### Supporting Information

**A “waiting” carbon nitride radical anion: a charge storage material and key Intermediate in direct C-H thiolation of methylarenes using elemental sulfur as the “S”-source**

Aleksandr Savateev*, Bogdan Kurpil, Artem Mishchenko, Guigang Zhang and Markus Antonietti

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Experimental Section

Chemicals

Acetonitrile-\textit{d}_3 (≥99.8 atom % D), chloroform-\textit{d} (99.8 atom % D), toluene (99.8%), 4-methylanisole (99%), 2-methylanisole (99%), \textit{p}-tolunitrile (98%), ethylbenzene (99.8%), \textit{p}-iodotoluene (99%), methylviologen dichloride hydrate (98%), sulfur (≥99.5%), triphenylphosphine (99%), 1,2-diphenylethane (99%), TiO\textsubscript{2} (99.5%, a mixture of rutile and anatase) were purchased from Sigma-Aldrich. 1,2-dibenzylidisulfane (98+%), benzylthiol (99%) were purchased from Alfa Aesar. Acetonitrile (hypergrade for LC-MS) and \textit{N},\textit{N},4-trimethylaniline (for synthesis) were purchased from Merck. \textit{P}-fluorotoluene (97%) and dibenzylsulfide (98%) were purchased from Acros Organics.

Materials characterization

Powder X-Ray diffraction patterns were measured on a Bruker D8 Advance diffractometer equipped with a scintillation counter detector with CuKa radiation (λ = 0.15418 nm) applying 2θ step size of 0.05° and counting time of 3s per step. Optical absorbance spectra of powders were measured on a Shimadzu UV 2600 equipped with an integrating sphere. The emission spectra were recorded on Jasco FP-8300 instrument. The excitation wavelength was 350 nm. The TEM measurements were acquired using a double-corrected Jeol ARM200F, equipped with a cold field emission gun and a Gatan GIF Quantum. The used acceleration voltage was 200kV and the emission was set to 10µA in order to reduce beam damage. An objective aperture with a diameter of 60µm was introduced into the beam to improve the contrast while still allowing for atomic resolution.

Time-resolved fluorescence measurements were performed by using a single photon counting setup (TCSPC) with a Becker&Hickl PML-spectrometer (modified Oriel MS-125) with a laser repetition rate of 2 MHz. The detector comprises a Becker&Hickl PML-16-C-1 (modified Hamamatsu) multi-alkaline photomultiplier. The excitation wavelength was 405 nm. The excitation was carried out using a pulsed laser diode at ~30 nl/cm\textsuperscript{2} (LDH-P-C405, PicoQuant GmbH). The emission was recorded in the range of 460-600 nm, while blocking the secondary detection of the excitation pulses with a 450 nm cut-off-filter. Raw decay data presented as logarithm of photon counts versus time were analyzed with data analysis software of PicoQuant GmbH (Germany). The decay times were extracted by means of a reconvoluation fit based on a double and triple exponential model. Considering that

\[
I_{PL}(t) = \sum_{i=1}^{\infty} a_i e^{-t/\tau_i}
\]

where \(\tau_i\) is the lifetime and \(a_i\) is the amplitude of the \(i\)th component, the intensity-averaged fluorescence lifetime \(\tau\) was calculated as

\[
\langle \tau \rangle = \sum_{i=1}^{\infty} \frac{a_i \tau_i^2}{\sum_{i=1}^{\infty} a_i \tau_i}
\]
Fourier transform infrared (FT-IR) spectra were recorded on Thermo Scientific Nicolet iD5 spectrometer.

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

Scanning electron microscopy (SEM) images were obtained on a LEO 1550-Gemini microscope.

The 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 \(hν=21.23 \text{ eV}\)) 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.

Quenching K-PHI• with Methylviologen

A mixture of K-PHI (10.39 mg), 4-methylanisole (0.6 mL) in acetonitrile (6.05 mL) was stirred under blue (461 nm, 0.0517±3·10⁻⁵ W·cm⁻²) light irradiation at +50 °C under N₂ gas flow for 24 hours. Reaction mixture has changed its color to green. Irradiation was stopped and methylviologen dichloride dihydrate (6.9 mg, 24 µmol) was added in one portion. K-PHI immediately precipitated, while the solution has changed its color to blue. Reactor was transferred into the glow box. Supernatant layer was transferred into screw capped quartz cuvette and UV-vis absorbance of the solution was measured (Fig. 1g). The number of transferred electrons was calculated using the equation:

\[
n = \frac{1}{m} \cdot A \cdot V = \frac{1}{m} \cdot \varepsilon \cdot l \cdot V
\]

where \(m\) – mass of K-PHI, g; \(A\) – absorbance of the sample at 606 nm; \(\varepsilon\) – extinction, (mol·L)⁻¹·cm⁻¹; \(l\) – optical path, cm.

AQY calculation

A glass tube with a side arm was charged with 4-methylanisole (610.4 mg, 5 mmol), K-PHI (10.22 mg), \(S_8\) (3.78 mg, 118 µmol of S atoms) and CD₃CN (5.005 g, 6 mL). The mixture was degassed by freeze-pump-thaw method three times. The reactor was wrapped with aluminum foil with a window of 3 cm² (1.2x2.5 cm). The suspension was vigorously stirred at +50°C under flow of nitrogen and light irradiation with an emission maximum at 461 nm and irradiance 0.0517±3·10⁻⁵ W·cm⁻². The reaction mixture was sampled (3 times) at fixed period of time and yield of polysulfides was determined by \(^1\text{H}\) NMR and AQY values were calculated using equation:
AQY = \frac{N_{MA}}{N_{\text{photon}}} = \left( \frac{2 \cdot n_{PS}}{N_A} \right) \cdot \frac{T \cdot S \cdot E}{A} = \frac{2 \cdot \left( n_{di} + n_{tri} + n_{tetra} + n_{penta} \right)}{N_A} \cdot \frac{T}{\left( \frac{\int_{\lambda_1}^{\lambda_2} W(\lambda) \, d\lambda}{h \cdot c \cdot \int_{\lambda_1}^{\lambda_2} W(\lambda) \, d\lambda} \right) \cdot \frac{1}{f_{\lambda_1}^{\lambda_2} l(t) \, dt}}

where AQY – apparent quantum yield; \(N_{MA}\) – number of 4-methylanisole molecules oxidized during time \(t\) of the reaction mixture irradiation; \(N_{\text{photon}}\) – number of photons that has reached the reactor; \(n_{PS}\) – amount of polysulfides formed during time \(t\) of the reaction mixture irradiation, mole; \(N_A\) – Avogadro’s number, mole\(^{-1}\); \(n_{di}, n_{tri}, n_{tetra}, n_{penta}\) – amounts of 1,2-bis(4-methoxybenzyl)disulfane, 1,3-bis(4-methoxybenzyl)trisulfane, 1,4-bis(4-methoxybenzyl)tetratosulfane and 1,5-bis(4-methoxybenzyl)pentasulfane formed during time \(t\) of the reaction mixture irradiation, mole; \(S\) – window size, cm\(^2\); \(E\) – amount of electromagnetic radiation received by the reactor during time \(t\), J; \(t\) – time of irradiation, s; \(l(t)\) – LED irradiance as a function of time (Fig. S8b); \(h\) – Planck’s constant, \(6.63 \times 10^{-34}\) J·s; \(c\) – speed of light, \(3 \times 10^8\) m·s\(^{-1}\); \(W(\lambda)\) – LED emission spectrum (Fig. S8a); \(\lambda\) – wavelength, nm; \(T\) – transmittance of the glass (Fig. S8a); \(\lambda_1\) and \(\lambda_2\) – designate limits of LED emission spectrum integration, nm.

Relative standard deviation of AQY measurements did not exceed 3%.

**Kinetics Study and Sulfur Content Determination**

The amount of polysulfides was calculated from \(^1\)H NMR spectra. Sulfur content determination is based on the oxidation of triphenylphosphine by S\(_8\) to give triphenylphosphine sulphide having different chemical shifts in \(^{31}\)P NMR (Fig. S7). A prepared glass reactor with a side inlet used to connect nitrogen, was charged with p-methylanisole (0.606 g, 4.97 mmol), S\(_8\) (3.11 mg, 97 µmol of S atoms), K-PHI (10 mg), CD\(_3\)CN (5.138 g, 6 mL) and a stir bar. The mixture was degassed repeatedly by freeze-pump-thaw method. The mass of the whole reaction mixture was measured to be 5.737 g. The reactor was connected to the nitrogen and condenser was mounted on the top of the reactor. The reaction mixture was stirred at +50 °C under blue (461 nm, \(0.0517 \pm 3 \times 10^{-5}\) W·cm\(^{-2}\)) light irradiation. A reaction mixture samples (exact mass, typically 160-170 mg or ca. 200 µL) at fixed time periods were taken. Three samples of the reaction mixture were taken for one measurement in order to calculate standard deviation. The sample was transferred into micro-NMR tube and \(^1\)H NMR spectrum was recorded. The data was then processed in MestReNova software to determine the content of (poly)sulfane (nPS) using the equation:

\[
n_{PS} = \frac{l_{PS}/P_{PS} \times M_{MA}}{l_{MA}/P_{MA} \times M_{MA} \times 10^6} = \frac{l_{PS}/4}{l_{MA}/3} \times \frac{m_{MA}}{M_{MA}} \times 10^6
\]

where \(l_{PS}\) – integral intensity of the peak related to the corresponding polysulfane CH\(_2\) groups; \(P_{PS}\) – number of protons in two CH\(_2\) groups of the corresponding polysulfane; \(l_{MA}\) – integral intensity of the peak related to p-methoxyanisole OCH\(_3\) group; \(P_{MA}\) – number of protons in p-methoxyanisole OCH\(_3\) group; \(m_{MA}\) – mass of p-methoxyanisole taken for the reaction, g; \(M_{MA}\) – molar mass of p-methoxyanisole, g·mol\(^{-1}\).

Relative standard deviation of polysulfane content determination did not exceed 5%.
For the sulfur content determination the slurry from the NMR tube was transferred into 5 mL screw-capped vial. NMR tube was thoroughly washed with toluene and washings were combined in the vial. The exact mass (typically in the range 174-177 mg or ca. 200 µL) of Ph₃P solution (27.23 mg·g⁻¹) in toluene was added to the vial. A stir bar (10x5 mm) was placed into the vial. The vial was closed with the cap and suspension was vigorously stirred at +70 °C for 3 hours. The solvent was gently evaporated, CDCl₃ (3x0.25 mL) was added to the vial and the residue was quantitatively transferred into the NMR tube and ³¹P NMR was recorded. Sulfur content (µmol of S atoms) in the reaction mixture was calculated using the equation:

\[ n = n_p \cdot \omega_S \cdot \left( \frac{m_{\text{mix}}}{m_a} \right) = \left( \frac{m_{\text{Ph}_3\text{P}} \cdot \omega_p}{M_p} \right) \left( \frac{l_S}{l_S + l_O + l_P} \right) \left( \frac{m_{\text{mix}}}{m_a} \right) \]

where \( n_p \) – amount of Ph₃P added to the reaction mixture, mole; \( \omega_S \) – mole fraction of Ph₃P(S) in the mixture; \( m_{\text{mix}} \) – mass of the whole reaction mixture in the reactor, g; \( m_a \) – mass of the aliquot taken for the analysis, g; \( m_{\text{Ph}_3\text{P}} \) – mass of the standard Ph₃P solution in toluene added to the reaction mixture, g; \( \omega_p \) – mass fraction of Ph₃P in its standard solution in toluene; \( M_p \) – molar mass of Ph₃P, g·mol⁻¹; \( l_S \) – integral intensity of Ph₃P(S) with respect to Ph₃P signal in ³¹P NMR spectrum (Fig. S7); \( l_O \) – integral intensity of Ph₃P(O) with respect to Ph₃P signal in ³¹P NMR spectrum (Fig. S7); \( l_P \) – intensity of Ph₃P signal in ³¹P NMR spectrum (Fig. S7).

**K-PHI Photocatalyst Characterization**

![XPS spectra](image)

- **a)** Raw data: C 1s, K 2p, Sum curve
- **b)** Raw data: C 1s, N 1s, O 1s, Sum curve
- **c)** Binding energy (eV)
- **d)** Binding energy (eV)
Preliminary Reaction Conditions Screening of Toluene Oxidative Thiolation

A screw-capped tube was charged with K-PHI (10 mg), toluene (0.3 mL), elemental sulfur (0.96 mg, 30 µmol of S atoms) and acetonitrile (2.7 mL). The teflon coated stir bar was placed as well. The suspension was frozen in liquid nitrogen to solid state and evacuated till the residual pressure 0.1 mbar. The solid was warmed using the heating gun until the solid has melted. The procedure was repeated 3 times and the tube was refilled with argon. The suspension was vigorously stirred at +50°C under blue LED (461 nm, 0.0517±3·10⁻⁵ W·cm⁻²) irradiation for 24 hours. The reaction mixture was allowed to cool to room temperature and the tube was opened in the fume hood. Attention! Evolution of H₂S! Catalyst was separated by centrifugation (13000 min⁻¹) and washed with acetonitrile (2x0.5 mL). The washings were combined and transferred into 5 mL calibrated flask. Standard naphthalene solution (0.25 mL, 52 mg·mL⁻¹) was added into the calibrated flask. The calibrated flask was filled with MeCN until the mark, solution was mixed and composition was analyzed using GC-MS. The yield of dibenzylidisulfane was calculated using the calibration graph. The results are presented in Table S1.
| Entry | K-PHI, mg | Solvent | T, °C | Dibenzyldisulfane yield, µmol |
|-------|----------|---------|-------|-------------------------------|
| 1     | 5        | MeCN    | 30    | 0.9293                        |
| 2     | 5        | PhCH₃   | 30    | 1.3588<sup>a</sup>            |
| 3     | 5        | Hexane  | 30    | <0.1                          |
| 4     | 5        | CH₂Cl₂  | 30    | <0.1                          |
| 5     | 5        | MeCN    | 50    | 5.855                         |
| 6<sup>b</sup> | 5    | MeCN    | 50    | 4.45                          |
| 7<sup>b</sup> | 10   | MeCN    | 50    | 5.105                         |
| 8<sup>b</sup> | 20   | MeCN    | 50    | 3.940<sup>c</sup>            |
| 9     | 5        | PhCH₃   | 50    | 1.486<sup>a</sup>            |
| 10    | 5        | 1,4-dioxane | 50 | <0.1                        |
| 11    | 5        | Pyridine | 50    | <0.1                          |
| 12    | 5        | CH₂Cl₂  | 50    | 0.2195                        |
| 13    | 5        | DMF     | 50    | <0.1                          |
| 14    | 5        | DMSO    | 50    | <0.1                          |
| 15    | 5        | MeOH    | 50    | <0.1                          |
| 16    | 5        | tBuOH   | 50    | <0.1                          |
| 17    | 5        | MeCN    | 80    | 2.213                         |
| 18    | 5        | PhCH₃   | 80    | 2.652<sup>a</sup>            |
| 19    | 5        | 1,4-dioxane | 80 | <0.1                       |
| 20    | 5        | pyridine | 80    | 0.9164                        |

<sup>a</sup> 1,2-diphenylethane was detected by GC-MS;

<sup>b</sup> PhCH₃ 0.2 mL; S₈ 31 µmol;

<sup>c</sup> significant amount of Bn₂S was detected by GC-MS.
Table S2. Oxidative thiolation of toluene. Reaction conditions and photocatalysts screening tests.

\[
\begin{align*}
\text{Entry} & \quad \text{Photocatalyst} & \quad T, ^\circ \text{C} & \quad \text{Light} & \quad \text{Bn}_2\text{S}_2 \text{ yield,}^a \% \\
1 & \quad \text{K-PHI} & \quad 30 & \quad 461 \text{ nm} & \quad 9.3 \\
2 & \quad \text{K-PHI} & \quad 50 & \quad 461 \text{ nm} & \quad 74.5 \\
3 & \quad \text{K-PHI} & \quad 80 & \quad 461 \text{ nm} & \quad 22.1 \\
4 & \quad \text{K-PHI} & \quad 50 & \quad 372 \text{ nm} & \quad 50.2 \\
5 & \quad \text{TiO}_2 & \quad 50 & \quad 372 \text{ nm} & \quad 0.0 \\
6 & \quad \text{mpg-CN} & \quad 50 & \quad 461 \text{ nm} & \quad 2.4
\end{align*}
\]

\(^a\) determined by GC-MS with respect to naphthalene as an internal standard. \(^b\) reaction conditions (unless other specified): catalyst – 10 mg; elemental sulfur – 30 µmol; toluene – 0.3 mL; acetonitrile – 2.7 mL; temperature – 50°C. Each photocatalytic test was repeated 3 times, the variance was estimated to be not more than 10%; average yield of \text{Bn}_2\text{S}_2 is given.
Figure S2. a) FT-IR spectrum of reference dibenzyldisulfane and the one synthesized photocatalytically using K-PHI; (b) $^{13}$C NMR spectra of the reaction mixture recorded after solvent evaporation and reference dibenzyldisulfane; (c) chromatogram of the reaction mixture recorded after catalyst separation and internal standard (naphthalene) addition; (d) ECI mass spectra of the synthesized dibenzyldisulfane using K-PHI as a photocatalyst and a reference compound.
a) The time dependent $^1$H NMR spectra of the reaction mixture of 4-methylanisole photocatalytic oxidative thiolation. Reaction conditions were: 4-methylanisole 604 mg; $S_8$ 10.09 mg; K-PHI 10.02 mg; CD$_3$CN 6 mL; temperature +50 °C; light source LED module 461 nm, 0.0517±3·$10^{-5}$ W·cm$^{-2}$. b) Time dependent yield of 1,2-bis(4-methoxybenzyl) polysulfides. The amount of polysulfides was calculated from $^1$H NMR spectra using eq. 1.

Figure S4. PXRD patterns of silver (I) sulfide (black continuous line) obtained after gases evolved during the photocatalytic reaction were absorbed by silver nitrate in comparison with PXRD pattern obtained from Natl. Bur. Stand. (U. S.): 1960; Vol. 10, p 51. (red bars).
Figure S5. Mass-spectra of benzylthiols detected by GC-MS.

Figure S6. PXRD patterns (a) and FT-IR spectra (b) of K-PHI before and after photocatalytic tests.
Figure S7. Example $^{31}$P NMR spectrum of the reaction mixture upon Ph$_3$P addition.

Figure S8. a) Normalized emission spectrum of the LED module and normalized transmission of the glass. b) Time dependent irradiance of LED module used as a light source in the photocatalytic experiments studied in the present work.
Table S3. The ratio between products (1,2-bis(4-methoxybenzyl)disulfane, 1,3-bis(4-methoxybenzyl)trisulfane, 1,4-bis(4-methoxybenzyl)tetrasulfane and 1,5-bis(4-methoxybenzyl)pentasulfane) versus 1,5-bis(4-methoxybenzyl)pentasulfane over the time based on data from Figure S3.

| Time, h  | 1,5-bis(4-methoxybenzyl)pentasulfane | 1,4-bis(4-methoxybenzyl)tetrasulfane | 1,3-bis(4-methoxybenzyl)trisulfane | 1,2-bis(4-methoxybenzyl)disulfane |
|---------|----------------------------------|---------------------------------|---------------------------------|----------------------------------|
| 2.63    | 1.0                              | 1.5                             | 1.7                             | 0.0                              |
| 5.10    | 1.0                              | 1.7                             | 2.0                             | 0.0                              |
| 8.23    | 1.0                              | 1.8                             | 2.6                             | 0.0                              |
| 17.28   | 1.0                              | 1.8                             | 2.6                             | 0.5                              |
| 29.27   | 1.0                              | 1.6                             | 2.4                             | 0.6                              |
| 41.95   | 1.0                              | 1.7                             | 2.3                             | 0.9                              |
| 50.33   | 1.0                              | 1.7                             | 2.3                             | 1.0                              |
| 92.53   | 1.0                              | 1.5                             | 2.2                             | 1.5                              |
| 112.13  | 1.0                              | 1.5                             | 2.3                             | 1.9                              |
Details of the DFT Calculations

In order to estimate the most preferable position of the potassium cation in the central cavity, preliminary calculations were performed for the closed-shell monoanion containing one K atom at PBE0-D3/DZP level\(^*\) in the Firefly\(^2\) program package. Assuming that the K\(^+\) ion is located on the C2 axis, two isomers (denoted as “A” and “B”) were found (Figure S9). Their relative energies are almost equal, with A-isomer being more stable by \(\sim 2.5\) kJ/mol. Two isomers are separated by a \(\sim 170\) kJ/mol potential barrier. The charge on potassium atom in both isomers is close to +0.9 (Mulliken) and +0.8 (Lowdin) indicating the primarily ionic bonding between the metal and the PHI matrix.

Figure S9. Potential energy surface (PES) of the K\(^+\) ion translation along the line segment connecting 2 imide nitrogen atoms. The position of the “top” nitrogen and the energy of the A-isomer are set to zero. Both parts of the PES curve are obtained by a rigid scan from the optimized geometry of the corresponding isomer. K, N, C and H atoms are represented by green, blue, black and white spheres respectively.

The rest of calculations were performed for the neutral K-PHI system containing two potassium cations in the GAMESS (US) package. The basis set was extended by adding diffuse functions to nitrogen atoms. The geometry of K-PHI was optimized using several functionals with the gradient convergence threshold of \(4 \cdot 10^{-5}\) Hartree/Bohr.

\(^*\) DZP stands for Dunning–Hay double zeta valence basis with one \(p\)-type polarization function on hydrogen atoms and one \(d\)-type function on other atoms\(^4\).
NMR Spectra of Disulfanes
References

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