Supplementary Information

# **Electric fields drive bond homolysis**

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#### Supplementary Notes: Synthesis.

For the synthesis of 4-(methylthio)benzoic peroxyanhydride 1, 4-(methylthio)benzoic acid 2 was transformed to the corresponding acyl chloride, and the resulting crude was converted to the aroyl peroxyanhydride using sodium peroxide to yield 1 after crystallization. All steps were performed according to literature reports and characterized by <sup>1</sup>H-NMR and <sup>13</sup>C-NMR, showing product formation in accordance with reported values.<sup>1</sup>

### Supplementary Notes: HPLC.

Reference chromatograms of compounds were performed in triplicate by injecting 5  $\mu$ L of a 1mM solution of the compound in propylene carbonate. To ensure there was no solvent dependence on the retention time, we compared the chromatograms to 1 mM solutions in acetone, dichloromethane and tetradecane.

Quantification of the relative concentrations was obtained by first making a calibration curve (25  $\mu$ M to 2 mM). For each compound, the peak area integration was automated using predefined Agilent Tangent Skim mode with no further value changes. We found that manual integration afforded values within 5% of the automated integration mode. In order to increase accuracy and lower detection limits, chromatograms were recorded at/near the absorption maxima for each compound, i.e. 300 nm for 1, 280 nm for 2, and 250 nm for thioanisole.

## **Additional Figures**.



Figure S1. (a) Logarithm-binned 1D and (b) 2D conductance-displacement histograms of conductance traces measured with 2, 4,4'-bis(methylthio)biphenyl and 4,4'-(methylthio)benzoic acid phenyl ester, compiled from thousands of measured traces without data selection. All measurements were performed using  $\sim$ 1 mM in tetradecane at room temperature in the dark.



**Figure S2.** (a) Schematic representation of reference compounds 1, 2, 4,4'bis(methylthio)biphenyl and 4,4'-(methylthio)benzoic acid phenyl ester forming molecular junctions. (b) DFT-calculated transmission functions plotted against energy relative to Fermi energy.



Figure S3. (a) HR-MS calculated for 4-(methylthio)benzoic acid  $C_8H_8O_2S$ . (b) HR-MS measured for formation of 2 from 1 solution in PC under 2 mV bias for 1 hour.



**Figure S4.** (a) Logarithm-binned 1D and (b) 2D conductance-displacement histograms of 1 mM 1 compared to 1 mM reference 4,4'-bis(methylthio)biphenyl in tetradecane. (c) Logarithm-binned 1D and (d) 2D conductance-displacement histograms of 1 mM 1 with acetic acid after 2 h compared to 1 mM reference 2 in tetradecane. (e) Logarithm-binned 1D and (f) 2D conductance-displacement histograms of conductance traces of 1 mM 1 with acetic acid after 4 h compared to 1 mM reference 4,4'-bis(methylthio)biphenyl in tetradecane.



**Figure S5.** Logarithm-binned 1D and 2D conductance-displacement histograms of conductance traces of 1 mM 1 in the dark in (a)-(b) DMF, (c)-(d) DMSO and (e)-(f) NMF.



Figure S6. Study of the homolysis of 1 in PC:NMF (50:50) mixed solution in the STM-BJ, with rate of consumption of 1 in the standard push-pull measurement using coated tip, without electrolyte (red circle), in the hold measurement using plain tip, without electrolyte (red dot) and in the standard push-pull measurement using coated tip, with 100 mM TBAPF<sub>6</sub> electrolyte (orange dot).



Figure S7. DFT calculated molecular orbitals for 1 (a) LUMO, (b) HOMO, (c) HOMO-1.



Figure S8. UV-vis spectra of all compounds: 1, 2, 4,4'-(methylthio)biphenyl, 4,4'-(methylthio)benzoic acid phenyl ester and thioanisole.



**Figure S9.** HPLC chromatograms detected at 280 nm for **2**, 4,4'-bis(methylthio)biphenyl, 4,4'- (methylthio)benzoic acid phenyl ester and thioanisole.



Figure S10. <sup>1</sup>H NMR spectrum (500 MHz, 298 K) of 1 in CDCl<sub>3</sub>.



Figure S11. <sup>13</sup>C NMR spectrum (500 MHz, 298 K) of 1 in CDCl<sub>3</sub>.

# **References.**

(1) Hashimoto, J.-i.; Segawa, K.; Sakuragi, H. Effects of a sulfur substituent on the behavior and generation mode of aroyloxyl radicals in the photolysis of diaroyl peroxides, *Chem. Phys. Lett.* **1999**, *314*, 261.