | ![Chemical Structure](image4.png) | 60 | 23 | 90(100) | 93(100) | - | - |
| ![Chemical Structure](image5.png) | ![Chemical Structure](image6.png) | - | - | - | - | 73(100) | 93(94) |
| ![Chemical Structure](image7.png) | ![Chemical Structure](image8.png) | 16 | 61 | - | - | - | - |
| ![Chemical Structure](image9.png) | ![Chemical Structure](image10.png) | 75 | 30 | 95(100) | 95 (100) | - | - |
| ![Chemical Structure](image11.png) | ![Chemical Structure](image12.png) | - | - | - | - | 57 (79) | 48 (58) |
| ![Chemical Structure](image13.png) | ![Chemical Structure](image14.png) | 55 | 65 | - | - | - | - |
| ![Chemical Structure](image15.png) | ![Chemical Structure](image16.png) | 33 | 19 | 82 (100) | - | - | - |
| ![Chemical Structure](image17.png) | ![Chemical Structure](image18.png) | - | - | - | 76 (90) | 84 (100) | 84 (86) |

**Scheme S1.** Chromoselective thioacetate oxidation with K-PHI.
Mechanism investigation

Table S5. S-phenylthioacetate photolysis

| Entry | $\lambda_{\text{max}}$, nm | Conversion, % | Yield, % |
|-------|-----------------|--------------|---------|
| 1     | 365             | 0            | 0       |
| 2     | 465             | 0            | 0       |
| 3     | 523             | 0            | 0       |

[a] S-Phenylthioacetate 0.035 mmol; HCl (36 wt. %) 50 μL; H$_2$O 0.2 mL; MeCN 0.5 mL; T = 25 °C; electron scavenger – O$_2$; irradiation with LED; [b] traces of deacetylated thiophenol (the product of S-Phenylthioacetate hydrolysis) was detected.

Table S6. Sulfonyl chlorides photolysis

| Entry | $\lambda_{\text{max}}$, nm | K-PHI | Conversion, % | Yield, % |
|-------|-----------------|------|--------------|---------|
| 1     | 365             | 5 mg | 0            | 0       |
| 2     | 465             | 5 mg | 0            | 0       |
| 3     | 523             | 5 mg | 0            | 0       |
| 4     | 365             | -    | 0            | 0       |
| 5     | 465             | -    | 0            | 0       |
| 6     | 525             | -    | 0            | 0       |

[a] Phenylsulfonyl chloride 0.035 mmol; K-PHI 5 mg; HCl (36 wt. %) 50 μL; H$_2$O 0.2 mL; MeCN 0.5 mL; T = 25 °C; electron scavenger – O$_2$; irradiation with LED;
Photon flux was calculated as follows:

\[ \Phi = \frac{I \cdot \lambda}{h \cdot c \cdot N_a} \]

Where \( \Phi \) – photon flux, \( \mu \text{mol s}^{-1} \text{cm}^{-2} \); \( I \) – irradiance, \( \text{W cm}^{-2} \); \( \lambda \) – wavelength, m; \( h \) – Planck constant, J s; \( c \) – speed of light, m s\(^{-1} \); \( N_a \) – Avogadro constant, mol\(^{-1} \).

**Figure S9.** Photon flux of the used LED

**Figure S10.** Cyclic voltammetry investigation of thioacetates.
Steady-state fluorescence

Figure S11. Steady-state fluorescence spectra of K-PHI suspension in MeCN (left) and reaction mixture (right) under different excitation wavelengths.
**Figure S12.** 2D-fluorescence spectra of: a) MeCN; b) K-PHI suspension in HCl (36 %)/MeCN; c) solution of 2-CF₃C₆H₄Sac in MeCN; d) reaction mixture with 2-CF₃C₆H₄Sac; e) solution of PhSac in MeCN; f) reaction mixture with PhSac; g) solution of 4-OMeC₆H₄Sac in MeCN; h) reaction mixture with 4-OMeC₆H₄Sac; reaction mixture stands for: Substrate 0.04 mmol; K-PHI 4 mg; HCl (36 wt. %) 0.1 mL; H₂O 0.1 mL; MeCN 0.5 mL; T = 25 °C; electron scavenger – O₂; irradiation with LED module.
Comments to Figure S12

All experiments were performed at the same concentrations as in the photocatalytic experiments. The intensity of K-PHI fluorescence in reaction mixtures is lower compared to the K-PHI in MeCN. At the same time, the fluorescence of thioacetates (shown on the left side) is quenched by photocatalyst and is not present anymore upon addition of K-PHI (on the right). Additionally, stronger quenching effect is seen for OMe-substituted substrate, followed by PhSAc, and 2-CF₃C₆H₄SAC.

Figure S16. Fluorescence spectra of K-PHI and Na-PHI. EQE – external quantum efficiency, IQE – internal quantum efficiency.
Time resolved photoluminescence study

Figure S17. TRES map of solid K-PHI under excitation with 375 nm.

Figure S18. TRES map of solid K-PHI under excitation with 470 nm.
Figure S19. TRES map of solid K-PHI under excitation with 640 nm.
Singlet oxygen detection

Figure S20. Singlet oxygen detection at different excitation wavelengths.
Transient absorption spectroscopy

Figure S21. Transient absorption spectroscopy (TAS) measurements of K-PHI and Na-PHI in MeCN under Ar and oxygen atmosphere (λ_{ex} = 387 nm / 2 µJ).
Figure S22. Transient absorption spectroscopy (TAS) measurements of K-PHI and Na-PHI in H$_2$O/MeCN (7:3) under Ar and oxygen atmosphere ($\lambda_{ex} = 387$ nm / 2 $\mu$L).
**Supplementary discussion on TAS experiments**

Addition of water to the K-PHI suspension gave rise to the positive transient absorption signal forming directly after photoexcitation with maxima at around 630 and 750 nm, that merge into one maximum at 690 nm similarly to the behavior under O$_2$. However, no positive transient, seen under O$_2$ atmosphere between 850 and 1000 nm and ascribed to the diffusion-dependent process, is detected for water. This can be explained by quenching of the exited state of K-PHI with water, where diffusion apparently does not play a role.

Formation of the signals at 630 and 750 nm is also seen for Na-PHI, however with significantly weaker intensity. These brings the idea, that exited state of Na-PHI can also be quenched at a certain level with water, but not with oxygen.

Addition of hydrochloric acid and phenylthioacetate resulted in stronger scattering of the samples and hardly interpretable data. No additional signals upon addition of these reagents were detected.

**Supplementary discussion of the mechanism**

In the ground state, apart from the valence band (VB), K-PHI has occupied intraband states (IBS) (Figure S23).$^{16}$

![DOS plot](image)

*Figure S23.* Partial (C, N, K) and total DOS in K-PHI ground state. Fermi energy is located at 0 eV. Reproduced with permission from *Angew. Chem. Int. Ed.* **2020**, *59*, 15061.$^{16}$

Therefore, two electron excitation events are possible: i) low-energy electron transfer from the IBS to the conduction band (CB) (a band of ca. 1.9 eV seen in the UV-vis spectrum, previously denoted as “n-π*” transfer) and ii) high-energy electron transfer from the valence band to the conduction band (an intrinsic band gap of CN materials, ca. 2.7 eV, previously denoted as “π-π*” transfer) (Figure S24).
Excitation of electron with the photons of low energy (green light) to the CB is only enough for the “IBS-CB” electron transfer and leaves holes with relatively low oxidation power in the IBS, which is not sufficient for the oxidation of S-Arylthioacetates. Therefore, relaxation of this state only allows for the energy transfer, for example, to oxygen with formation of \( \text{^1O}_2 \). Irradiation with the high-energy photons (>2.64 eV), on the other hand, is enough for the effective exciton separation and excitation of electron form the VB to the CB. In this case, two further possibilities for relaxation exist. First, a classic electron transfer pathway, and second, an intersystem crossing of electron form the IBS to VB and further energy transfer and \( \text{^1O}_2 \) sensitization.
Figure S25. EPR spectra of: a-c) K-PHI, TEMP, MeCN, O₂ and d-f) K-PHI, DMPO, MeCN, H₂O, O₂ under 530 nm, 465 nm, 415 nm irradiation. Dark blue represents a mixture with catalyst, oxygen trigger, and irradiation; aquamarine – mixture with oxygen trigger and irradiation; beige – mixture with catalyst, oxygen trigger in dark
Chlorine detection

**Figure S26.** Detection of active chlorite with Quantofix® Chlor test strips.

**Figure S27.** The local structure of the adduct between poly(heptazine imide) anion and ‘active chlorine’.
Intermediate detection

Participation of the thyl radical in the photocatalytic mechanism was confirmed by irradiating a deaerated mixture of DMPO, PhSH and K-PHI in MeCN with white LED. GC-MS analysis of the reaction mixture revealed presence of several fragments with m/z 204.1, 190.1, and 144.1, which could be assigned to the decomposition of the DMPO-SPh adduct during the mass spectrum acquisition.

Reaction conditions: Substrate 0.04 mmol; K-PHI 4 mg; MeCN 1 mL; T = 25 °C; Ar; irradiation with LED module 465 nm (46.2 mW cm$^{-2}$);

![Figure S28. GC chromatogram of the reaction mixture after 24 h irradiation.](image)

![Figure S29. MS spectra of the DMPO-phenylthiyl adduct (product with the retention time 10.67 min and M$_2$ 204.1)](image)
Figure S30. Possible fragmentation of the DMPO-phenylthiyl adduct

The formation of DMPO-thiyl radical was also evidenced by EPR. The EPR capillary was filled with the deaerated mixture of DMPO, PhSH and K-PHI in MeCN. The measurement was performed in dark and under 415 nm LED irradiation.

Figure S31. Experimental and simulated EPR spectra of the DMPO-thiyl radical adduct (K-PHI 4 mg, PhSAc 5 mg, DMPO 5 µL in 0.5 mL deaerated MeCN under 415 nm irradiation
Synthesis of phenylsulfonyl chloride from phenylsulfenyl chloride

Coupling of phenyltyil radical with chlorine gives benzenesulfenyl chloride that is further oxidized to sulfonyl chloride.

The benzenesulfenyl chloride was synthesized and tested under the photocatalytic conditions in order to confirm the proposed transformation.

In a glass vial, a solution of phenyl sulfenyl chloride (0.5 mL, 1 M) was diluted with dichloromethane (0.5 mL) and K-PHI (4 mg) was added. The reaction mixture was stirred under light irradiation ($\lambda_{\text{max}} = 465$ nm, at 10 cm distance) at room temperature for 24 h under O2 atmosphere. After the irradiation, catalyst was removed by centrifugation and reaction mixture analyzed by GC-MS. The reaction mixture consist of 10% sulfonyl chloride and 90% disulfide.*

* Formation of disulfide is promoted due to the instability of phenyl sulfenyl chloride under light irradiation (evolution of Cl$_2$ molecule and coupling of two thiyl fragments) and slow kinetics of catalytic reaction. Thus, in the photocatalytic reaction of sulfonyl chloride synthesis, sulfenyl chloride is formed only as a transient specie, presumably bound to the photocatalyst surface, and it does not accumulate in the reaction mixture.

**Figure S32.** GC chromatogram of the reaction mixture after 24 h irradiation.
NMR spectra
$^{19}$F NMR (DMSO)

$^{13}$C NMR (DMSO)
$^{1}H$ NMR (CDCl$_3$)
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