Supplementary Information

Origins of the Photoinitiation Capacity of Aromatic Thiols As Photoinitiators: A Computational Study

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1- Assesing the Level of Theory

Table S1. Calculated absorption wavelength in DMSO by using the ground state geometry sampling based on the Wigner distribution, compared with the experimental UV/Vis data in DMSO.

	λ_{abs} Values of Molecules					
TDA-TDDFT Method	**RSH**		**PhSH**		***p*-CF_3PhSH**	
τHCTHhyb/def2-TZVP	200nm	6.19eV	265nm	4.67eV	256nm	4.84eV
ωB97XD/def2-TZVP	210nm	5.90eV	243nm	5.10eV	260nm	4.76eV
Experimental Data[1*]	260nm	4.76eV	278nm	4.45eV	272nm	4.55eV

1 Love, D. M.; Fairbanks, B. D.; Bowman, C. N. Evaluation of Aromatic Thiols as Photoinitiators. Macromolecules 2020, 53, 13, 5237–5247

*Experimental data obtained in DMSO solvent.

2- Spin-Orbit Coupling Constants

Table S2. Spin Orbit Coupling Constants (cm^{-1}) of S_0 minimum geometries by ωB97X-D3/def2-TZVP in DMSO (ORCA Software).

Molecule	**S1-T1**	**S1-T2**	**S1-T3**	**S1-T4**	**S2-T1**	**S2-T2**	**S2-T3**	**S2-T4**
Hexanethiol	2.10	51.22	151.65	8.33	45.43	1.39	19.55	5.71
Thiophenol	5.25	116.42	20.50	3.04	3.67	1.83	0.50	2.57
paratrifluorothiophenol	1.01	0.10	0.37	0.02	17.63	2.06	6.74	0.50

Molecule	**S3-T1**	**S3-T2**	**S3-T3**	**S3-T4**
Hexanethiol	16.54	8.73	6.83	0.57
Thiophenol	20.90	19.31	5.42	6.28
paratrifluorothiophenol	0.28	0.63	0.15	0.83

Table S3. Spin Orbit Coupling Constants (cm^{-1}) of S_1 minimum geometries by ωB97X-D3/def2-TZVP in DMSO (ORCA Software).

Molecule	**S1-T1**	**S1-T2**	**S1-T3**	**S1-T4**	**S2-T1**	**S2-T2**	**S2-T3**	**S2-T4**
Hexanethiol	1.98	128.62	144.02	69.27	142.77	91.44	26.78	6.90
Thiophenol	5.25	116.42	20.50	3.04	3.67	1.83	0.50	2.57
paratrifluorothiophenol	0.98	0.27	0.30	0.01	0.18	0.71	0.13	0.76

Molecule	**S3-T1**	**S3-T2**	**S3-T3**	**S3-T4**
Hexanethiol	82.48	36.77	65.94	5.57

Thiophenol	20.90	19.31	5.42	6.28
paratrifluorothiophenol	18.34	4.37	8.07	0.25

3- Natural Transition Orbitals

Table S4. Natural transition orbitals of RSH molecule at critical distances (ωB97XD/def2-TZVP level of theory)

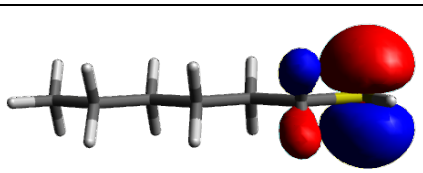
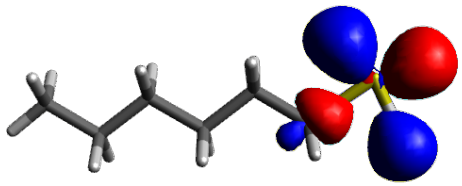
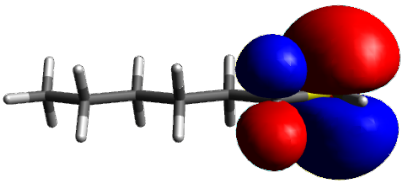
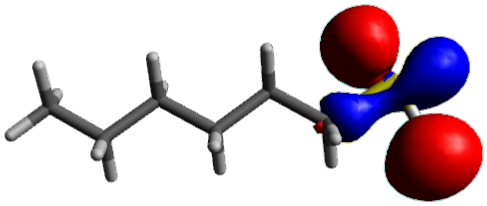
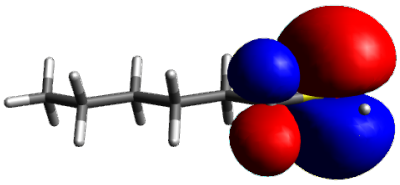
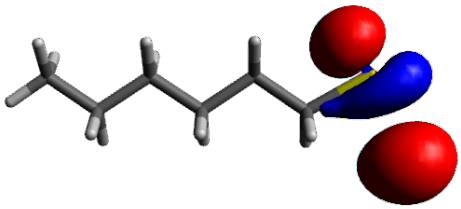
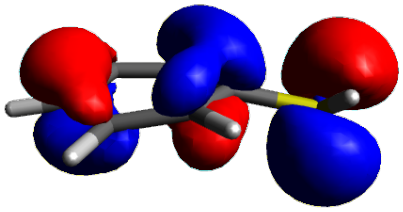
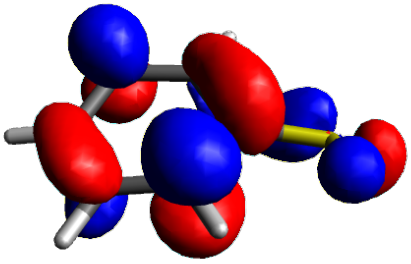
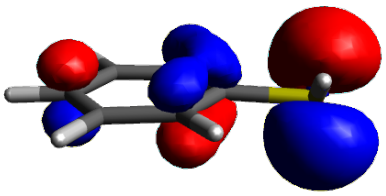
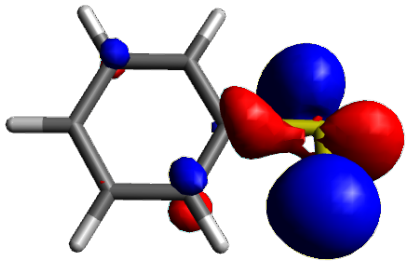
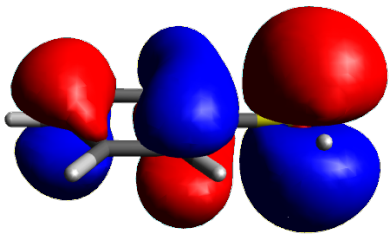
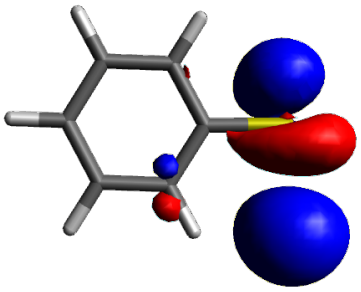
	oNTO	vNTO
Distance= 1.30 S_0 to S_1 f= 0.0000 5.1913 eV ϕ_s(Mul.)= 0.0259 ϕs(Löw.)= 0.0282		
Distance= 1.50 S_0 to S_1 f= 0.0001 4.4854 eV ϕ_s(Mul.)= 0.0265 ϕ_s(Löw.)= 0.0275		
Distance= 1.90 S_0 to S_1 f= 0.0000 2.7023 eV ϕ_s(Mul.)= 0.0300 ϕ_s(Löw.)= 0.0283		

Table S5. Natural transition orbitals of PhSH molecule at critical distances (ωB97XD/def2-TZVP level of theory)

	oNTO	vNTO
Distance= 1.31 S_0 to S_1 f= 0.0700 4.5791 eV ϕ_s(Mul.)= 0.5442 ϕs(Löw.)= 0.5708		

Distance= 1.51 S_0 to S_1 f= 0.0222 4.2780 eV ϕ_s(Mul.)= 0.3502 ϕ_s(Löw.)= 0.3980		
Distance= 1.91 S_0 to S_1 f= 0.0022 2.5944 eV ϕ_s(Mul.)= 0.1580 ϕ_s(Löw.)= 0.1743		

4- Potential Energy Surfaces of Aromatic Thiols

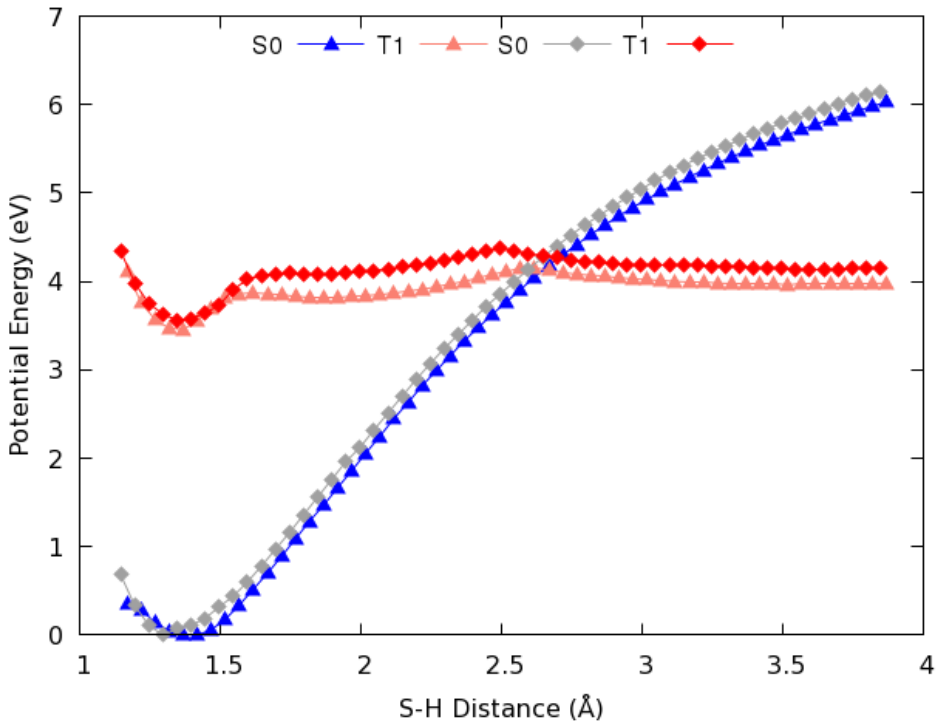


Figure S1. Potential energy surface of thiophenol (S_0: Blue, T_1: Light Red) and parafluorothiophenol (S_0: Gray, T_1: Dark Red) relaxed on the T1 potential at ωB97XD/def2-TZVP level of theory,in DMSO (SMD).

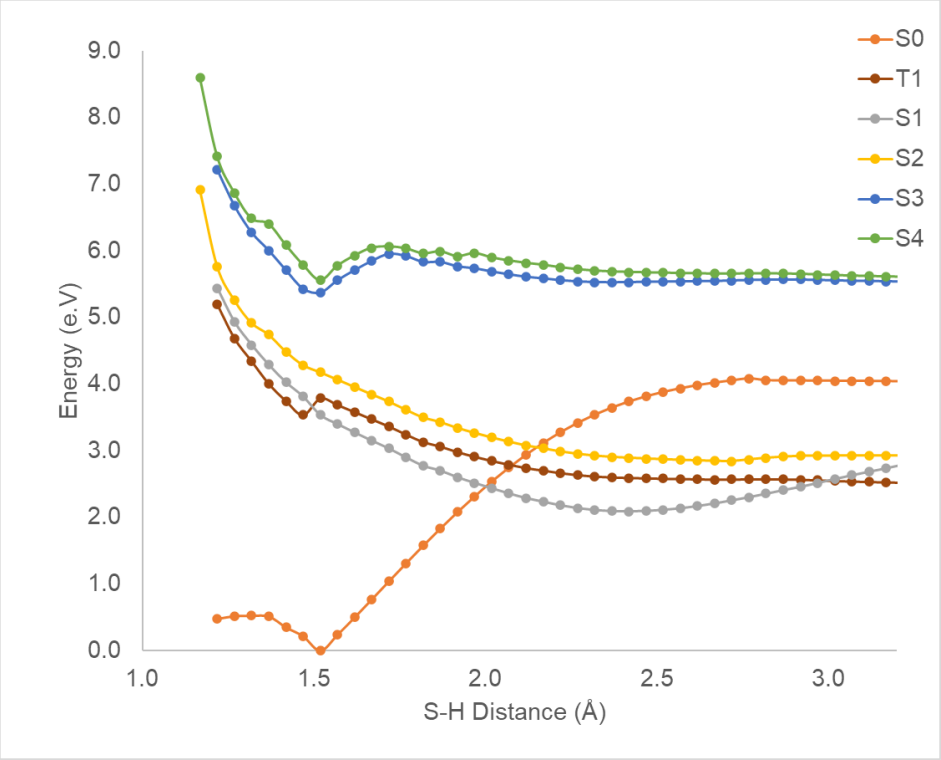


Figure S2. SF-TDDFT potential energy surface, relaxed on the S1 surface, of thiophenol relaxed scan at ωB97X/TZ2P level of theory.

5- Coordinates

Optimized geometry of RSH

C	4.304951	-0.425636	-0.000001
H	4.325107	-1.070612	0.882706
H	5.222046	0.167759	-0.000004
H	4.325106	-1.070619	-0.882703
C	3.068250	0.461333	-0.000004
H	3.088545	1.117096	-0.876615
H	3.088549	1.117107	0.876598
C	1.767986	-0.332749	0.000004
H	1.746571	-0.989132	0.877369
H	1.746568	-0.989146	-0.877351
C	0.524938	0.547397	-0.000001
H	0.544369	1.202304	-0.877860

H	0.544371	1.202316	0.877850
C	-0.771240	-0.254843	0.000006
H	-0.795519	-0.906350	0.879344
H	-0.795523	-0.906358	-0.879326
C	-1.994974	0.647283	0.000004
H	-1.997759	1.283518	-0.885212
H	-1.997758	1.283522	0.885217
S	-3.513784	-0.363052	0.000008
H	-4.394283	0.648041	0.000007

Optimized geometry of PhSH

C	-0.929629	0.859289	-0.000823
C	-0.232449	-0.340814	0.003320
C	1.153740	-0.348444	0.003287
C	1.856431	0.854161	-0.000925
C	1.159967	2.059418	-0.005084
C	-0.226917	2.055812	-0.005012
S	3.624302	0.779421	-0.000739
H	-0.768628	-1.282011	0.006616
H	1.686540	-1.292369	0.006544
H	1.695671	3.001133	-0.008381
H	-0.759069	2.999371	-0.008270
H	-2.012407	0.861875	-0.000785
H	3.845894	2.102234	-0.005367

Optimized geometry of *p*-CF_3PhSH

C	-0.224657	-0.354678	0.100752
C	1.158119	-0.349434	0.106011
C	1.858152	0.852190	0.012080
C	1.146524	2.048579	-0.087145
C	-0.233365	2.036943	-0.091596

C	-0.928080	0.836351	0.002164
H	-0.760057	-1.291197	0.174034
H	1.699248	-1.283560	0.183671
H	1.676343	2.989506	-0.160786
H	-0.778943	2.969207	-0.168777
S	3.612498	0.788562	0.024168
H	3.814005	2.108271	-0.079763
C	-2.422627	0.862794	-0.005681
F	-2.914848	1.593332	1.012676
F	-2.906838	1.418934	-1.132095
F	-2.958759	-0.360164	0.091577