Supporting information for:

Sulfur Radical Cations. Kinetic and Products Study of the Photo-Induced Fragmentation Reactions of (Phenylsulfanylalkyl)trimethylsilanes and Phenylsulfanylacetic Acids Radical Cations.

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Preparation and characterization of 2 and 4.

*Phenyl(phenylsulfanyl)acetic acid (**4**).*[S1] Butyllithium, (1.6 M in hexane, 6.4 mL, 10 mmol) was slowly added in a 50 mL three necked round bottom flask containing a stirred solution of benzyl phenyl sulfide (2 g, 10 mmol) in 30 mL of anhydrous THF at 0 °C under Ar atmosphere. The mixture was allowed to react for 1 h after which a slurry of diethyl ether and crunched solid CO_2 was slowly added. After the removal of CO_2 water was added and the aqueous layer was separated, filtered and acidified with diluted HCl. The obtained white solid was then filtrated, treated with dilute aqueous Na_2CO_3. Filtration and acidification of the aqueous solution gave 1.7 g (70 % yield) of a white solid. m. p. 101-103 °C (lit. 102-103 °C)[S1]

^{1}H-NMR (300 MHz, $CDCl_3$): δ: 7.2-7.5 (m, 10 H), 4.9 (s, 1 H).[S2]

*[Phenyl(phenylsulfanyl)methyl]trimethylsilane (**2**).*[S3] Butyllithium, (1.6 M in hexane, 6.4 mL, 10 mmol) was slowly added in a 50 mL three necked round bottom flask containing a stirred solution of benzyl phenyl sulfide (2 g, 10 mmol) in 30 mL of anhydrous THF at 0 °C under Ar atmosphere. The mixture was allowed to react for 1 h after which trimethylsilyl chloride (1.4 mL, 10 mmol) was slowly added. The mixture was stirred 30 min at room temperature, poured in a saturated NH_4Cl aqueous solution (40 mL) and extracted three times with diethyl ether. The recombined organic layers were dried over anhydrous Na_2SO_4 and evaporated. After silica gel chromatography purification (eluant: hexane/ethyl acetate 9:1) 2.6 g of a colorless oil were obtained (96 % yield).

^{1}H-NMR (300 MHz, $CDCl_3$): δ: 7.0-7.4 (m, 10 H), 3.8 (s, 1 H), 0.1 (s, 9 H).[S3]

EI-MS (70 V): 73(100 %) [$^+SiMe_3$], 272 (50 %) [M^+], 199 (23 %), 195 (27 %), 167 (27 %), 135 (28 %), 122 (22 %).

(S1) Lehto, S.; Shirley, D. A. *J. Org. Chem.* **1957**, *22*, 989.

(S2) Ogura, K.; Itoh, H.; Morita, T.; Sanada, K.;Iida, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 1216.

(S2) Ager, D. J. *J. Chem. Soc., Perkin Trans.* I **1986**, 195.

Table S1. Absorption maxima and transients produced by LFP of NMQ^+/toluene/sulfide in N_2-saturated CH_3CN.

compd	R	X	λ_{max} (nm)	transient
1	H	$Si(CH_3)_3$	330-340	$1^{+\bullet}$; $C_6H_5SCH_2^\bullet$
			400	$NMQ^\bullet$
			540-560	$1^{+\bullet}$, $NMQ^\bullet$
			>700	$1_2^{+\bullet}$
			330,550 [a]	$1^{+\bullet}$
2	C_6H_5	$Si(CH_3)_3$	330-360	$2^{+\bullet}$; $C_6H_5SC(C_6H_5)H^\bullet$
			400	$NMQ^\bullet$
			540	$2^{+\bullet}$, $NMQ^\bullet$
			>700	$2_2^{+\bullet}$
			<350, 530 [a]	$2^{+\bullet}$
3	H	COOH	325-340	$3^{+\bullet}$; $C_6H_5SCH_2^\bullet$
			400	$NMQ^\bullet$
			540	$3^{+\bullet}$, $NMQ^\bullet$
			> 700	$3_2^{+\bullet}$
			325, 530 [a]	$3^{+\bullet}$
4	C_6H_5	COOH	330-360	$4^{+\bullet}$; $C_6H_5SC(C_6H_5)H^\bullet$
			400	$NMQ^\bullet$
			520	$4^{+\bullet}$, $NMQ^\bullet$
			>700	$4_2^{+\bullet}$
			530 [a]	$4^{+\bullet}$

[a] In O_2-saturated CH_3CN.

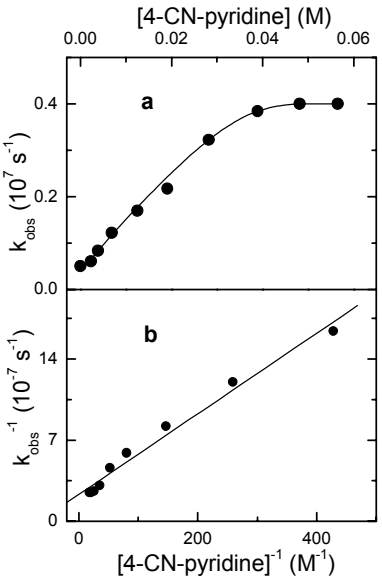

Figure S1. Observed rate constant (k_{obs}) *vs* [4-CN-pyridine] (a) and $1/k_{obs}$ *vs* 1/[4-CN-pyridine] (b) for the decay of $\mathbf{3}^{+\bullet}$ in CH_3CN.

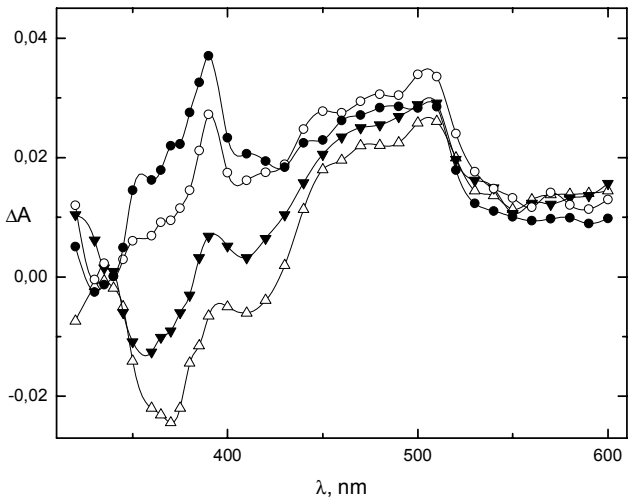

Figure S2. Time-resolved absorption spectra of the 1,4-dicyanonaphthalene (1.0×10^{-4} M)/ $PhSCH(Ph)CO_2NMe_4$ (0.01 M) system in N_2-saturated MeCN recorded 0.14 (△), 0.18 (▲), 0.33 (o) and 3.2 (•) μs after the laser pulse. λ_{ecc} =355 nm.