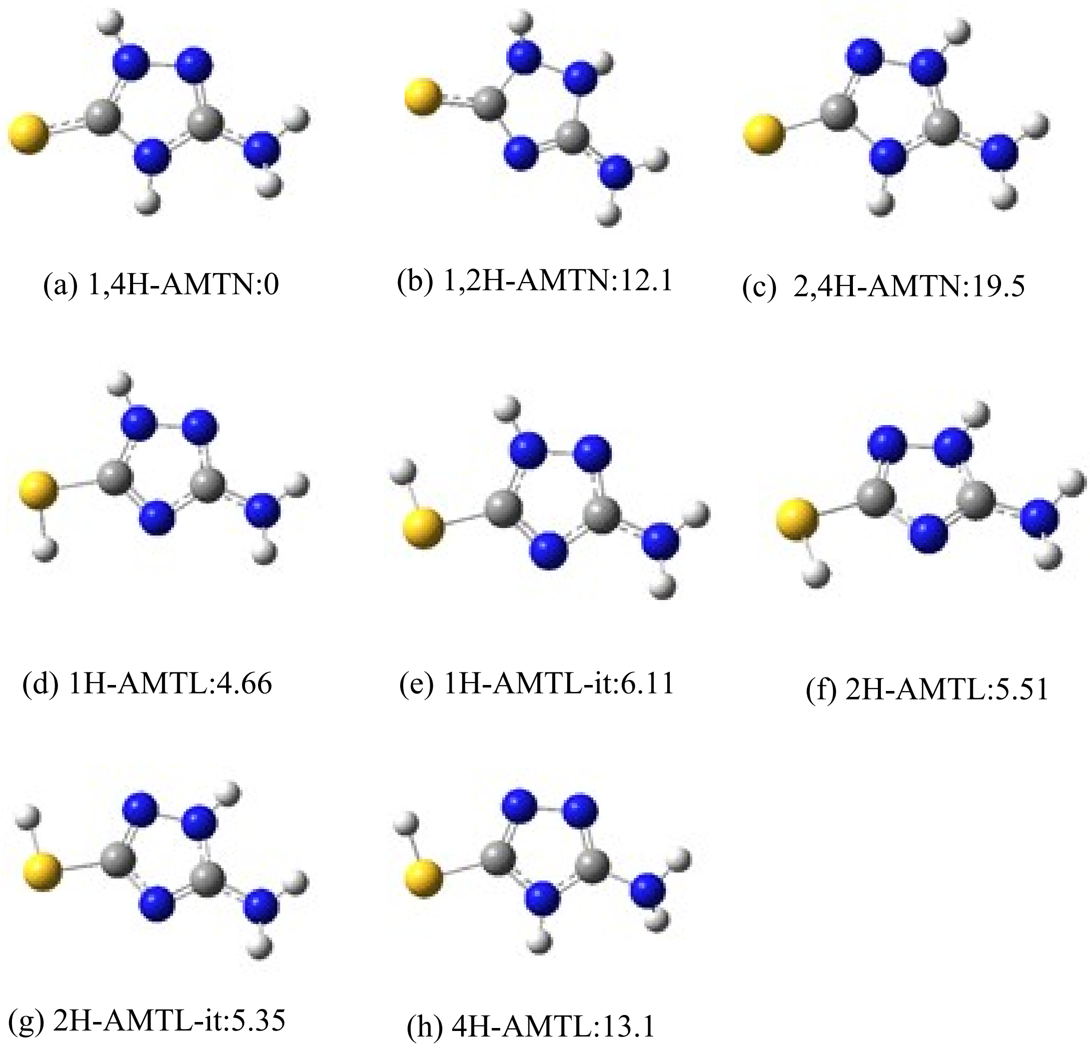


Figure S1. Optimized tautomers of AMT and the energies (in kcal/mol) relative to structure (a) at B3LYP-D3(BJ)/6-311++G(d, p) level.

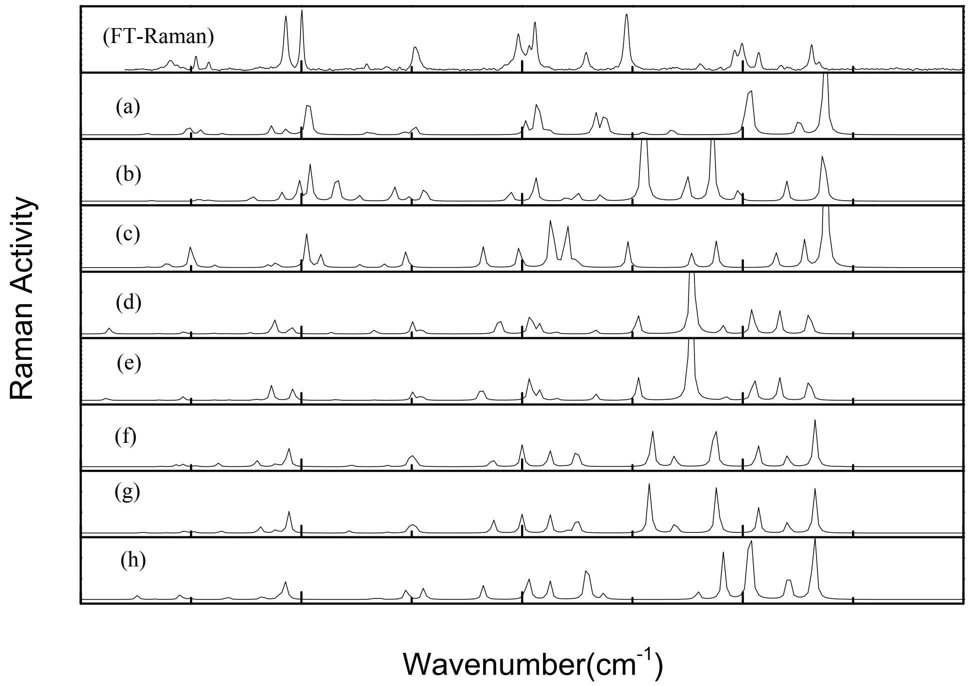


Figure S2. FT-Raman and calculated Raman activities (a), (b), (c), (d),(e), (f), (g) and (h) for the optimized isomers in Figure S1 at B3LYP-D3(BJ)/6-311++G(d, p) level.

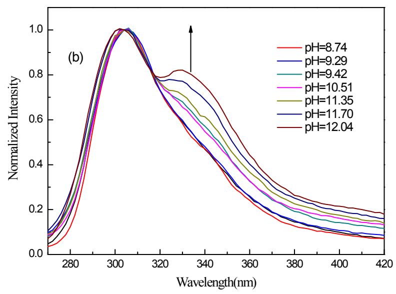


Figure S3. (a) UV absorption and (b) emission (λ_{ex}=230 nm) spectra for AMT (4.78×10^{-5} mol/L) in CH_3OH with different volume of $[(Bu)_4\ N]^+OH^-$ (**1.53** mol/L).

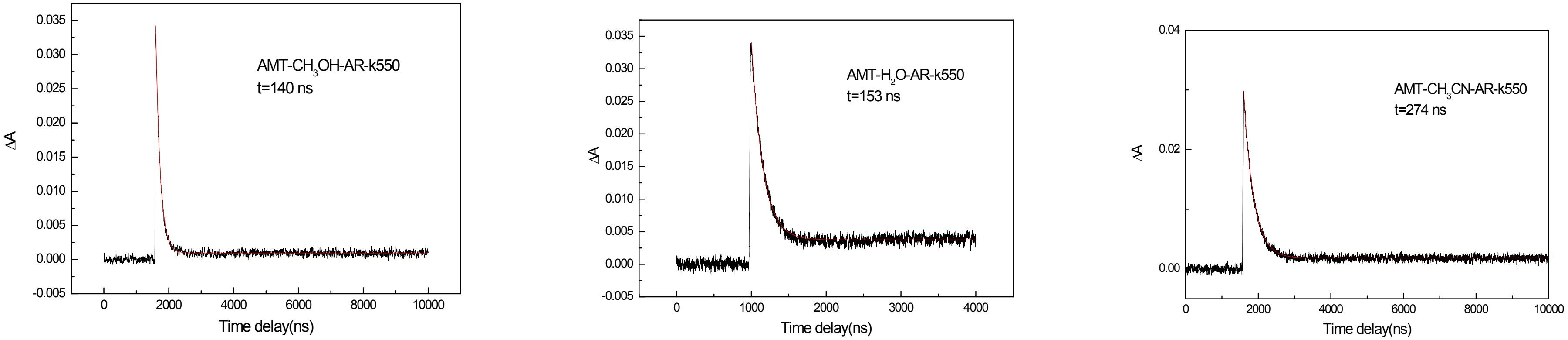


Figure S4. Kinetics of ^{3}AMT measured at 550 nm in CH_3CN, CH_3OH and H_2O and fitted with a single exponential function, the time constants are listed close to the curves.

Notes: Based on the experimental results, as shown in Figure S4, the solvents induce transient absorption spectra not return to the baseline due to its polarity, especially the hydrogen bonding interaction effect on the excited state structure.

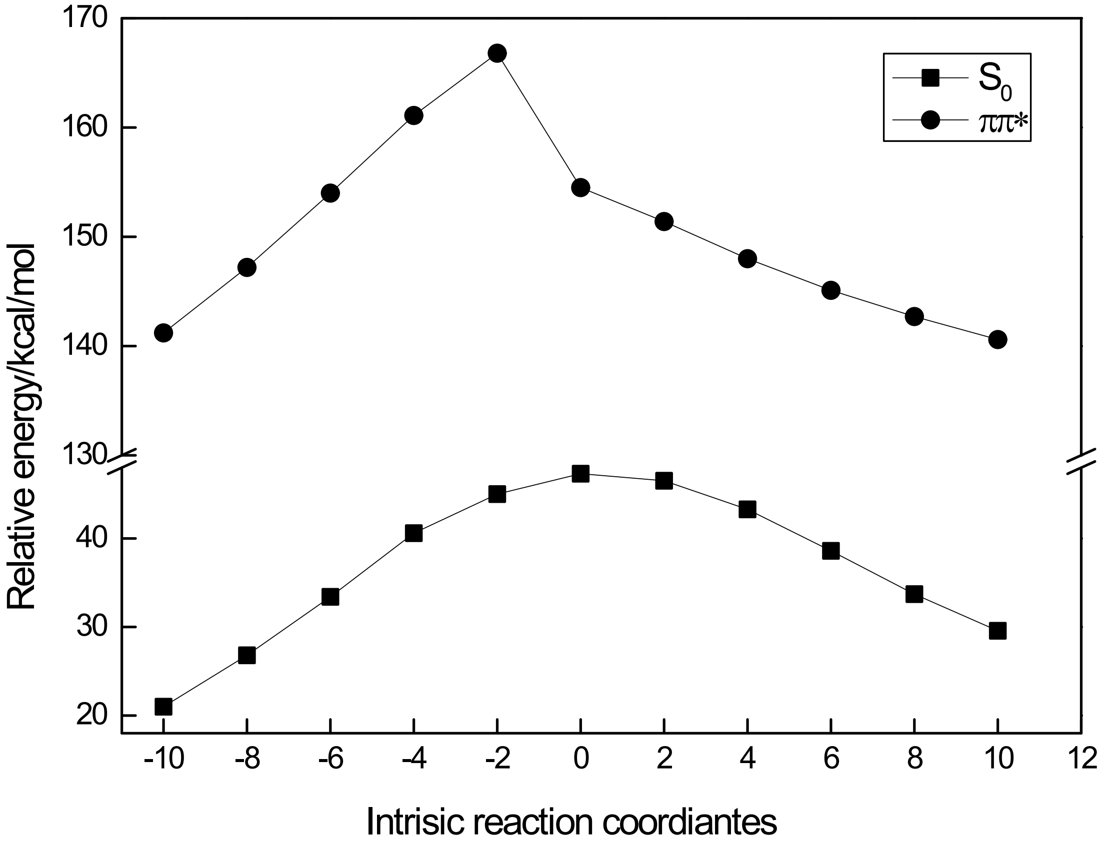


Figure S5. Calculated energies (kcal/mol) of S_0 (circle) and $\pi\pi^*$ (rectangular) states relative to ground state thione AMT on the selected IRC points at B3LYP(TD)-D3(BJ)/6-31G* level.

Table S1. Experimental and calculated vibrational frequencies at B3LYP-D3(BJ)/6-311++G(d, p) level and assignments of thione AMT in gas phase.

Modes	Calc	Exp		Desciption（PED%）
	(Raman activity /IR activity)	FT-raman	FT-IR	
ν_1	3684(88.1/104)			N_1H_6(99)strech
ν_2	3662(57.3/65.9)			N_4H_{11}(99) strech
ν_3	3644(73.1/37.8)			N_7H_8(58)+N_7H_9(42) strech
ν_4	3549(242/30.9)			N_7H_8(42)+N_7H_9(58) strech
ν_5	1686(53.0/333)	1655	1647	N_2C_3(35) strech +N_7C_3(23) strech +$H_9N_7H_8$(19)bend
ν_6	1628(9.39/31.8)	1585	1589	N_2C_3(13)strech+$H_9N_7H_8$(59)bend
ν_7	1517(26.2/505)	1498	1546	N_1C_5(33)strech+N_4C_3(14)strech+$H_6N_1N_2$(18)bend+$H_{11}N_4C_3$(13) bend
ν_8	1508(12.9/8.97)		1482	N_4C_3(19)strech+N_7C_3(15)strech+$H_6N_1N_2$(19)bend+$N_1N_2C_3$(14)bend
ν_9	1340(3.24/21.4)	1402	1391	$H_6N_1N_2$(32)bend +$H_{11}N_4C_3$(30) bend +$C_5N_1N_2$(12) bend
ν_{10}	1275(1.46/2.19)	1344		N_1C_5(32)strech + $C_5N_1N_2$(29) bend
ν_{11}	1188(12.2/49.4)	1236	1239	N_7C_3(11)strech+N_1N_2(12)strech+$H_{11}N_4C_3$(19)bend+$H_8N_7C_3$(10) bend
ν_{12}	1166(9.87/109)	1144	1143	N_1N_2(21)strech+$S_{10}C_5$(18)strech+$H_{11}N_4C_3$(13)bend+$H_8N_7C_3$(25) bend
ν_{13}	1060(2.37/45.1)		1068	N_4C_3(17)strech + N_1N_2(36)strech + $H_8N_7C_3$(23) bend
ν_{14}	1035(19.2/11.8)	1028		N_2C_3(18)strech+N_4C_3(15)strech+N_1N_2(10)stretch+$N_4C_3N_2$(42)bend
ν_{15}	1008(4.83/8.83)	991		N_4C_3(15)strech +$N_1N_2C_3$(42)bend
ν_{16}	757(4.38/8.96)	758	755	N_7C_3(27)strech +$N_4C_3N_2$(19)bend +$N_1N_2C_3$(42)bend
ν_{17}	732(1.40/83.0)	723	706	$H_9N_7C_3N_4$(11)tors+$N_4C_3N_2N_1$(25)tors+$N_7N_4N_2C_3$(34)out
ν_{18}	660(0.795/154)	692		$H_8N_7C_3N_4$(24)tors+$H_9N_7C_3N_4$(11)tors+$C_5N_1N_2C_3$(12)tors+$S_{10}N_1N_4C_5$(29)out

ν_{19}	649(0.804/47.7)	646	639	$H_6N_1N_2C_3$(11)tors+$H_8N_7C_3N_4$(22)tors+$C_5N_1N_2C_3$(24)tors+ $S_{10}N_1N_4C_5$(16)out
ν_{20}	518(9.56/94.7)	501	513	$S_{10}C_5$(21)strech+$C_5N_1N_2$(10)bend+$H_6N_1N_2C_3$(13)tors+$H_{11}N_4C_3N_7$(31)tors
ν_{21}	513(7.47/72.1)		497	$S_{10}C_5$(22)stretch+$C_5N_1N_2$(11)bend+$H_6N_1N_2C_3$(11)tors+$H_{11}N_4C_3N_7$(25)tors
ν_{22}	467(2.15/28.2)	465	467	$N_7C_3N_2$(12)bend+$C_5N_1N_2$(45)bend+$H_{11}N_4C_3N_7$(16)tors
ν_{23}	432(2.85/4.25)	399		$N_7C_3N_2$(37)bend+$S_{10}C_5N_4$(18)bend+$H_{11}N_4C_3N_7$(16)tors
ν_{24}	322(0.471/5.10)			$N_4C_3N_2N_1$(36)tors+$N_7N_4N_2C_3$(36)out
ν_{25}	271(1.68/38.6)	289		$N_7C_3N_2$(12)bend+$S_{10}C_5N_4$(20)bend+$H_8N_7C_3N_4$(16)tors+$H_9N_7C_3N_4$(41)tors
ν_{26}	244(3.78/10.6)	260		$N_7C_3N_2$(14)bend+$S_{10}C_5N_4$(44)bend+$H_8N_7C_3N_4$(14)tors+$H_9N_7C_3N_4$(13)tors
ν_{27}	149(0.576/2.28)			$C_5N_1N_2C_3$(43)tors+ $N_4C_3N_2N_1$(17)tors + $S_{10}N_1N_4C_5$(26)out

Table S2. 266 nm resonance Raman spectra and calculated vibrational frequencies at B3LYP-D3(BJ)/6-311++G(d, p) level using H_2O PCM model and assignments of thione AMT in solvents

Modes	Calc.(Raman activity /IR activity)[a]	Exp.		Desciption（PED%）
		CH_3OH	H_2O	
ν_5	1669(113/681)	1646	1656	N_2C_3(25)stretch+N_7C_3(26)stretch+$H_9N_7H_8$(27)bend
ν_6	1627(31/112)	1619	1615	N_2C_3(16)stretch+$H_9N_7H_8$(55)bend
ν_7	1519(104/359)	1524	1528	N_1C_5(23)stretch+$H_6N_1N_2$(39)bend+$N_4C_5N_1$(10)bend
ν_8	1501 (147/387)	1491	1490	N_2C_3(16)stretch+N_4C_3(30)stretch+$H_{11}N_4C_3$(11)bend+$H_8N_7C_3$(12)bend
ν_9	1363(25/23)	1378	1386	N_4C_5(21)stretch+$H_6N_1N_2$(23)bend+$H_{11}N_4C_3$(33)bend
ν_{10}	1303(6/3)	1307	1319	N_1C_5(38)stretch+ $H_6N_1N_2$(18)bend
ν_{11}	1194(117/117)	1210	1220	**N_1C_5(12)**stretch+$S_{10}C_5$(10)stretch+$H_6N_1N_2$(11)bend+

				$H_{11}N_4C_3$(19)bend+ **$N_4C_5N_1$(19)**bend
ν_{12}	1165(24/196)			N_2C_3(15)stretch+N_4C_5(24)stretch+$H_8N_7C_3$(19)bend+ **$N_4C_5N_1$(10)**bend
ν_{13}	1056(7.8/73)			$N_2C_3N_4$(10)bend+$H_8N_7C_3$(36)bend+$C_3N_4C_5$(29)bend
ν_{14}	1042(59/1)			N_4C_5(14)stretch+ **$N_4C_5N_1$(41)**bend
ν_{15}	1010(11/47)	989	1004	N_4C_3(52)stretch+ $N_2C_3N_4$(16)bend
ν_{16}	759(9.7/10)		804	N_7C_3(29)stretch+$N_2C_3N_4$(32)bend+$C_3N_4C_5$(12)bend
ν_{17}	724(2.8/13.8)	754	724	$N_2C_3N_4C_5$(32)tors+$N_7N_4N_2C_3$(49)out
ν_{18}	659(3/43)	643	658	$H_6N_1N_2C_3$(13)tors+$C_3N_4C_5N_1$(39)tors+$S_{10}N_1N_4C_5$(37)out
ν_{19}	574(1/478)			$H_9N_7H_8$(11)bend+$H_8N_7C_3N_4$(49)tors+$H_9N_7C_3N_4$(26)tors
ν_{20}	541(0.3/260)			$H_6N_1N_2C_3$(17)tors+$H_{11}N_4C_3N_7$(56)tors+$S_{10}N_1N_4C_5$(10)out
ν_{21}	506(20/38)		509	$S_{10}C_5$(50)stretch+ $C_3N_4C_5$(18)bend
ν_{22}	481(1.6/35)			$H_6N_1N_2C_3$(61)tors+ $H_{11}N_4C_3N_7$(26)tors
ν_{23}	448(14.8/13.5)		457	$N_7C_3N_2$(51)bend+$S_{10}C_5N_4$(21)bend
ν_{24}	337(1/20)			$N_2C_3N_4C_5$(36)tors+$C_3N_4C_5N_1$(11)tors+$N_7N_4N_2C_3$(32)out
ν_{25}	279(1.6/52)			$H_8N_7C_3N_4$(31)tors+ $H_9N_7C_3N_4$(51)tors
ν_{26}	249(10/2.5)			$N_7C_3N_2$(17)+ $S_{10}C_5N_4$(61)bend

Table S3. Experimental and calculated triplet electronic transition energies, corresponding orbitals and oscillator strengths with the electronic transition character for the optimized T_1 state at B3LYP(TD)-D3(BJ)/6-31G* level.

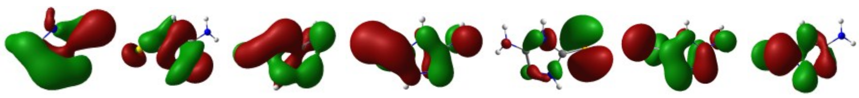
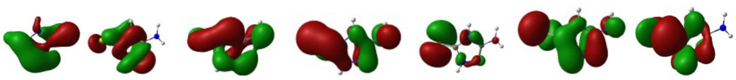
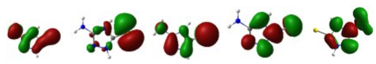
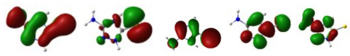
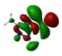
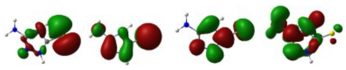
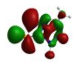
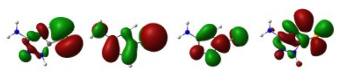
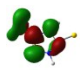
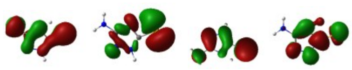
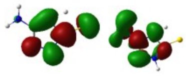
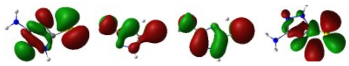
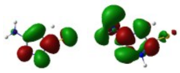
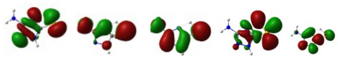
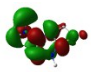
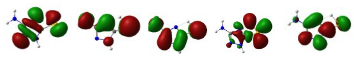
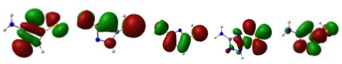
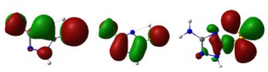
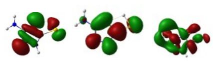
States	Orbitals(coefficient)	Electronic transition	Transition Energy(nm)		Oscillator strength(f)	
			Calc	Expt	Calc	Expt
AMT in CH_3CN						
T_1	29→30(0.99635)	π→π*	1125.57		0.0000	
T_2	**28→30(0.97857)**	**π→π***	**565.44**	**613**	**0.1494**	
T_3	27→30(0.78374)	π→π*	357.42		0.0028	
T_4	**27→30(0.49870)**	**π→π***	**356.35**	**328.2**	**0.0238**	
T_5	26→30(0.89785)	π→π*	322.97		0.0063	
T_6	29→31(0.94498)	π→π*	297.46		0.0064	
T_7	25→30(0.29788) 28→31(0.32522)	π→π* π→π*	273.86	295.07	0.0398	
 25π 26π 27π 28π 29π 30π* 31π*						
AMT in H_2O						
T_1	29→30(0.99632)	π→π*	1112.52		0.0000	
T_2	**28→30(0.97863)**	**π→π***	**564.82**	**600**	**0.1489**	
T_3	27→30(0.87456)	π→π*	357.50		0.0024	
T_4	**27→30(0.31013)** **28→30(0.15798)** **28→31(-0.14434)**	**π→π*** **π→π*** **π→π***	**355.57**	**317.3**	**0.0243**	
T_5	26→30(0.89856)	π→π*	323.12		0.0062	
T_6	29→31(0.94623)	π→π*	297.15		0.0064	
T_7	25→30(0.30532) 28→31(0.33513)	π→π* π→π*	273.18	292.21	0.0399	
 25π 26π 27π 28π 29π 30π* 31π*						

Table S4. Transition orbital nature and energy (kcal/mol) corresponding to the ground structures in Figure S1

	States	Orbitals(coefficient)	Electronic transition	Transition Energy (kcal/mol)	
-10(thione)	S_1	29→31(0.70424)	n→π*	133.2	 28π 29n 30π 31π* 32π*
	S_2	30→31(0.67205) 30→32(0.17648)	π→π* π→π*	141.2	
	S_3	30→32(0.63838) 28->31(-0.23277)	π→π* π→π*	156.8	
-8	S_1	29→31(0.70315)	n→π*	141.6	 28π 29n 30π 31π* 32π*  33π*
	S_2	30→31(0.66720) 30→32(0.17646) 29→33(-0.11105)	π→π* π→π* n→π*	147.2	
	S_3	28→31(-0.19022) 30->31(-0.11702) 30->32(0.50303) 30->33(-0.42931)	π→π* π→π* π→π* π→π*	162.9	
-6	S_1	29→31(0.68931) 30→31(0.11686)	n→π* π→π*	152.1	 29n 30π 31π* 32π*  33π*
	S_2	30→31(0.64839) 29→31(-0.12649) 29→33(0.15282)	π→π* n→π* n→π*	154.0	
	S_3	30→32(0.27441) 30→33(0.63972)	π→π* π→π*	162.4	
-4	S_1	30→32(0.63128) 30→31(0.23986) 29→31(0.16847)	π→π* π→π* n→π*	159.3	 29n 30π 31π* 32π*  33π*
	S_2	30→31(0.59728) 29→32(0.21265) 30→32(-0.24480) 30→33(0.15849)	π→π* n→π* π→π* π→π*	161.1	
	S_3	29→31(0.68285) 30→32(-0.17108)	n→π π→π*	164.8	
-2	S_1	30 ->32 (0.67820) 28 -> 32(0.11368) 30 -> 31(0.15010)	π→π* π→π* π→π*	157.1	 28π 29n 30π 31π*  32π* 33π*
	S_2	30 ->31 (0.61272) 29 ->32 (0.25959) 30->32(-0.13736) 30 -> 33(0.14017)	π→π* n→π* π→π* π→π*	166.8	
	S_3	29→31(0.68760) 29→32(-0.11689)	n→π* n→π*	176.3	

0	S_1	30 ->31 (0.69063) 29 -> 31(0.14302)	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	154.5	 28n 29π 30π 31π*  32π* 33π*
	S_2	30 ->32 (0.61848) 28 -> 31(0.28304) 29 -> 32(0.11623) 30 ->33 (0.12864)	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	170.7	
	S_3	28→32(0.13753) 29→31(0.67328) 30→31(-0.14716)	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	179.8	
2	S_1	30 ->31 (0.68505) 29 -> 31(0.16922)	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	151.4	 28n 29π 30π 31π*  32π* 33π*
	S_2	30 ->32 (0.61071) 28 ->31 (0.29529) 29 -> 32(0.12970) 30 -> 33(0.12200)	$\pi\rightarrow\pi^*$ $n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	172.2	
	S_3	29→31(0.68087) 30→31(-0.17085)	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	174.9	
4	S_1	30 ->31 (0.67888) 29 -> 31(0.19129)	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	148.1	 28n 29π 30π 31π* 32π*  33π*
	S_2	29 ->31 (0.67540) 30->31(-0.19254)	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	170.0	
	S_3	28→31(0.29526) 29→32(0.12345) 30→32(0.61112) 30→33(0.11399)	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	171.3	
6	S_1	29 ->31 (0.20580) 30 -> 31(0.67405)	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	145.1	 28n 29π 30π 31π* 32π*  33Ryd
	S_2	29 ->31 (0.67254) 30->31(-0.20789)	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	165.8	
	S_3	28→31(-0.27753) 30→32(0.62486) 30→33(0.11105)	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ π→Ryd	168.8	
8	S_1	29 ->31 (0.21251) 30 -> 31(0.67141)	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	142.7	 28n 29π 30π 31π* 32π*  33Ryd
	S_2	29 ->31 (0.67018) 30->31(-0.21527)	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	162.6	
	S_3	28→31(-0.23729) 30→32(0.64449)	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	165.6	
10(thiol)	S_1	29 -> 31(0.21347) 30 -> 31(0.67073)	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	140.6	 29π 30π 31π*  28n 32π* 33Ryd
	S_2	29 ->31 (0.66943) 30->31(-0.21673)	$\pi\rightarrow\pi^*$ $\pi\rightarrow\pi^*$	160.4	
	S_3	28→31(-0.18657) 30→32(0.66030) 30→33(0.10832)	$n\rightarrow\pi^*$ $\pi\rightarrow\pi^*$ π→Ryd	162.4	