Supporting Information

Photodissociation Dynamics of *ortho*-Substituted Thiophenols at 243 nm

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Table S1. Adiabatic radical energy gaps for thiophenol and *ortho*-substituted thiophenols. The optimization was performed using the B3LYP/aug-cc-pVTZ and CASPT2(9,8)/cc-pVTZ methods. The values in parentheses are the vertical excitation energies calculated by the TD-B3LYP/aug-cc-pVTZ. The experimentally reported values are also given.

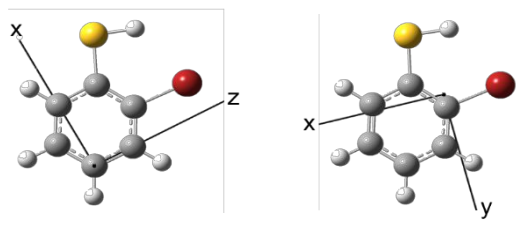| Molecules	$\Delta E(\tilde{A}\text{-}\tilde{X})$ (cm^{-1})		
	Calc.		Exp.
	B3LYP	CASPT2	
Thiophenol	3099 (3492[a])	2976[a]	3000[c]
2-FTP	2884 (3391)	2752[b]	2800[b]
2-CTP	2159	2148[b]	2100[b]
2-BTP	1850	1967	
2-MTP	2994 (3628)	2760	

[a] from Ref [1]. [b] from Ref [2]. [c] from Ref [3].

Table S2. Relative energies including zero-point energy correction for 2-BTP and 2-MTP calculated by the B3LYP and MP2 methods. The basis sets for 2-BTP and 2-MTP are aug-cc-pVTZ and 6-311++G(3df,3pd), respectively.

	Relative energies (cm^{-1})			
	2-BTP		2-MTP	
	Cis	Trans	Cis	Trans
B3LYP	0	97	0	251
MP2	0	186	0	312

Table S3. Calculated vertical excitation energies, oscillator strengths, and transition dipole moments of the singlet states of 2-BTP. The Cartesian axes are given for the EOM-CCSD (left), and HCTH (right) methods.

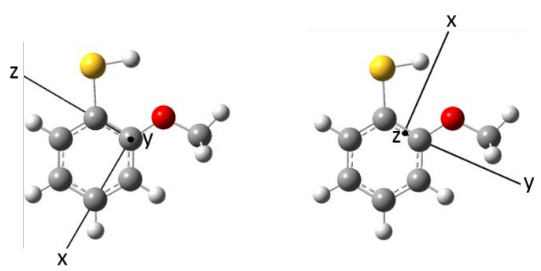| State	Excitation energy (eV)	Oscillator strength	Transition dipole moment (a.u.)		
			μ_x	μ_y	μ_z
EOM-CCSD/aug-cc-pVTZ					
$1^1\pi\pi^*$	4.76	0.00782	-0.0658	0.0000	0.2508
$1^1\pi\sigma^{*a}$	5.29	0.00006	0.0000	0.0207	0.0000
$2^1\pi\pi^*$	5.63	0.18072	1.1194	0.0000	0.2429
$2^1\pi\sigma^{*a}$	5.77	0.02273	0.0000	0.4009	0.0000
TD-HCTH/6-311++G(3df,3pd)					
$1^1\pi\sigma^{*b}$	4.22	0.0000	0.0000	0.0000	0.0048
$1^1\pi\pi^*$	4.23	0.0165	0.3971	0.0347	0.0000
$2^1\pi\pi^*$	4.78	0.1565	-0.0001	-1.1563	0.0000
$2^1\pi\sigma^{*a}$	4.97	0.0030	0.0000	0.0000	0.1557
$3^1\pi\sigma^{*a}$	5.02	0.0119	0.0000	0.0000	0.3115

[a] The transition character is σ^*_{SH}, greater than σ^*_{CBr}. [b] The transition character is σ^*_{CBr}, greater than σ^*_{SH}.

Table S4. Calculated vertical excitation energies, oscillator strengths, and transition dipole moments. The Cartesian axes are given for the EOM-CCSD and CASPT2 (left), and HCTH (right) methods.

State	Excitation energy (eV)	Oscillator strength	Transition dipole moment (D)		
			μ_x	μ_y	μ_z

State	Excitation energy (eV)	Oscillator strength	μ_x	μ_y	μ_z
EOM-CCSD/aug-cc-pVTZ					
$1^1\pi\pi^*$	4.78	0.0387	-0.3533	0.0000	1.4186
$1^1\pi\sigma^{*a}$	5.35	0.0091	0.0000	0.6682	0.0000
$2^1\pi\sigma^{*a}$	5.54	0.0056	0.0000	0.5173	0.0000
$2^1\pi\pi^*$	5.64	0.1815	-1.5401	0.0000	2.4745
CASPT2//SA4-CASSCF(12,11)/6-311++G(3df,3pd)					
$1^1\pi\pi^*$	4.30	0.0099	0.3425	0.0000	-0.6993
$1^1\pi\sigma^{*a}$	5.15	0.0001	0.0000	-0.0527	0.0000
$2^1\pi\pi^*$	5.16	0.2552	-0.6674	0.0000	3.5480
TD-HCTH/6-311++G(3df,3pd)					
$1^1\pi\pi^*$	4.34	0.0588	1.8581	-0.3477	0.0000
$1^1\pi\sigma^{*a}$	4.43	0.0012	0.0000	0.0000	0.2664
$2^1\pi\sigma^{*a}$	4.74	0.0045	0.0000	0.0000	-0.4987
$2^1\pi\pi^*$	4.80	0.1501	-2.0610	1.9987	0.0000

[a] The transition character has both $\sigma_{O\text{-}CH_3}^*$ and $\sigma_{S\text{-}H}^*$ characters.
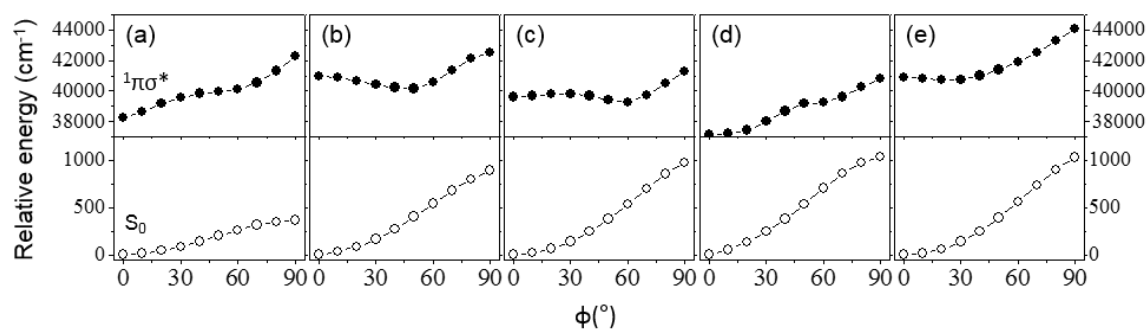
Figure S1. Torsion potential energy curves (PECs) along ϕ for S_0 and $^1\pi\sigma^*$ states of (a) thiophenol, (b) 2-FTP, (c) 2-CTP, (d) 2-BTP, and (e) 2-MTP calculated by the TD-B3LYP method (vertical excitation energies). The basis set is 6-311++G(3df,3pd), except for 2-BTP (aug-cc-pVTZ). The S_0 geometries were optimized by fixing ϕ but relaxing other geometry parameters. The state having the dominant character of $^1\pi\sigma^*_{S-H}$ for 2-BTP and 2-MTP is the S_4 and S_3 state, respectively, while that for other molecules is the S_2 state.
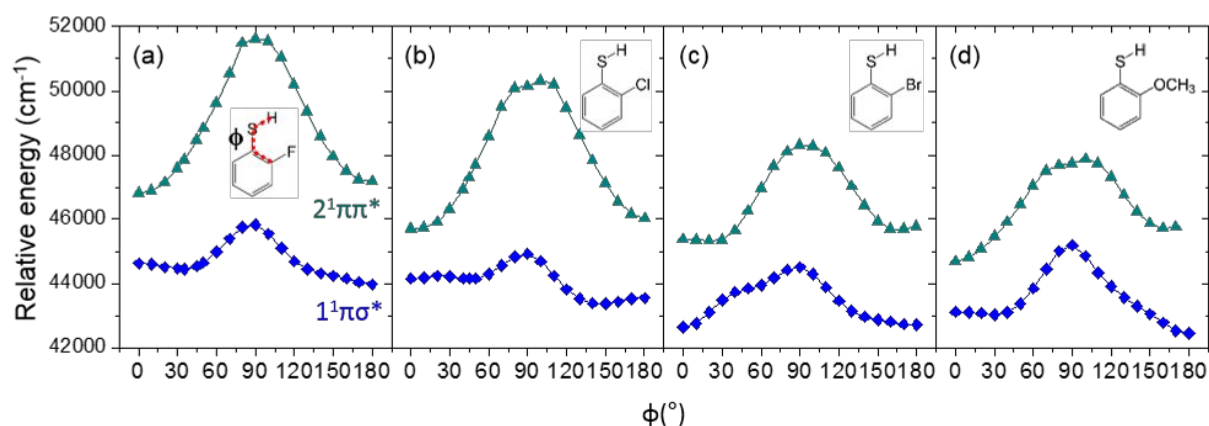

Figure S2. The enlarged torsion potentials of Figure 3 calculated at the EOM-CCSD/aug-cc-pVTZ level of theory. The $1^1\pi\sigma^*$ (S_2) and $2^1\pi\pi^*$ (S_3) states of (a) 2-FTP, (b) 2-CTP, (c) 2-BTP, and (d) 2-MTP are plotted as blue diamond and dark cyan triangle symbols, respectively. The S_3 state for 2-MTP is the $2^1\pi\sigma^*$ state, exceptively.
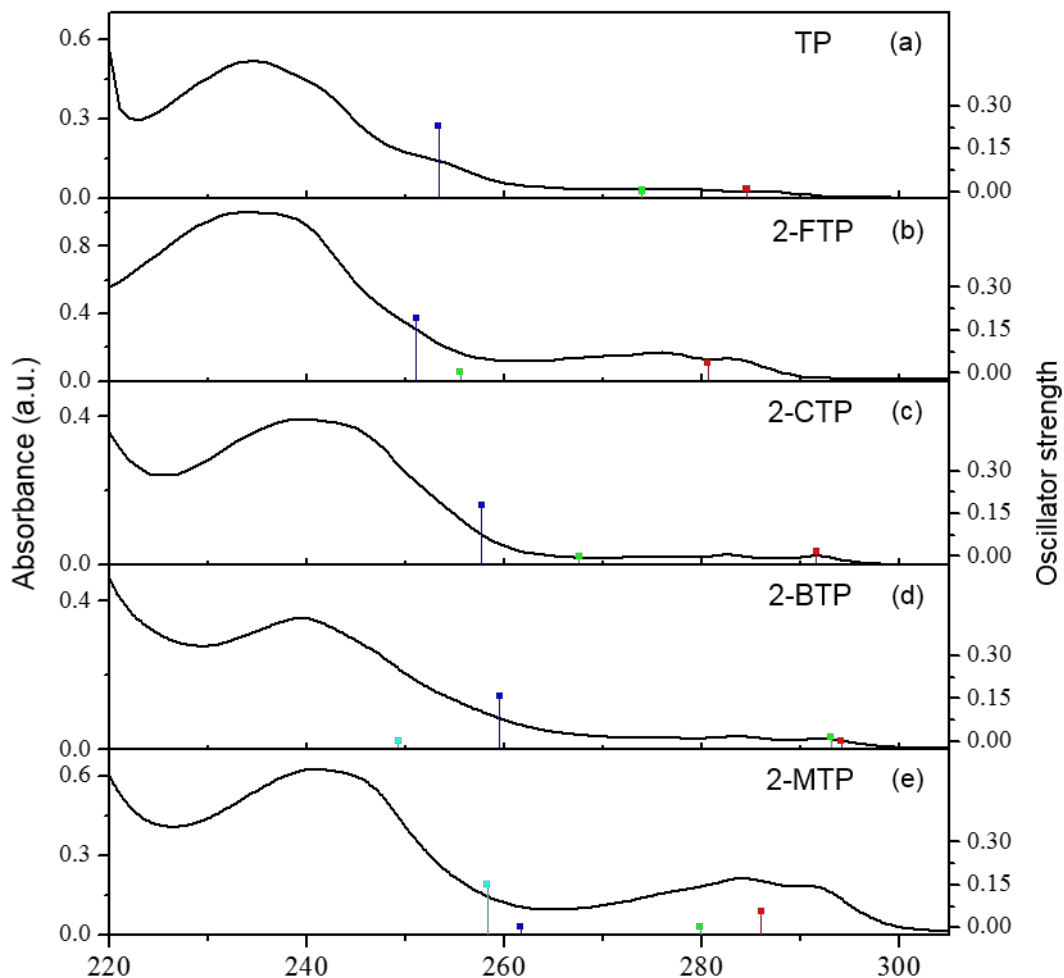
Figure S3. UV absorption spectra of (a) thiophenol, (b) 2-FTP, (c) 2-CTP, (d) 2-BTP, and (e) 2-MTP in hexane at room temperature. The vertical excitation energies for the singlet states calculated by the TD-HCTH/6-311++G(3df,3pd) method are overlaid as sticks.

Details in the fitting procedure

The $\tilde{X}$ and $\tilde{A}$ states of the fragment radical originating from the direct $1^1\pi\sigma^*$ state were fitted with two Gumbel functions:

$$P_{signal}(E) = a_1\exp\left(-exp\left(\frac{E-b_1}{c_1}\right)+\left(\frac{E-b_1}{c_1}\right)+1\right) + a_2\exp\left(-exp\left(\frac{E-b_2}{c_2}\right)+\left(\frac{E-b_2}{c_2}\right)+1\right)$$

(Equation S1)

where a_1, b_1, and c_1 (a_2, b_2, and c_2) are the amplitude, maximum position, and width of the Gumbel functions, respectively. The position of the Gumbel distributions was determined as the middle of the movable range. It was assumed that the width of the $\tilde{A}$ state peak, resulting from the adiabatic pathway, is larger than that of the $\tilde{X}$ state peak from the nonadiabatic transition. The component at the center of the image (the lowest translational energy, green dashed line) which is minor for 2-BTP and 2-MTP was fitted with a Boltzmann-like function:

$$P_{bg\_center}(\text{E}) = A_1 \left(\frac{E}{\pi C_1^3}\right)^{\frac{1}{2}} e^{\left(\frac{-E}{C_1}\right)} \qquad \text{(Equation S2)}$$

where A_1 is the amplitude and C_1 is the width. Only the amplitude was adjusted across the series of *ortho*-substituted thiophenols. The component at the high translational energy (olive dashed line) for 2-CTP and 2-BTP was fitted with a Gaussian function:

$$P_{bg\_high}(\text{E}) = \frac{A_2}{C_2\sqrt{\pi/2}} e^{\left(-\frac{2(E-B_2)^2}{C_2^2}\right)} \qquad \text{(Equation S3)}$$

where A_2, B_2, and C_2 are the amplitude, center, and width of the Gaussian distribution, respectively. After subtracting the backgrounds (green and olive dashed lines) and fitting with the two Gumbel functions (red and blue lines) from the total translational energy distributions, the leftover originated from the $1^1\pi\pi^*$ state (grey dashed line) was expressed as a Gaussian function (Equation S3). The error range of the $\tilde{X}/\tilde{A}$ branching ratio was obtained by the fitting procedure.

References

1.   Cheng, C.-W.; Lee, Y.-P.; Witek, H. A. Theoretical Investigation of Molecular Properties of the First Excited State of the Thiophenoxyl Radical. *J. Phys. Chem. A* **2008,** *112*, 11998-12006.

2.   Han, S.; You, H. S.; Kim, S.-Y.; Kim, S. K. Dynamic Role of the Intramolecular Hydrogen Bonding in Nonadiabatic Chemistry Revealed in the UV Photodissociation Reactions of 2-Fluorothiophenol and 2-Chlorothiophenol. *J. Phys. Chem. A* **2014,** *118*, 6940-6949.

3.   Kim, J. B.; Yacovitch, T. I.; Hock, C.; Neumark, D. M. Slow Photoelectron Velocity-Map Imaging Spectroscopy of the Phenoxide and Thiophenoxide Anions. *Phys. Chem. Chem. Phys.* **2011,** *13*, 17378-17383.