Supporting Information

Synthesis of Tautomerization-inhibited Diamino Substituted Tetraphenylethene Derivatives with Different Mechanochromism: The Vital Role of Chlorine

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Materials and Methods

Benzophenone (99%), 4-Chlorobenzophenone (99%), 4,4'-Dichlorobenzophenone (99%), 4-Aminobenzophenone (99%), Titanium tetrachloride (99%), Tetrahydrofuran (THF, Extra Dry, 99.5%) and Palladium carbon (10 %) were purchased from Sigma-Aldrich. Zinc powder (AR) was purchased from Aladdin. Glacial acetic acid (AR), Fuming nitric acid (AR), Hydrazine hydrate (80%, AR), and other organic solvents were purchased from Kelong Chemical Reagent Co, Ltd (Chengdu). All reagents were used without further purification unless otherwise stated.

The NMR spectra were recorded using an AV Ⅲ HD 400 MHz NMR spectrometer (Bruker, Germany). A UV spectroscopy analysis was carried out using a UV-1800PC spectrophotometer (MAPADA, Shanghai, China). Fluorescence spectra of three molecules in THF solution were obtained using a Horiba Jobin Yvon FluoroMax-4. High-resolution mass spectra (HRMS) were obtained on a LCMS-IT-TOF (ESI; Shimadzu, Japan). X-ray diffraction spectra were determined on an Ultima IV X-ray diffractometer (XRD; Rigaku, Cu-Ka radiation). Absolute fluorescence quantum yields measurements were performed on an integrating sphere (Quanta-phi) of Fluorolog-3 (HORIBA, Japan). Fluorescence Spectroscopy were recorded using a FluoroMax-4 spectrophotometer (HORIBA, Japan) for solution and FL7000 spectrophotometer (HITACHI, Japan) for solid. The crystallographic data collection was performed without any inert gas protection at room temperature on an Oxford Xcalibur EOS CCD area detector using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å). The data reduction and integration and global unit cell refinements were performed using the CrysAlis Pro program and the Olex2 software package, respectively.

Synthesis and Characterization

Synthesis

Synthesis of *E/Z*/S-2Cl-2NH_2-TPE

The synthetic route was shown in **Scheme 1**. Firstly, compound **1** was synthesized by McMurry coupling of 4-chlorobenzophenone. In a 500ml Schlenk flask, 4-chlorobenzophenone (12.00 g, 55.4 mmol), zinc powder (7.97 g, 121.9 mmol) anhydrous THF (200 mL) was added. Nitrogen was bubbled into the solution to remove

oxygen at -20 ℃ for 30 minutes. $TiCl_4$ (23.12 g, 121.9 mmol) was added dropwise and keep the reaction at a constant temperature of -20 ℃ for 1 hour. Then the mixture was heated to reflux for 5 h. After completion of the reaction, the solution was cooled to room temperature and filtered to get filtrate. After solvent evaporation, the residue was extracted with ethyl acetate, washed with brine, and dried with Na_2SO_4. Compound **1** was obtained as a light white solid by rotary evaporation. Yield: 10.1 g, (92%). Secondly, compound **2** was synthesized by nitration of fuming nitric acid. In a 100ml flask, glacial acetic acid (30.0 ml) and fuming nitric acid (10.0 ml) were added under 0 ℃. After well mixed, the dichloromethane (15 ml) solution of compound **1** (2.0 g, 5.0 mmol) added into the flash dropwise, and then the mixture was kept below 0 ℃ for 25 minutes. The solution was quenched by adding into 800 ml ice water. Then filtered to get residue and washed with distilled water three times. Compound 2 was obtained as a yellow solid by Natural drying. Yield: 2.2 g, (91%). Lastly, *Z/E*-2Cl-2NH2-TPE was synthesized by nitroreduction reaction of hydrazine hydrate. In a 250ml flask, hydrazine hydrate (10.3 g, 163 mmol) was added to an ethanol (100 mL) solution of compound **2** (8.0 g, 16.3 mmol) under N_2 atmosphere at 0 ℃. Nitrogen was bubbled into the solution to remove oxygen for 20 minutes. Then palladium on carbon (100 mg) was added and the mixture was heated at 60 ℃ for 6 h. The solution was cooled to room temperature and filtered to get filtrate. After solvent evaporation, the residue was extracted with ethyl acetate, washed with brine. The organic phase was collected and dried over anhydrous Na_2SO_4. After solvent evaporation, the residue was purified on a silica-gel column using ethyl acetate/petroleum ether mixture (1: 4, v/v) to afford *E*-2Cl-2NH_2-TPE as light green solid in 39 % yield (2.73 g) and *Z*-2Cl-2NH_2-TPE as orange solid in 41 % yield (2.87 g). E-2Cl-2NH_2-TPE: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.23 – 7.13 (m, 4H), 7.02 – 6.89 (m, 4H), 6.59 – 6.49 (m, 4H), 6.35 – 6.25 (m, 4H), 5.07 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.75, 144.04, 138.43, 133.12, 132.18, 130.80, 130.72, 128.09, 113.79. HRMS: calc. for [M+H^+] 431.1076, found 431.1074. Z-2Cl-2NH_2-TPE: ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 7.21 – 7.11 (m, 4H), 6.98 – 6.87 (m, 4H), 6.66 – 6.54 (m, 4H), 6.37 – 6.27 (m, 4H), 5.05 (s, 4H). ^{13}C NMR (100 MHz,

DMSO-d_6) δ 147.67, 143.81, 138.30, 133.26, 131.98, 131.13, 130.95, 128.18, 113.72, 39.69, 39.47. HRMS: calc. for [M-H$^+$] 429.0931, found 429.0924.

Synthesis of S-2Cl-2NH_2-TPE.

The synthetic route was shown in **Scheme 1**. The synthetic procedure of S-2Cl-2NH_2-TPE was similar to *Z/E*-2Cl-2NH_2-TPE. The difference is that compound **3** is synthesized by McMurry coupling of benzophenone and 4,4'-dichlorobenzophenone. What's more, compound **4** was synthesized by nitration without dichloromethane. glacial acetic acid (20.0 ml) successively and fuming nitric acid (10.0 ml) were added under 0 ℃. After well mixed, compound **3** was added in portions, and the mixture was kept below 0 ℃ for 45 minutes. S-2Cl-2NH_2-TPE: ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) = 7.21 – 7.12 (m, 4H), 6.95 – 6.87 (m, 4H), 6.64 – 6.56 (m, 4H), 6.34 – 6.26 (m, 4H), 5.08 (s, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 148.01, 144.02, 143.90, 133.16, 132.94, 132.41, 130.78, 130.57, 128.30, 113.57. HRMS: calc. for [M-H$^+$] 429.0931, found 429.0929.

Synthesis of *E/Z*-2NH_2-TPE

The *E/Z*-2NH_2-TPE molecules synthesized through the McMurry coupling reaction of 4-aminobenzophenone as reported.[1]

The image of *E*-2NH_2-TPE molecule and *Z*-2Cl-2NH_2-TPE molecule in thin-layer chromatography (TLC) were shown in **Figure S1.**

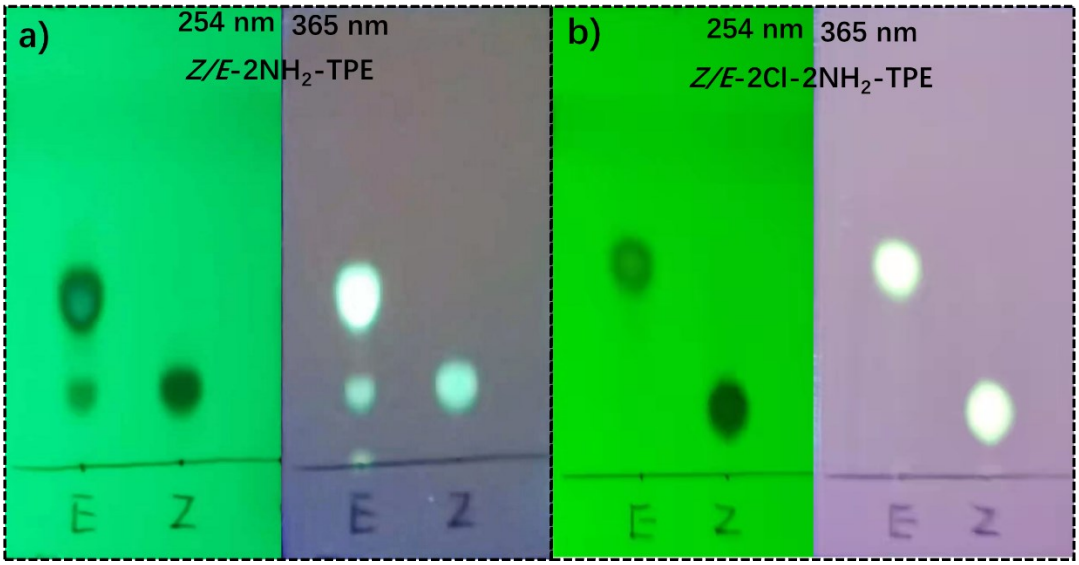

Figure S1. The image of *Z/E*-2NH_2-TPE molecules and *Z/E*-2Cl-2NH_2-TPE molecules

in TLC.

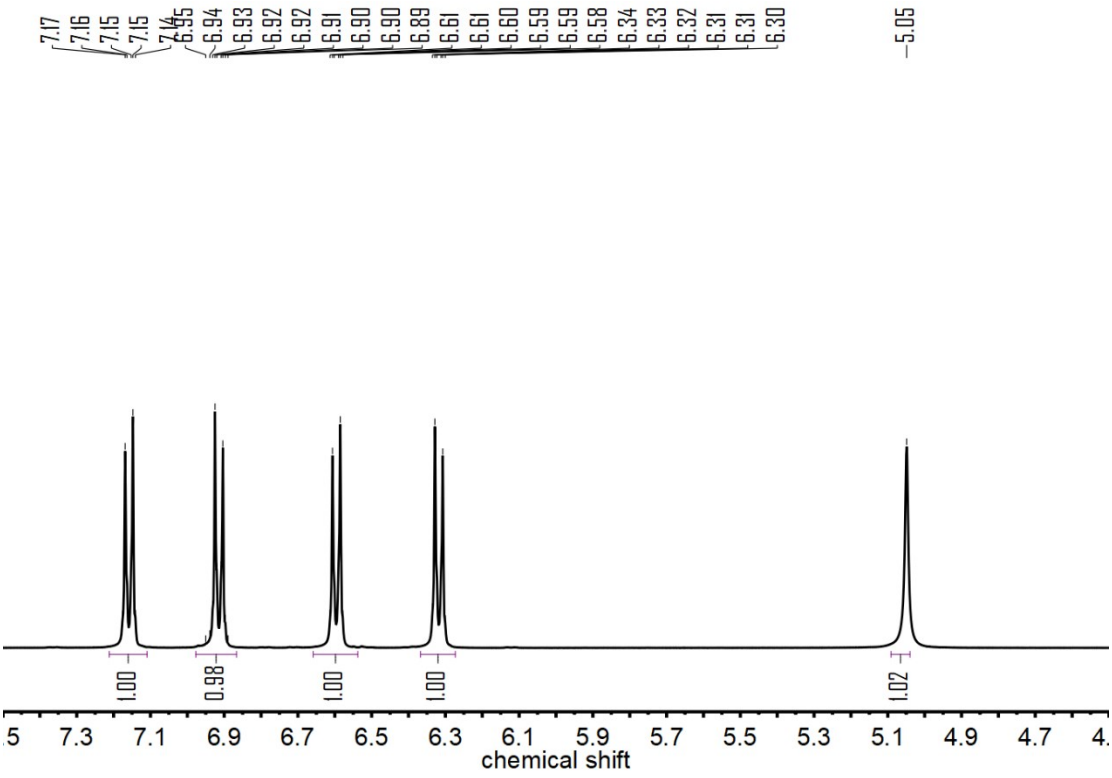

Figure S2. ^{1}H NMR spectrum of *E*-2Cl-2NH$_2$-TPE in DMSO-d_6.

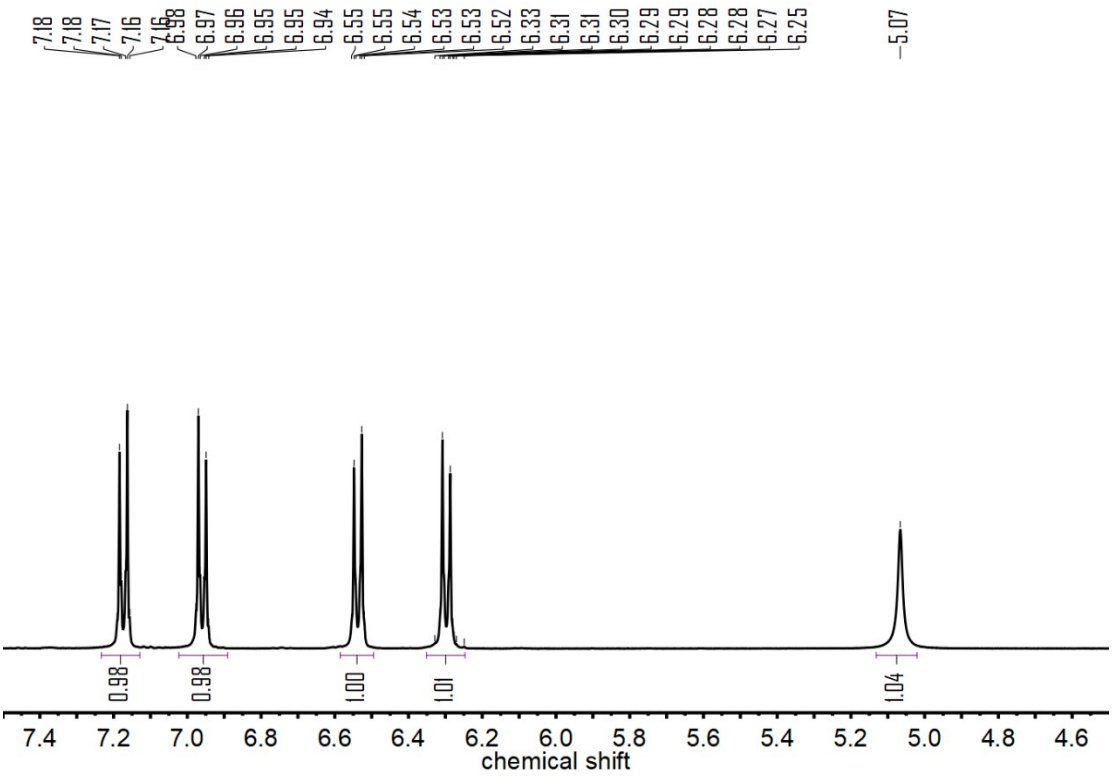

Figure S3. ^{1}H NMR spectrum of *Z*-2Cl-2NH$_2$-TPE in DMSO-d_6.

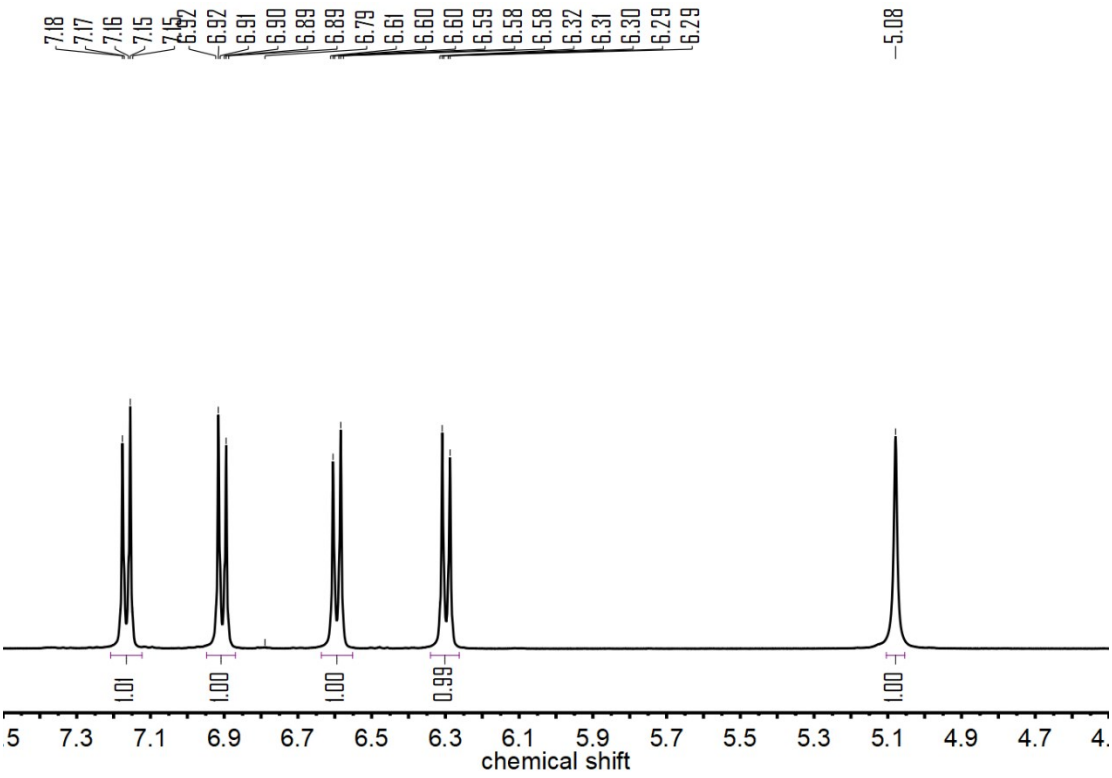

Figure S4. ^{1}H NMR spectrum of S-2Cl-2NH$_2$-TPE in DMSO-d_6.

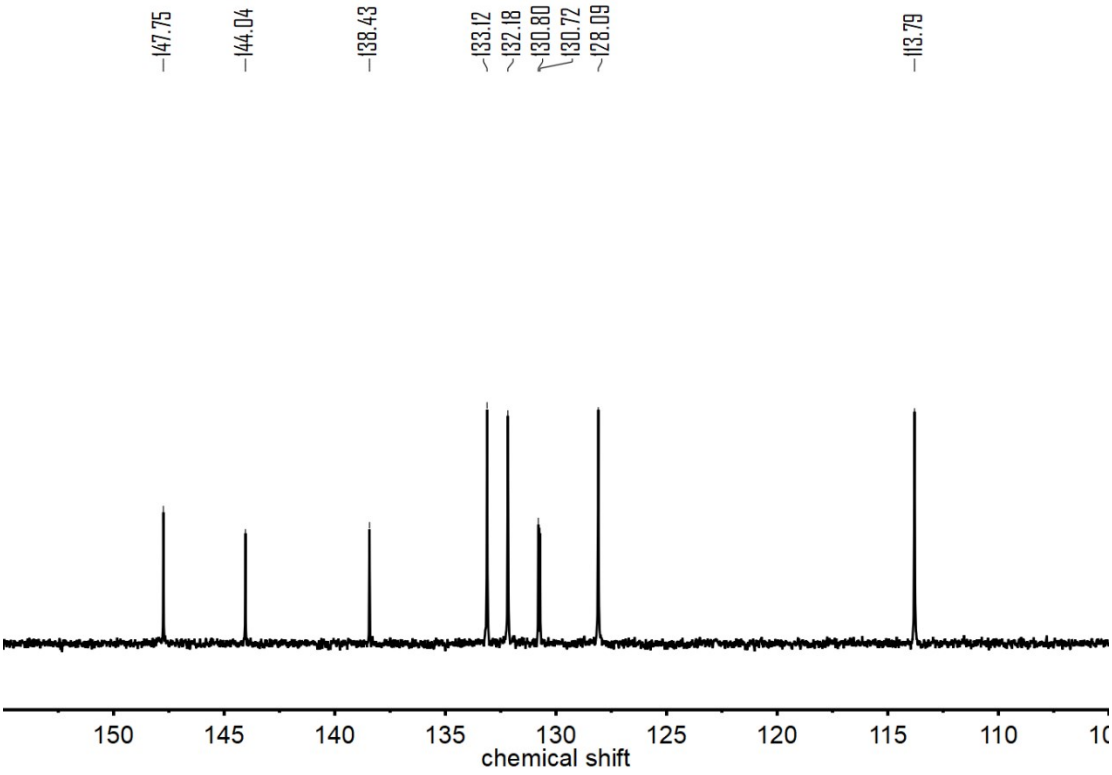

Figure S5. ^{13}C NMR spectrum of *E*-2Cl-2NH$_2$-TPE in DMSO-d_6.

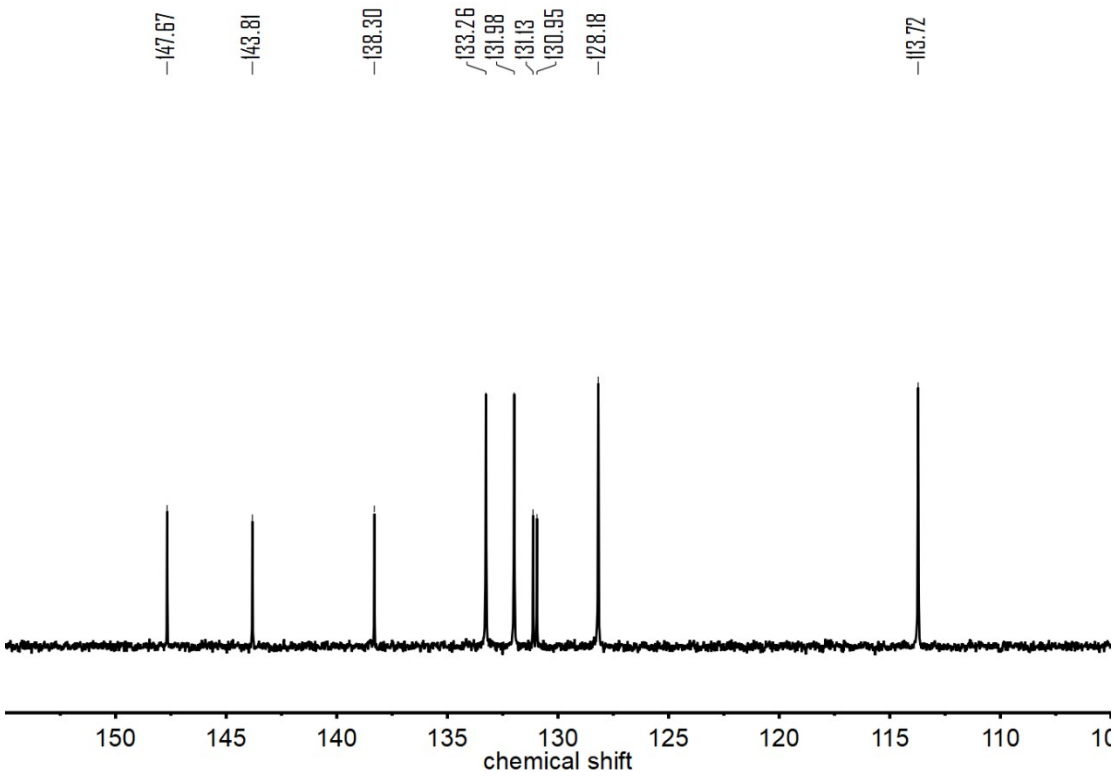

Figure S6. ^{13}C NMR spectrum of *Z*-2Cl-2NH$_2$-TPE in DMSO-d_6.

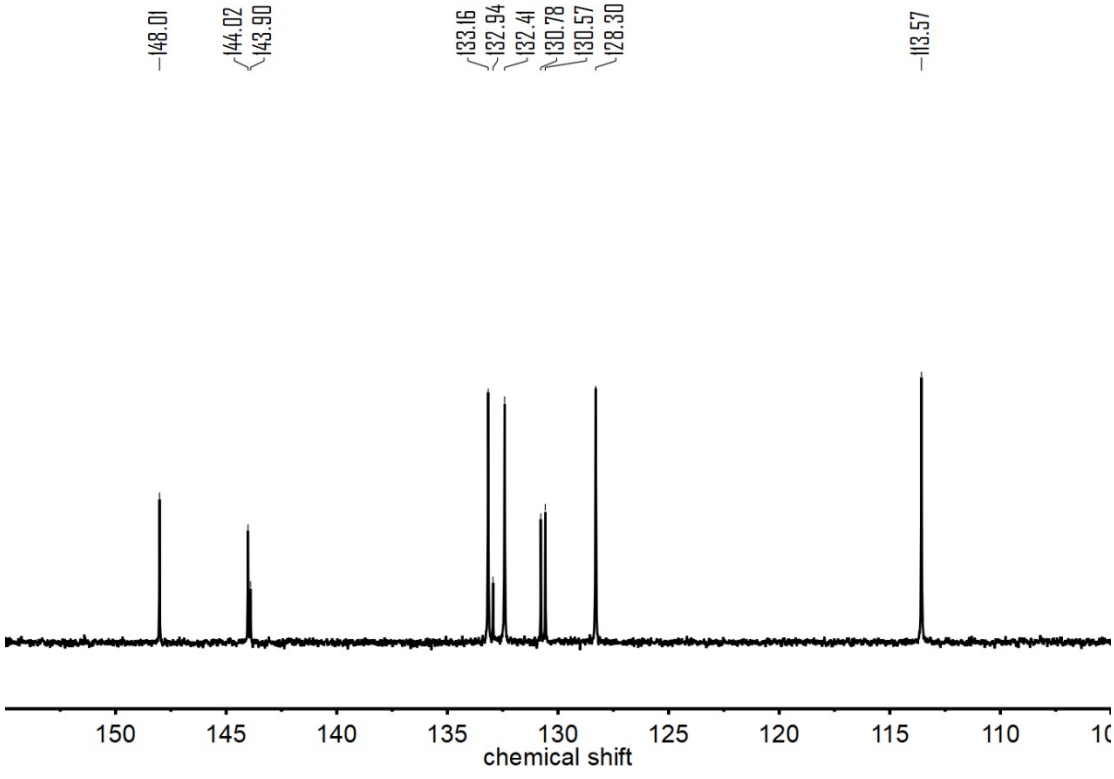

Figure S7. ^{13}C NMR spectrum of S-2Cl-2NH$_2$-TPE in DMSO-d_6.

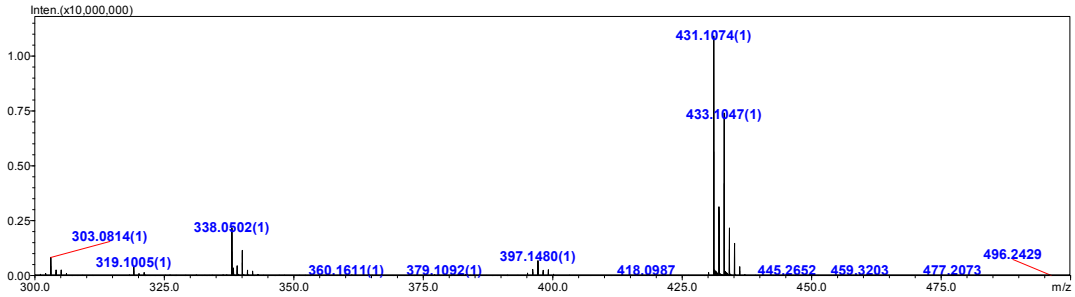

Figure S8. High-resolution mass spectrum of *E*-2Cl-2NH_2-TPE.

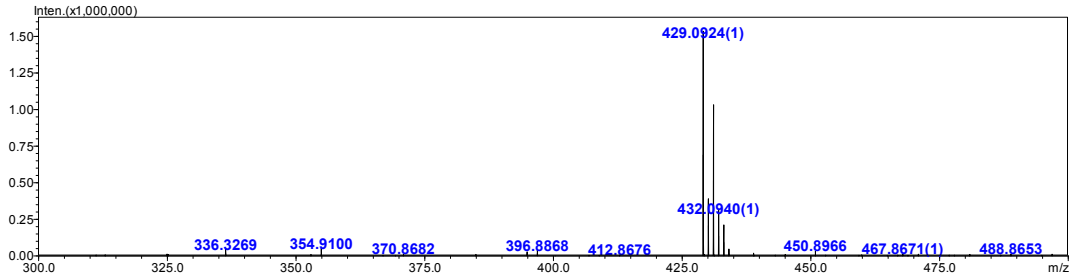

Figure S9. High-resolution mass spectrum of *Z*-2Cl-2NH_2-TPE.

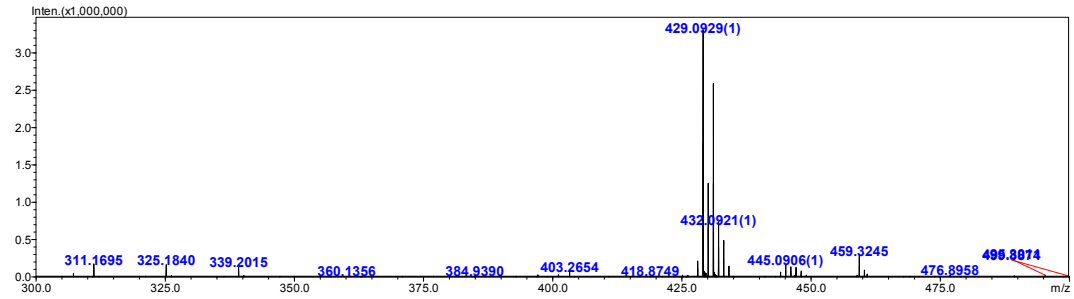

Figure S10. High-resolution mass spectrum of S-2Cl-2NH_2-TPE.

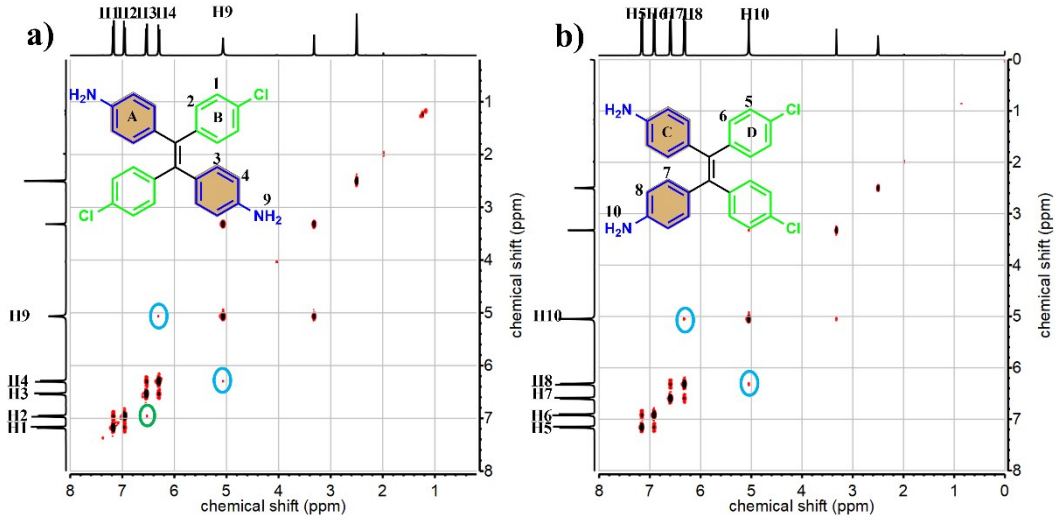

Figure S11. NOESY-NMR of **a)** *E*-2Cl-2NH_2-TPE and **b)** *Z*-2Cl-2NH_2-TPE

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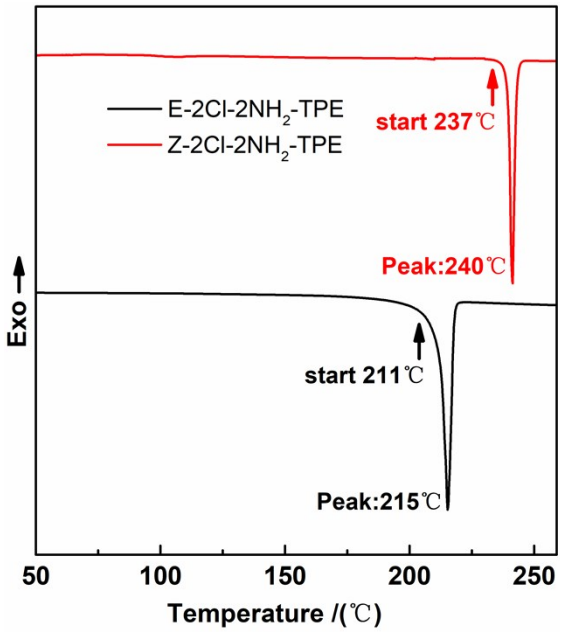


Figure S12. DSC curve of *E/Z*-2Cl-2NH_2-TPE

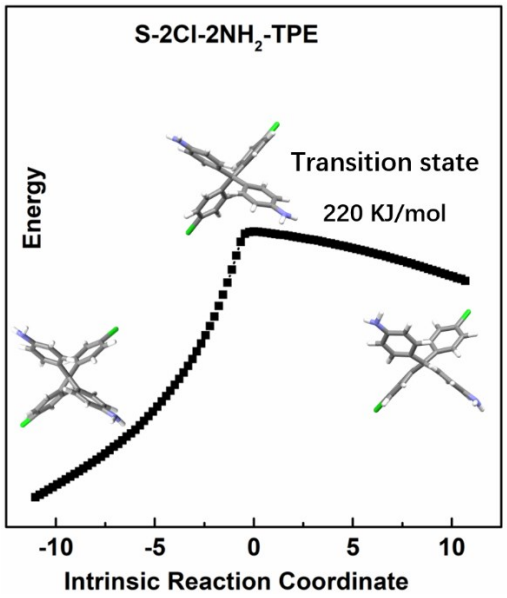


Figure S13. IRC curve of S-2Cl-2NH_2-TPE was calculated in the $\mathbf{S_0}$ at M06-2X/6-311G (d,p) level.

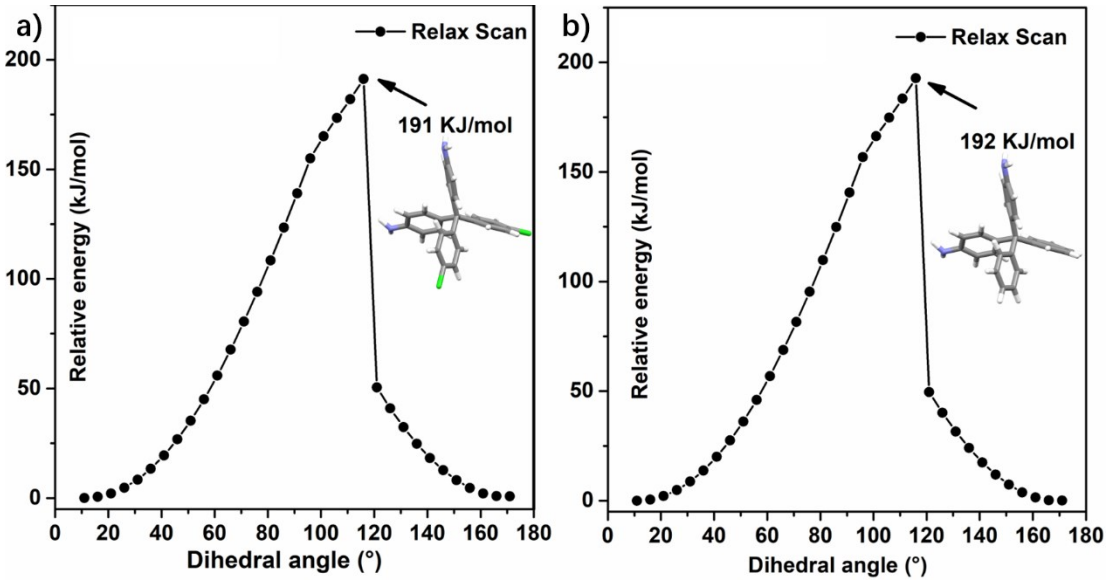


Figure S14. Relax scan curve of *E*-2Cl-2NH_2-TPE (a) and *E*-2NH_2-TPE (b) was calculated in the **PES** of $\mathbf{S_0}$ at M06-2X/6-311G (d,p) level.

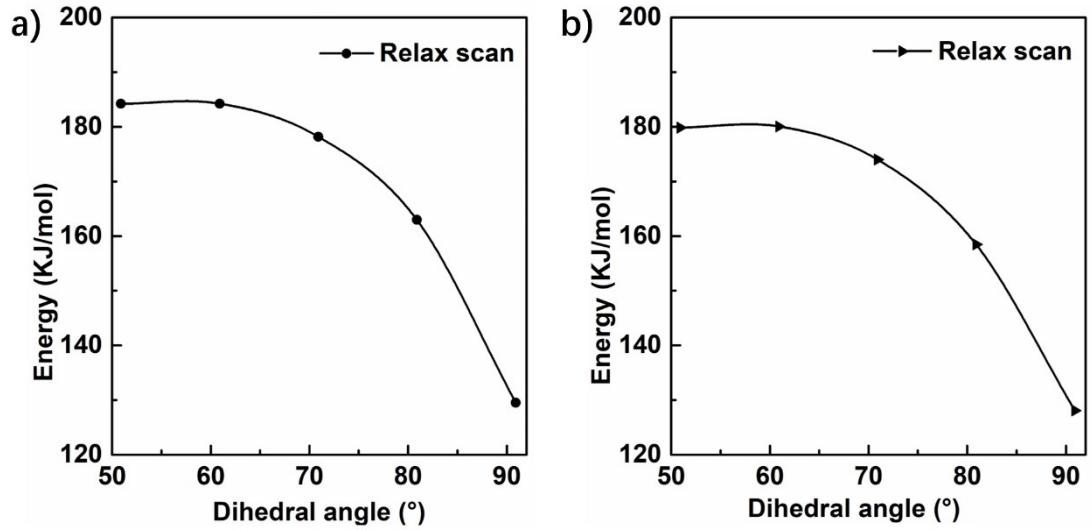


Figure S15. Relax scan curve of *E*-2Cl-2NH_2-TPE and *E*-2NH_2-TPE was calculated in the $\mathbf{S_1}$ at M06-2X/6-311G (d,p) level. Energy was obtained compared to the $\mathbf{S_1}$ energy of *E*-2Cl-2NH_2-TPE and *E*-2NH_2-TPE, respectively.

In **PES** of $\mathbf{S_0}$, the geometric *E/Z*-2Cl-2NH_2-TPE molecules with up to 220 kJ/mol energy barrier was hard to tautomerize at room temperature. Our analysis was as followed. Relax scan curve of *E*-2Cl-2NH_2-TPE was obtained in THF solvent at M06-2X/6-311G (d,p) level. The max energy point about 190 kJ/mol in the relax scan give the minimum energy barrier of tautomerization process in **Figure S15**. The TS of *E/Z*-2Cl-2NH_2-TPE molecules was not searched in **PES** of $\mathbf{S_0}$ at M06-2X/6-311G (d,p) level. However, **TS** of geometric S-2Cl-2NH2-TPE has been calculated at M06-2X/6-

311G (d,p) level and intrinsic reaction coordinate (**IRC**) has confirmed in **Figure S14**. Energy barrier 220 kJ/mol was calculated and tautomerization process would not occur at room temperature without excitation. Collectively, the barrier energy of geometric *Z/E*-2Cl-2NH_2-TPE may be about 220 kJ/mol.

TS of E-2NH_2-TPE was not found. Relax scan curve of *E*-2Cl-2NH_2-TPE and E-2NH_2-TPE was calculated in the **PES** of $\mathbf{S_1}$ at M06-2X/6-311G (d,p) level in **Figure S16**. Combined similar **CI** and **FL** energy, the **TS** conformation and energy of *E*-2Cl-2NH_2-TPE and *E*-2NH_2-TPE might be similar.

Table S1. Crystal data and structure refinement

	E-2Cl-2NH_2-TPE	*Z* -2Cl-2NH_2-TPE	S-2Cl-2NH_2-TPE
CCDC number	2042607	2042606	2042605
Formula	$C_{26}H_{20}Cl_2N_2$	$C_{26}H_{20}Cl_2N_2$	$C_{26}H_{20}Cl_2N_2$
Formula weight	431.34	431.34	431.34
Crystal system	monoclinic	Triclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a /Å	15.4602(11)	9.5711(3)	11.2845(10)
b /Å	10.5768(7)	19.8121(8)	9.1406(5)
c /Å	26.8575(19)	24.9957(15)	21.8173(16)
α /°	90	107.268(4)	90
β /°	95.143(6)	100.656(4)	104.065(8)
γ /°	90	91.625 (3)	90
Volume /$Å^3$	4362.8(5)	4430.5(4)	2182.9(3)
Z	8	8	4
ρ_{calc} /g*cm^{-3}	1.313	1.298	1.312
μ /mm^{-1}	0.313	0.308	0.313
Temperature /K	293.15	293.15	293.15
2Θ range for data	5.876-52.744	5.854-52.744	5.826-52.744

collection /°			
Reflections collected R_1/ R_w	0.0621/0.0854	0.0792/0.1899	0.0536/0.1151
Reflections collected	20849	21250	10207
Rint	0.0946		0.0305
F (000)	1792	1792	896

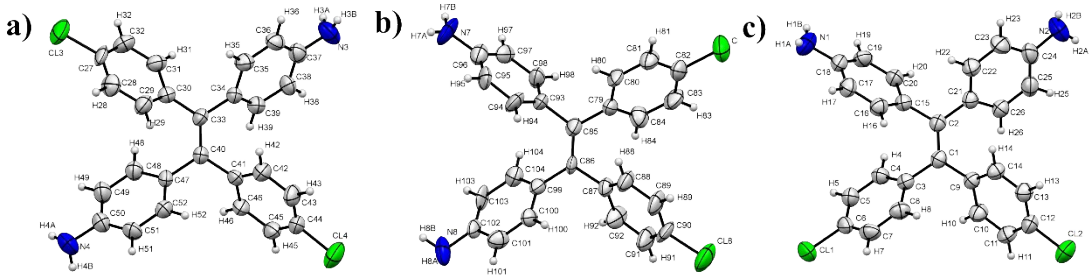


Figure. S16 Crystal structures of **a)** *E*-2Cl-2NH_2-TPE, **b)** *Z*-2Cl-2NH_2-TPE, **c)** S-2Cl-2NH_2-TPE

Table S2. Summary of the intermolecular interactions in three single crystals

Crystal	Conformation	Intermolecular interactions/ (d Å^{-1})					
		N-H…N	C-H…N	N-H…π	C-H…π	C-H…Cl	N-H…Cl
E-2Cl-2NH_2-TPE	one	2.719(1) [a] 2.341(1)	2.980(2)			2.991(1) 3.189(1) 3.103(1) 2.964(1) 3.099(1)	
	two	2.719(1) 2.808(2) 2.341(1)	3.133(1) 3.010(1)			3.103(1) 2.991(1) 3.009(1) 3.189(1) 2.964(1)	3.187(1)
Z-2Cl-2NH_2-TPE	one	2.781(1)	2.960(1) 3.008(2) 3.026(1) 3.030(1)	2.851(1)	3.051(2)	3.089(1) 2.960(1) 3.040(1) 3.148(1) 3.016(1) 3.098(1) 3.150(1)	
	two		2.875(2) 2.861(1) 2.947(1) 3.006(1) 2.999(1)	2.818(2)	3.174(2)	3.110(1) 3.198(1) 3.120(1) 3.150(2) 3.077(1) 3.058(1) 2.918(1)	

						3.077(1) 3.089(1) 3.134(1)
	three		2.902(1) 2.714(1)	2.735(2) 3.125(1)	3.175(2)	3.058(1) 3.134(1) 3.081(1) 3.029(1) 3.110(1) 3.014(1) 3.081(1) 3.029(1) 3.198(1) 3.120(1) 2.985(1) 2.918(1)
	four	2.781(1)	3.013(1) 2.714(1) 3.006(1) 2.943(1) 2.861(1)	2.893(2)	2.653(1)	3.062(1) 3.049(1) 2.969(1) 2.960(1) 3.040(1) 3.016(1) 3.162(1) 3.062(1) 3.049(1) 3.148(1) 3.150(1)
Z-2Cl-2NH_2-TPE	one	2.474(2)	3.034(2)	3.003(2)		3.146(2) 3.308(2)

[a] The number of hydrogen bonds. The bond length of the N-H…π/ C-H…π interaction is the distance between the hydrogen atom and the plane of the benzene ring.

Single crystal structures of the three isomers were deciphered with detailed information listed in **Table S1**, and **Figure S16**. *Z*-2Cl-2NH_2-TPE belongs to a triclinic system with a centrosymmetric $P\bar{1}$ space group, whereas *E*-2Cl-2NH_2-TPE and S-2Cl-2NH_2-TPE belong to monoclinic system with a centrosymmetric *P*21/*c* and *P*21/*n* space group, respectively. All molecules adopt a highly twisted conformation. Molecules in the unit cell of *Z*-2Cl-2NH_2-TPE showed four conformations, while *E*-2Cl-2NH_2-TPE and S-2Cl-2NH_2-TPE showed two conformations and one conformation, respectively. The intermolecular hydrogen bonds shorter than 3.2 Å in these single crystals were analyzed shown in **Table S2**. There was no π-π stacking between molecules in three single crystals due to the highly twisted TPE moiety. Each conformation of *E*-2Cl-2NH_2-TPE molecule interacts with nine neighbouring molecules. There are three kinds (six numbers) of N-H…N bonds with distances ranging from 2.341 to 2.809 Å and three kinds (four numbers) of C-H…N bonds with distances ranging from 2.980 to 3.010 Å (includes two conformations). Compared to *Z*-2Cl-2NH_2-TPE and S-2Cl-2NH_2-TPE molecules, *E*-2Cl-2NH_2-TPE molecule lacked N-H…π and C-H…π intermolecular

interactions. Abundant intermolecular interactions were also present in crystal *Z*-2Cl-2NH_2-TPE, three kind (four numbers) of N-H…N bonds with distances 2.781 Å, thirteen kinds (fifteen numbers) of C-H…N bonds with distances ranging from 2.714 to 3.030 Å, five kinds (eight numbers) of N-H…π bonds with distances ranging from 2.735 to 3.125 Å and four kinds (seven numbers) of C-H…π bonds with distances of 2.653 and 3.175Å (includes four conformations). Each S-2Cl-2NH_2-TPE molecule interacts with six neighbouring molecules, one kind (two numbers) of N-H…N bonds with distances of 2.472 Å, one kind (two numbers) of C-H…N bonds with distances of 3.034 Å and one kind (two numbers) of N-H…π bonds with distances of 3.003 Å. Together with the presence of strong hydrogen bonding N-H…N (C-H…N, N-H…π and C-H…π are weak hydrogen bonding), it could be concluded that *E*-2Cl-2NH_2-TPE exhibited stronger intermolecular interactions, followed by S-2Cl-2NH_2-TPE, and finally *Z*-2Cl-2NH_2-TPE. Thus, the ordered packing of *Z*-2Cl-2NH_2-TPE would be more vulnerable to external pressure than those of *E*-2Cl-2NH_2-TPE and S-2Cl-2NH_2-TPE.

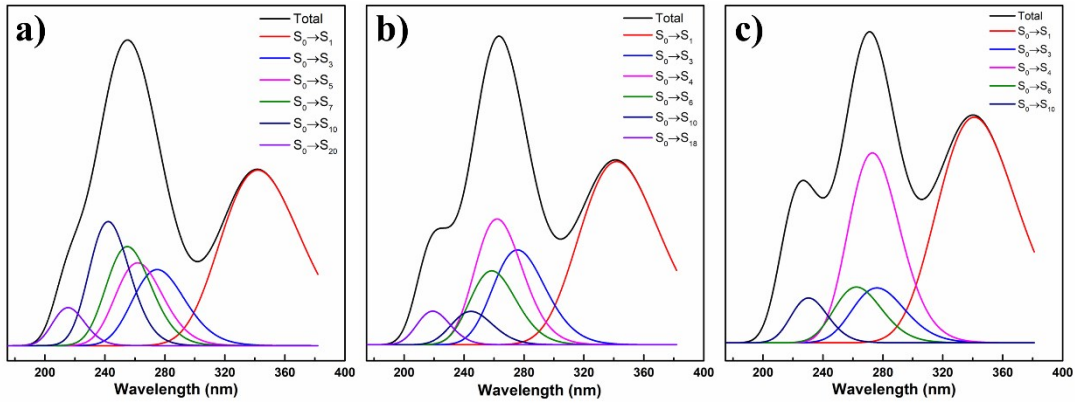


Figure S17. The simulated absorption spectrum of *E/Z*/S-2Cl-2NH_2-TPE contribution to each transition

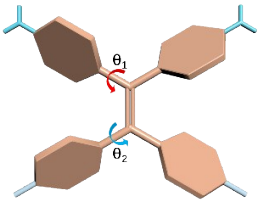
Table S3. Transition wavelength, oscillator strengths and the assignment of $\mathbf{S_0}$ to $\mathbf{S_i}$ transitions for *E/Z*/S-2Cl-2NH_2-TPE[1]

	Excited state	Transition wavelength (nm)	Oscillator strength	Orbitals	Contribution
***E*-2Cl-2NH_2-TPE**	1	343.37	0.5469	HOMO→LUMO	0.94

	3	274.44	0.2276	HOMO→LUMO+2 HOMO→LUMO+8	0.54 0.16
	5	268.15	0.2700	HOMO-1→LUMO+1 HOMO→LUMO+2 HOMO→LUMO+8	0.12 0.28 0.23
	6	257.31	0.3158	HOMO→LUMO+5	0.64
	10	241.91	0.3721	HOMO-2→LUMO	0.49
***Z*-2Cl-2NH$_2$-TPE**	1	345.10	0.5384	HOMO→LUMO	0.93
	3	275.11	0.3187	HOMO-1→LUMO+5	0.65
	5	263.54	0.2854	HOMO→LUMO+2 HOMO→LUMO+4 HOMO→LUMO+9	0.17 0.25 0.17
	7	257.42	0.3564	HOMO-1→LUMO	0.75
S-2Cl-2NH$_2$-TPE	1	342.58	0.5875	HOMO→LUMO	0.95
	4	272.39	0.5731	HOMO-1→LUMO HOMO→LUMO+5	0.63 0.11
	6	263.32	0.1716	HOMO→LUMO+4	0.47
	10	240.38	0.0119	HOMO-1→LUMO+3 HOMO→LUMO+6	0.13 0.39

[1]Other prohibited transitions and contribution below 0.1 are not listed.

Table S4. Dihedral angle and vinyl bond length of three molecules



	θ_1[1]	θ_2[2]	length of vinyl bond
E-2Cl-2NH$_2$-TPE	45.32°	46.03°	1.3600 Å
Z-2Cl-2NH$_2$-TPE	45.23°	47.03°	1.3606 Å
S-2Cl-2NH$_2$-TPE	44.61°	45.62°	1.3613 Å

[1, 2] As S-2Cl-2NH$_2$-TPE molecule for example, θ_1 (θ_2) is the dihedral angle between vinyl plane and benzene ring connected with amino (chlorine)

The ultraviolet-visible absorption spectrum analysis was as follows. The peak shape and trend of the simulated absorption spectrum were in good agreement with the experimental absorption spectrum. The calculated structure of the isomer in THF solvent was in **Table S4**. A stronger absorption peak at a wavelength of 271.0 nm, 285.5 nm and 308.5 nm of *E*/*Z*/S-2Cl-2NH$_2$-TPE molecules were shown in **Figure 5**. These results from Rydberg excitation, and the contribution for each transition in the simulated absorption were illustrated in **Figure S17**, **Figure S18**, and **Table S4**.

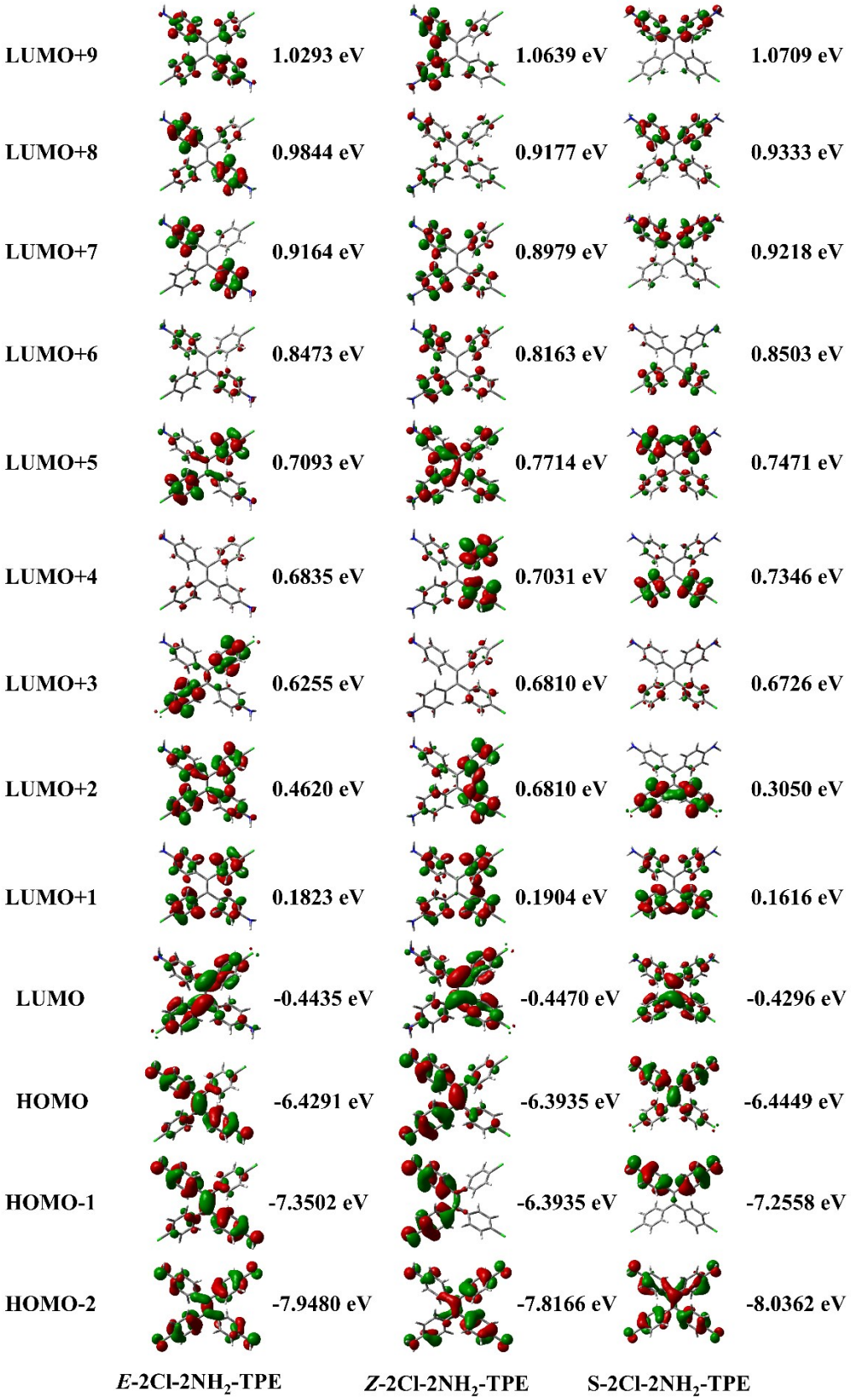


Figure S18. The frontier molecular orbitals of *E/Z*/S-2Cl-2NH_2-TPE

The three molecules were verified to be typical AIE molecules. The three isomers

exhibit good solubility in tetrahydrofuran (THF), but they are insoluble in water (H_2O). The fluorescence spectra of the luminogens in THF and THF/H_2O mixtures were obtained (see **Figure S19**). *Z/E*-2Cl-2NH_2-TPE in pure THF and THF/H_2O mixtures with water fractions (f_w) lower than 80% shows no emission, which is a result of the free rotation and vibration of benzene ring in these mixtures. A fluorescence peak at 516 nm and 517 nm was detected for *E/Z*-2Cl-2NH_2-TPE when the water content reached 95%. As for S-2Cl-2NH_2-TPE, water fractions lower than 85%, no emission was detected. A fluorescence peak at 521nm was detected for S-2Cl-2NH_2-TPE when the water content reached 99%. As water fractions increase, the molecules begin to aggregate and the interaction among molecules has played more and more important roles.

As for fluorescent molecule, electronic coupling between fluorescent molecules in the solid state quenched their emission.[2] Bulky and contorted structures were a common feature of fluorescent molecules that display aggregation-induced emission (AIE). Electronic coupling still occurs in AIE fluorescent molecules, once the spatially isolated fluorescent molecules are coupled from each other. As for *Z*/*E*-2Cl-2NH_2-TPE molecules, 99% of water fraction made them too tightly packed and electronic coupling occurred. The fluorescence intensity would be weakened.

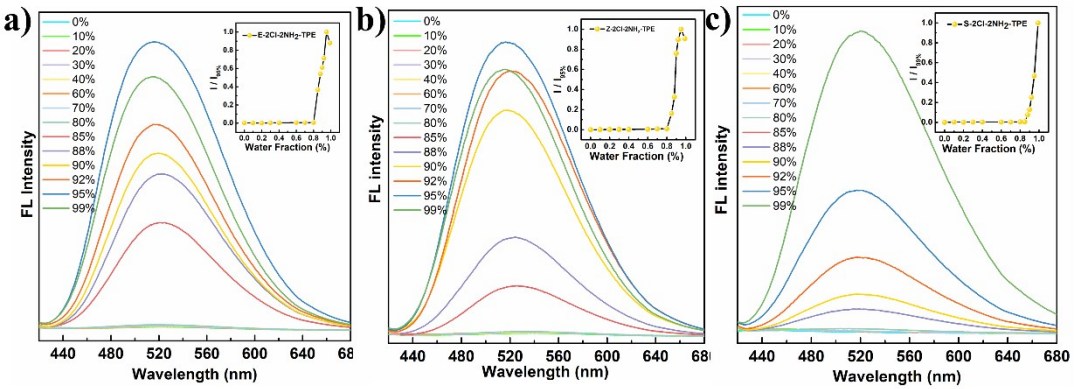


Figure S19. Fluorescence spectra of *E*-2Cl-2NH_2-TPE (**a**), *Z*-2Cl-2NH_2-TPE (**b**) and S-2Cl-2NH_2-TPE (**c**) (10 μM, excitation wavelength: 365 nm) in THF and water mixtures with different water fractions.

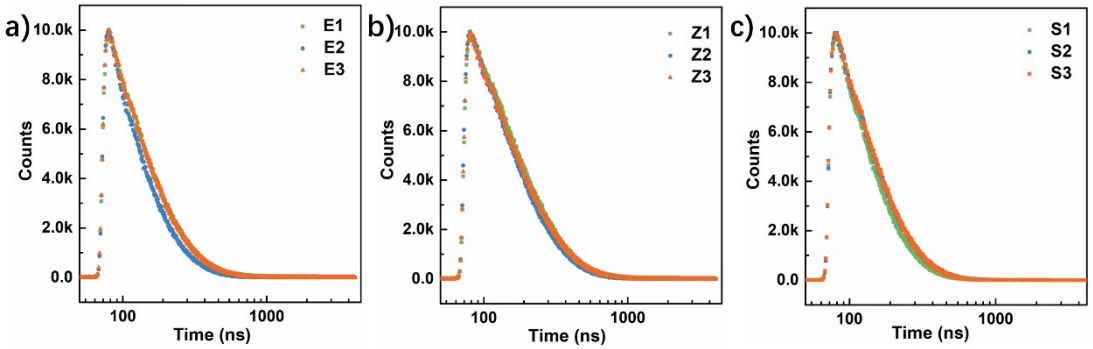


Figure S20. Fluorescence lifetime of *E/Z*/S-2Cl-2NH_2-TPE powders.

Table S5. Fluorescence lifetime and fluorescence efficiency of *E/Z*/S-2Cl-2NH_2-TPE

	Fluorescence lifetime τ (ns)	**Fluorescence quantum yield Φ_F (%)**
E1	98	27.62
E2	88	26.63
E3	97	22.54
Z1	137	56.78
Z2	121	40.80
Z3	133	53.17
S1	85	22.27
S2	97	28.16
S3	98	26.16

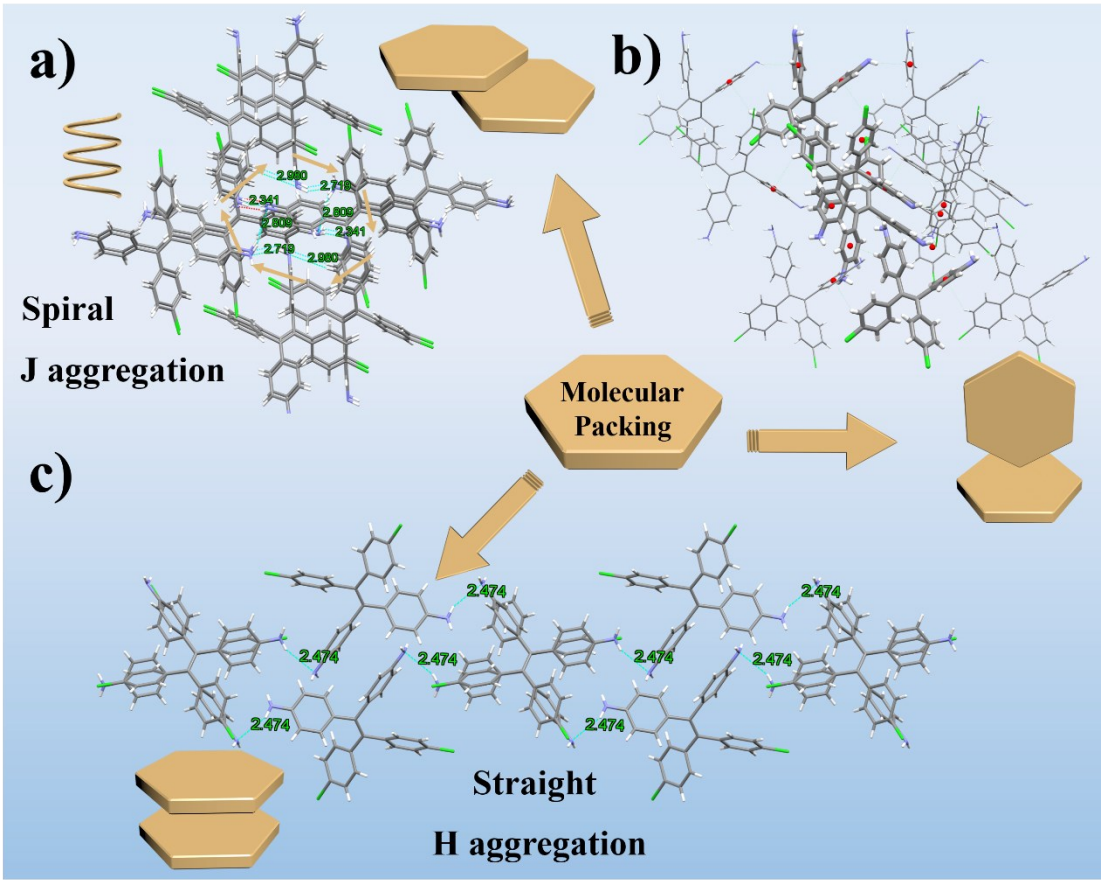


Figure S21. Molecular stacking pattern of three isomers. Molecular packing data was obtained from single crystal.

Theoretical calculations

All quantum-chemistry calculations were performed using the Gaussian 16 suite of programs.[3]

In the calculation of mechanism of non-tautomerization, the optimized conformation $\mathbf{S_0}$, $\mathbf{S_1}$, Cyclic isomer and **TS** of *Z/E*-2Cl-2NH_2-TPE molecules were calculated in THF solvent at M06-2X[4]/6-311G (d,p) level[5]. The conformation CI-twist and CI-cyclic is a method of approximation as reported[6, 7]. Energy calculation were at M06-2X/6-311G (d,p) level. **TS** of S-2Cl-2NH_2-TPE in the **PES** of $\mathbf{S_0}$ at M06-2X/6-311G (d,p) level and **TS** of *Z/E*-2Cl-2NH_2-TPE molecules in the PES of $\mathbf{S_0}$ at HF/6-311G (d,p) level were calculated, giving the vibration form and conformation of the **TS** in shape of scissors. The **TS** calculation of *Z/E*-2Cl-2NH_2-TPE molecules in PES of $\mathbf{S_1}$ were obtained but with a small false frequency of -59 at M06-2X/6-311G (d,p). This is related to the flat PES of $\mathbf{S_1}$ and lower energy barrier (22 kJ/mol).

In the calculation of simulated absorption spectrum, the geometries of the three isomers were optimized by using density functional theory (DFT) at M06-2X/6-31G+(d,p) level.[8] Based on the optimized geometries, time-dependent density functional theory (TDDFT) with the functional CAM-B3LYP[9] and 6-31G+(d,p) basis set was employed to calculate the excitation energies and the oscillator strength for electronic transitions from the ground to excited states. The simulated absorption spectrum was carried out with the aid of a Multiwfn program package.[10]

In the calculation of MC mechanism, the excited geometries conformation of three isomers were optimized by using TDDFT at M06-2X/6-31G+(d,p) level. The range-separated CAM-B3LYP functional was used to calculate the energy for three molecules. In the amorphous-phase calculations, the PCM was used to include the solid-state solvation effect and the state-specific solvation correction was employed.[11-13] In the crystal-phase calculations, the finite-size cluster model derived from the crystallographic data, crystal-phase geometry optimization for $\mathbf{S_1}$ was performed on the central molecule using TDDFT at the CAM-B3LYP/6-31+G(d,p) level while the adjacent molecules were fixed in the initial geometries and treated at the semiempirical PM7 level (two-layer ONIOM)[11, 14].

The optimized ground state or excited state special point of *Z/E*-2Cl-2NH_2-TPE molecular structure is in xyz format at M06-2X/6-311G (d,p) level.

$S_{0(Cl)}$

C	-0.56248100	1.85238200	0.16714600
C	-1.57599900	1.96337100	1.12508100
C	-2.35121100	3.10667900	1.22813700
C	-2.14069900	4.19240800	0.36607300
C	-1.11486200	4.09604700	-0.58437200
C	-0.33817700	2.95150300	-0.66923400
H	-1.76009300	1.13511600	1.80051800
H	-3.12521600	3.17079400	1.98534600
H	-0.92880100	4.92969600	-1.25281000
H	0.45289300	2.90260300	-1.41038000
C	0.26677800	0.62412800	0.04351300
C	-0.26185900	-0.62471100	0.04154000

C	-1.72938600	-0.86033400	-0.07735600
C	-2.48934400	-0.21983900	-1.06099600
C	-2.36950900	-1.76499400	0.77448500
C	-3.85270800	-0.45239700	-1.17903800
H	-2.00582600	0.47252800	-1.74018600
C	-3.73557800	-1.99939100	0.67925300
H	-1.79120000	-2.28697100	1.52853200
C	-4.46274200	-1.33628100	-0.29883500
H	-4.43603900	0.04193600	-1.94506700
H	-4.22953300	-2.68920700	1.35127100
C	0.56619000	-1.85408400	0.16056900
C	1.58154300	-1.96824800	1.11622400
C	0.33734400	-2.95220900	-0.67601700
C	2.35383500	-3.11366500	1.21691800
H	1.76712000	-1.14211000	1.79383800
C	1.11084700	-4.09910100	-0.59331900
H	-0.45716500	-2.90204100	-1.41339500
C	2.13737800	-4.19924700	0.35612100
H	3.13229100	-3.17860800	1.96946800
H	0.92353100	-4.93020200	-1.26477500
C	1.73390700	0.86184700	-0.07552200
C	2.49530700	0.22125900	-1.05809000
C	2.37201900	1.76930700	0.77488900
C	3.85811000	0.45655000	-1.17648700
H	2.01366800	-0.47357800	-1.73605000
C	3.73753600	2.00670000	0.67903500
H	1.79266000	2.29160200	1.52788800
C	4.46606300	1.34355700	-0.29796400
H	4.44259700	-0.03849600	-1.94113900
H	4.22984600	2.69902600	1.34966300
Cl	6.18558500	1.64099000	-0.43470200
N	-2.88002000	5.36033800	0.49914300
H	-3.78824400	5.24620300	0.92552600
H	-2.92350100	5.93631300	-0.32921200
Cl	-6.18295000	-1.62981300	-0.43477500
N	2.95174600	-5.32233800	0.40874300
H	3.40928100	-5.47957000	1.29509700
H	2.54103200	-6.16847500	0.04126600

$S_{1(Cl)}$

C	-1.56553500	0.96350800	-0.36831300
C	-2.17591200	0.08594700	-1.29956700
C	-3.46343800	0.29442700	-1.76338500

C	-4.19308100	1.37756200	-1.28885200
C	-3.64827400	2.24815100	-0.34740500
C	-2.35793900	2.04151600	0.10250400
H	-1.61002500	-0.75644600	-1.67858900
H	-3.90199100	-0.37781700	-2.49021100
H	-4.24126200	3.06772000	0.03878500
H	-1.96330000	2.69653400	0.86933400
C	-0.24086100	0.69253100	0.14437400
C	0.24070400	-0.69260200	0.14431700
C	1.56544800	-0.96340800	-0.36844200
C	2.17548000	-0.08601000	-1.30004000
C	2.35811700	-2.04106400	0.10265200
C	3.46300100	-0.29433100	-1.76392900
H	1.60933600	0.75613700	-1.67922700
C	3.64846400	-2.24755000	-0.34732500
H	1.96368100	-2.69592500	0.86972400
C	4.19295800	-1.37714200	-1.28910500
H	3.90133200	0.37775000	-2.49104100
H	4.24169800	-3.06685200	0.03905200
C	-0.61338600	-1.73749200	0.63942400
C	-1.67042400	-1.45216000	1.54512100
C	-0.50683800	-3.08849400	0.21238200
C	-2.50693500	-2.43299800	2.02771100
H	-1.80158900	-0.43243400	1.88814400
C	-1.34939100	-4.07111500	0.67865100
H	0.23365700	-3.34956900	-0.53392600
C	-2.36347500	-3.77068800	1.61202200
H	-3.29175600	-2.17950900	2.73206100
H	-1.25250200	-5.08765800	0.31269600
C	0.61339800	1.73730000	0.63959900
C	1.67004100	1.45183200	1.54568500
C	0.50736000	3.08821900	0.21227500
C	2.50665700	2.43251400	2.02836200
H	1.80084800	0.43212700	1.88891900
C	1.35001800	4.07072800	0.67863600
H	-0.23280900	3.34934400	-0.53434300
C	2.36369500	3.77021700	1.61240400
H	3.29122700	2.17896600	2.73297200
H	1.25350600	5.08722300	0.31244800
N	3.22866300	4.73982000	2.04642900
H	2.94952500	5.70252200	1.93810700
H	3.76781800	4.55050600	2.87726200
N	-3.22835200	-4.74052400	2.04584900
H	-2.94869100	-5.70312500	1.93790400

H	-3.76767900	-4.55122800	2.87658300
Cl	-5.82510600	1.63993500	-1.86132300
Cl	5.82497000	-1.63933000	-1.86168600

Cyclic isomer (Cl)

C	-2.74554900	3.03756700	-0.06629600
C	-1.30249800	2.95807600	-0.32818800
C	-3.35097900	4.23985400	0.12471500
C	-4.75547000	4.36179300	0.48347400
C	-2.54182100	5.51959300	0.14191200
C	-5.38499200	5.54811300	0.44242600
H	-5.30318500	3.46925000	0.76054700
C	-3.36916100	6.73696100	-0.19698700
H	-2.18185300	5.62439500	1.18657400
C	-4.70018000	6.75897800	-0.01809300
C	-0.59769400	4.08429700	-0.61957600
C	-1.29971400	5.42284200	-0.74421100
C	0.80726900	4.04615200	-0.99190200
C	-0.36315500	6.58123700	-0.48514500
H	-1.63961800	5.50395200	-1.79634900
C	1.54710800	5.16838900	-1.06041700
H	1.26448800	3.08595600	-1.19744500
C	0.94551400	6.43895800	-0.68295200
H	-0.77096100	7.53471400	-0.17401200
C	-3.52659300	1.77123500	0.04110100
C	-4.50221000	1.45864000	-0.90572500
C	-3.28671400	0.86981400	1.08151900
C	-5.22288800	0.27106500	-0.82785500
H	-4.69429600	2.14857200	-1.71982200
C	-3.99858300	-0.31786200	1.17638000
H	-2.52749300	1.09552600	1.82144900
C	-4.95818900	-0.60438000	0.21404100
H	-5.97565200	0.02817600	-1.56659400
C	-0.63533700	1.62660800	-0.29787200
C	0.32493900	1.33242500	0.67164700
C	-0.96079400	0.62763800	-1.22033000
C	0.93525600	0.08696100	0.72928800
H	0.59154600	2.09179900	1.39941800
C	-0.35355600	-0.61666900	-1.17767500
H	-1.70387500	0.82854800	-1.98474100
C	0.60381100	-0.91083700	-0.19552200
H	1.67250700	-0.12177800	1.49698300
H	-2.86037300	7.63088900	-0.54137100

H	-6.43746100	5.61895300	0.69690600
H	2.59290200	5.14447400	-1.33771700
H	-3.81192400	-1.01482800	1.98301300
H	-0.62024700	-1.37574500	-1.90514200
Cl	2.04410700	7.78599500	-0.44519000
Cl	-5.85395800	-2.10448800	0.32159600
N	-5.52383200	7.84329200	-0.33504600
H	-6.33006900	7.93254800	0.26889900
H	-5.03266100	8.72427400	-0.40526100
N	1.16203400	-2.18005800	-0.10487000
H	1.16332000	-2.70865700	-0.96528500
H	2.05711700	-2.22001100	0.36104800

CI-cyclic (Cl)

C	-0.21653700	-0.61806200	-0.04271200
C	0.20047600	0.72393400	-0.00052500
C	0.69954500	-1.64041200	-0.46334900
C	0.27707900	-2.96415900	-0.68382900
C	2.11913500	-1.33537500	-0.70329800
C	1.21536400	-4.00251000	-0.71801900
H	-0.79087100	-3.18105600	-0.73752900
C	3.04807800	-2.42871100	-0.80335000
H	2.32439600	-0.51108300	-1.40511800
C	2.61211500	-3.74100800	-0.70365100
C	1.56949800	1.03349000	0.23130600
C	2.38914200	-0.10683500	0.67552600
C	2.16472700	2.25108700	-0.16154200
C	3.78576700	0.17914900	0.91854500
H	1.86477400	-0.69523500	1.45056500
C	3.52381600	2.47417200	0.04094100
H	1.53896400	3.02926500	-0.60450400
C	4.31116700	1.41841400	0.58652800
H	4.42913900	-0.62903500	1.27949300
C	-1.62563000	-0.96847500	0.21556300
C	-2.12484400	-1.05837100	1.52905700
C	-2.47865200	-1.22988900	-0.86671000
C	-3.47209500	-1.37530700	1.74542100
H	-1.45132400	-0.88003500	2.37433400
C	-3.82061700	-1.54329600	-0.65659500
H	-2.06724300	-1.16586800	-1.87633800
C	-4.31690300	-1.61170200	0.65144800
H	-3.86392700	-1.43418000	2.76598100
C	-0.76547000	1.79491800	-0.24447200

C	-1.53250200	1.81501400	-1.42579500
C	-0.88783100	2.83601600	0.68910900
C	-2.42078500	2.86724400	-1.66049300
H	-1.40116200	1.02107400	-2.16549900
C	-1.79573400	3.87274000	0.46789400
H	-0.27386600	2.79540400	1.59196200
C	-2.56044700	3.88698600	-0.70677200
H	-3.01107500	2.88827900	-2.58172500
H	4.09129000	-2.19752300	-1.05826100
H	0.84328700	-5.03486700	-0.75577900
H	3.97841900	3.43211700	-0.21668700
H	-4.47115500	-1.72221700	-1.51510100
H	-1.90702700	4.66156400	1.21605700
N	3.49128100	-4.81258500	-0.65738200
H	3.15076300	-5.66920700	-1.07067200
H	4.43905300	-4.60421800	-0.93809200
N	-3.50511600	4.89118300	-0.90419100
H	-3.31951000	5.75431100	-0.41397200
H	-3.75711000	5.05596100	-1.86810700
Cl	6.01847600	1.72180500	0.84244000
Cl	-5.99707100	-1.99462600	0.92218700

$TS_{(Cl)}$

C	-0.30500500	1.55226000	0.67142700
C	-1.19514000	1.09722400	1.69534400
C	-1.77134400	1.95836900	2.57901100
C	-1.53485400	3.35684500	2.46857000
C	-0.69618600	3.84006500	1.42046200
C	-0.09964000	2.96653100	0.56520900
H	-1.37695400	0.03303000	1.76802600
H	-2.42166600	1.59664100	3.36581700
H	-0.56582800	4.90876400	1.30309800
H	0.48975700	3.35872000	-0.25291100
C	0.23557900	0.61997900	-0.22851400
C	-0.28444300	-0.74425800	-0.30332700
C	-1.33111700	-0.97808700	-1.22418800
C	-2.01754400	0.09740700	-1.87978100
C	-1.74348600	-2.28777600	-1.64272100
C	-3.02580300	-0.11330800	-2.80661300
H	-1.76238200	1.12350500	-1.64177700
C	-2.75142800	-2.48981700	-2.56172000
H	-1.21861200	-3.15430100	-1.26361900
C	-3.40839800	-1.40364200	-3.14020000

H	-3.52197900	0.73383200	-3.26609100
H	-3.02075600	-3.49842500	-2.85404600
C	0.30121600	-1.69126300	0.62630600
C	1.59115700	-1.49472100	1.17640000
C	-0.40142300	-2.81259500	1.13663600
C	2.14172100	-2.35339900	2.11840800
H	2.19294900	-0.65568000	0.84477000
C	0.15415300	-3.67715800	2.06434800
H	-1.42335900	-2.98438900	0.82241500
C	1.44219600	-3.47172300	2.57486800
H	3.14053900	-2.15985700	2.49781200
H	-0.42822100	-4.52161300	2.42116200
C	1.34870600	0.99530500	-1.11748300
C	1.42167800	0.43188100	-2.40221700
C	2.40500900	1.81002000	-0.67804300
C	2.47559500	0.73285300	-3.24793500
H	0.63114500	-0.22896600	-2.73308200
C	3.48750000	2.08083000	-1.50189900
H	2.40981100	2.18607600	0.33804900
C	3.50006300	1.55332000	-2.78626000
H	2.51820000	0.32323500	-4.24844700
H	4.31576900	2.68204000	-1.15117000
Cl	4.84696100	1.90196100	-3.83473300
N	-2.10555000	4.20740500	3.31746800
H	-2.71764400	3.88129000	4.04918900
H	-1.95273000	5.20117400	3.24576700
Cl	-4.70187500	-1.67379300	-4.30399300
N	2.02675100	-4.39057800	3.46485800
H	2.72606400	-3.97245400	4.06414200
H	1.34681800	-4.88578800	4.02677500

CI-twist (Cl)

C	0.63924600	0.20658100	0.31783600
C	-0.32414800	0.72576800	-0.70608700
C	2.03218400	0.06226800	0.00966900
C	2.99155300	-0.31318700	0.99143800
C	2.47409000	0.39872600	-1.30121900
C	4.34162100	-0.38897700	0.65466300
H	2.66790400	-0.52042100	2.01239700
C	3.82269300	0.30616800	-1.62964600
H	1.70353800	0.70692100	-2.01679700
C	4.74716200	-0.13798000	-0.67127000
C	-0.91519000	2.01493200	-0.59941000

C	-0.36915200	3.04024300	0.23300100
C	-2.03474000	2.39278100	-1.40592200
C	-0.95145700	4.30585900	0.31394000
H	0.52008200	2.81763400	0.83541800
C	-2.60210900	3.66068000	-1.31867400
H	-2.45699300	1.66383400	-2.10249400
C	-2.07582200	4.63695200	-0.45661200
H	-0.51583500	5.04941100	0.98837500
C	0.10765700	-0.29646200	1.58068800
C	-0.84653800	0.44012300	2.32366400
C	0.43929300	-1.60990700	1.99155400
C	-1.34432600	-0.08532600	3.51561500
H	-1.14295200	1.43345000	1.98093500
C	-0.10879300	-2.14434600	3.16276200
H	1.07338800	-2.22762900	1.35064600
C	-0.97654500	-1.37196500	3.94227700
H	-2.04582700	0.50225700	4.11297800
C	-1.07288500	-0.47872800	-1.10838800
C	-0.43416500	-1.58923900	-1.70901200
C	-2.43631500	-0.61901700	-0.74924300
C	-1.16088100	-2.73269500	-2.05408200
H	0.63163900	-1.52718000	-1.94967300
C	-3.16167800	-1.75389700	-1.11090900
H	-2.91236000	0.18868300	-0.18547800
C	-2.56708600	-2.76829900	-1.87063500
H	-0.65243700	-3.56493000	-2.54956100
H	4.16160200	0.54350700	-2.64055100
H	5.07714000	-0.67566300	1.40946900
H	-3.46896000	3.89644100	-1.94391300
H	0.13530800	-3.16731500	3.46077500
H	-4.21804900	-1.82773900	-0.83859800
N	-2.68192900	5.86984500	-0.33134300
H	-2.10716200	6.61550100	0.03206300
H	-3.26754500	6.15995300	-1.10043700
N	-1.54156600	-1.90809100	5.09359900
H	-1.00786000	-2.64410200	5.53261400
H	-1.87586500	-1.23175400	5.76446800
Cl	6.43113900	-0.28919200	-1.10189000
Cl	-3.49092200	-4.14195400	-2.40190000

$S_{0(H)}$

C	1.83276000	0.62470200	-0.09726200
C	2.51356600	-0.13834700	-1.05192700

C	3.89427200	-0.09876500	-1.15895800
C	4.65383000	0.71220900	-0.30442600
C	3.97866300	1.49339700	0.64288600
C	2.59570400	1.45439000	0.73152000
H	1.94742200	-0.77725700	-1.72069700
H	4.39787300	-0.69401700	-1.91307900
H	4.54800800	2.13602200	1.30591300
H	2.09472700	2.07273700	1.46913900
C	0.35088500	0.58304700	0.02683100
C	-0.35334600	-0.57591500	0.02812500
C	0.31094100	-1.90637400	0.15222300
C	1.25583300	-2.14962400	1.15429500
C	-0.03296900	-2.95176500	-0.71046000
C	1.85773500	-3.39608100	1.27510400
H	1.51893500	-1.34925500	1.83678800
C	0.57870400	-4.19557800	-0.59975700
H	-0.78085200	-2.78040000	-1.47726000
C	1.52708300	-4.42192600	0.39345900
H	2.58443000	-3.56818200	2.06043500
H	0.31124500	-4.98996700	-1.28670100
C	-1.83538000	-0.62033600	-0.09126400
C	-2.52191200	0.14622300	-1.03916400
C	-2.59298900	-1.45913500	0.73331500
C	-3.90265300	0.10144100	-1.14315400
H	-1.95999200	0.78955700	-1.70725000
C	-3.97589300	-1.50434200	0.64705200
H	-2.08763600	-2.08299100	1.46324500
C	-4.65666200	-0.72059900	-0.29408600
H	-4.41063600	0.70336400	-1.88905400
H	-4.54082700	-2.15210000	1.30885400
C	-0.31063000	1.91467000	0.15144300
C	-1.25840000	2.15886400	1.15065500
C	0.03904300	2.96045300	-0.70853500
C	-1.85771100	3.40653500	1.27091000
H	-1.52650200	1.35834400	1.83098400
C	-0.56991900	4.20561900	-0.59816700
H	0.78940100	2.78856600	-1.47276600
C	-1.52140400	4.43276800	0.39182800
H	-2.58742100	3.57895500	2.05332000
H	-0.29783900	5.00030900	-1.28293300
N	6.03497000	0.79449100	-0.44327600
H	6.46805700	-0.01626600	-0.86188100
H	6.52796000	1.09385900	0.38581300
N	-6.04582800	-0.71795400	-0.34974800

H	-6.43479900	-0.43763500	-1.23866600
H	-6.48784300	-1.55430100	0.00399300
H	-1.99198500	5.40447600	0.48295200
H	1.99937200	-5.39276100	0.48510400

$S_{1(H)}$

C	0.30244500	1.80961900	0.69752000
C	1.34603000	1.67760600	1.64684500
C	2.02860400	2.78315600	2.12894400
C	1.72378000	4.06312400	1.66959800
C	0.72237700	4.21674000	0.70793500
C	0.02676100	3.11985000	0.23026800
H	1.59410000	0.68926000	2.01626400
H	2.80908100	2.64568700	2.86880300
H	0.49579300	5.20214200	0.31647100
H	-0.71173400	3.25814000	-0.55028100
C	-0.36263400	0.63811700	0.16489700
C	0.36261700	-0.63812500	0.16494700
C	-0.30247800	-1.80960000	0.69760200
C	-1.34611700	-1.67754200	1.64686300
C	-0.02675900	-3.11985800	0.23044200
C	-2.02870700	-2.78307000	2.12899000
H	-1.59421500	-0.68917800	2.01621500
C	-0.72239000	-4.21672500	0.70813600
H	0.71177700	-3.25818900	-0.55006100
C	-1.72384700	-4.06306200	1.66973600
H	-2.80922600	-2.64556400	2.86879900
H	-0.49577700	-5.20214900	0.31674200
C	1.70488100	-0.68368900	-0.34430700
C	2.18272200	0.31050400	-1.24100800
C	2.65377900	-1.66100800	0.06167300
C	3.46836000	0.29630400	-1.73465700
H	1.50205800	1.08860800	-1.56648800
C	3.94438100	-1.67046400	-0.41619200
H	2.36745600	-2.39929700	0.80056800
C	4.38078200	-0.69956200	-1.34047800
H	3.79077200	1.06283700	-2.43126800
H	4.64677000	-2.41939800	-0.06574800
C	-1.70487000	0.68366600	-0.34442200
C	-2.18269100	-0.31058700	-1.24106900
C	-2.65376700	1.66103800	0.06143500
C	-3.46830300	-0.29639400	-1.73478500
H	-1.50202900	-1.08873200	-1.56645700

C	-3.94434400	1.67048700	-0.41649500
H	-2.36746300	2.39937800	0.80028600
C	-4.38072100	0.69952500	-1.34073000
H	-3.79069800	-1.06297200	-2.43135500
H	-4.64673400	2.41946300	-0.06614300
N	-5.68137100	0.68348600	-1.78349100
H	-6.20437000	1.54262100	-1.70804300
H	-5.87512500	0.15830900	-2.62266600
N	5.68145600	-0.68352500	-1.78317100
H	6.20447100	-1.54264100	-1.70762700
H	5.87523800	-0.15841300	-2.62238100
H	-2.26594500	-4.92446000	2.04051200
H	2.26586500	4.92453800	2.04035200

CI-twist (H)

C	-0.59124400	0.64608100	-0.21351500
C	0.62675800	0.55608100	0.65508800
C	-1.32272100	1.87400100	-0.32850600
C	-2.41004800	2.02753900	-1.23369800
C	-0.87986500	2.99895900	0.42333200
C	-3.05583100	3.25721300	-1.34644200
H	-2.72120100	1.18516500	-1.85308700
C	-1.54094600	4.21793000	0.31269200
H	-0.02324800	2.84076600	1.08813900
C	-2.65884000	4.33362300	-0.52833400
C	1.93444900	0.43520500	0.10920600
C	2.23183200	0.77540300	-1.24658000
C	3.05217500	0.06513400	0.92183300
C	3.52387500	0.66713500	-1.76263900
H	1.41808000	1.11317200	-1.89997100
C	4.33655700	-0.03362700	0.39486400
H	2.88973300	-0.15095900	1.98097900
C	4.59548000	0.26021100	-0.95415600
H	3.69798600	0.90978300	-2.81540000
C	-1.10828800	-0.57911000	-0.81518500
C	-0.25381900	-1.48826400	-1.48479800
C	-2.46010700	-0.93621200	-0.59383600
C	-0.78468200	-2.65749700	-2.02859500
H	0.80139300	-1.23856700	-1.61208600
C	-2.96637200	-2.13812300	-1.10064600
H	-3.08683200	-0.29799400	0.03410900
C	-2.13804200	-2.98513800	-1.84471900
H	-0.13481900	-3.33724500	-2.58521000

C	0.15795100	-0.22124600	1.81665800
C	-0.88062100	0.24458200	2.65708600
C	0.62954900	-1.54123900	2.02359000
C	-1.32871200	-0.52479300	3.73502800
H	-1.29977400	1.24108100	2.48677000
C	0.19270200	-2.29841100	3.11021800
H	1.35240200	-1.95356700	1.31344900
C	-0.69784600	-1.75700600	4.04485200
H	-2.10846300	-0.12882400	4.39216300
H	-1.21632000	5.07696200	0.90413100
H	-3.88915200	3.37422300	-2.04271400
H	5.15643000	-0.33772300	1.05309700
H	-4.00536500	-2.41649300	-0.90605500
H	0.58799100	-3.30710200	3.25792000
N	5.86154000	0.09862600	-1.48420500
H	6.05624900	0.61756200	-2.32782500
H	6.62422300	0.12640000	-0.82356300
N	-2.63117900	-4.19377200	-2.32947800
H	-3.62719800	-4.21219500	-2.49472300
H	-2.11693200	-4.58210700	-3.10702000
H	-3.18199900	5.27996900	-0.59650900
H	-1.00576700	-2.32686100	4.91241400

CI-cyclic (H)

C	-0.28650400	0.61085000	0.11281100
C	0.33697900	-0.64898400	0.13963600
C	-1.65478700	0.72463900	-0.30694600
C	-2.26167200	1.97722500	-0.51216200
C	-2.47234700	-0.47218700	-0.56202000
C	-3.65720800	2.08250700	-0.54555700
H	-1.63786500	2.87137800	-0.55457500
C	-3.89901400	-0.31983200	-0.66071100
H	-2.05227700	-1.20192200	-1.27277200
C	-4.48834500	0.92980800	-0.54575400
C	-0.44101600	-1.82004900	0.35671200
C	-1.82113500	-1.56503400	0.80362100
C	-0.03222200	-3.10731500	-0.05194800
C	-2.63538000	-2.73820300	1.03184600
H	-1.84746900	-0.78696800	1.58833900
C	-0.86264700	-4.20855300	0.13662100
H	0.95774800	-3.23380800	-0.49615100
C	-2.16109700	-3.99375900	0.68443800
H	-3.65876400	-2.60111100	1.39414800

C	0.49215500	1.83306700	0.38651300
C	0.79119500	2.22615400	1.70508000
C	0.92999300	2.62397400	-0.68589700
C	1.54817300	3.38200400	1.93603800
H	0.42613900	1.62211700	2.54281500
C	1.68557900	3.77370100	-0.46126500
H	0.67658300	2.30641200	-1.69962400
C	1.99732100	4.14927600	0.85163900
H	1.79095200	3.68220400	2.96048000
C	1.77515200	-0.75538100	-0.10512500
C	2.34489200	-0.22638800	-1.27978600
C	2.58139700	-1.43642300	0.82039200
C	3.71388800	-0.37287300	-1.51581900
H	1.70252300	0.26709500	-2.01367200
C	3.95390200	-1.55831800	0.59814800
H	2.10845300	-1.84156300	1.71812900
C	4.51792600	-1.02677100	-0.56982500
H	4.15619200	0.03034400	-2.43197100
H	-4.49494000	-1.20345600	-0.92679200
H	-4.09969700	3.08708800	-0.57104800
H	-0.53113000	-5.21250400	-0.13333000
H	2.03359400	4.36247800	-1.31242400
H	4.57822300	-2.06202400	1.34036200
N	-5.86697500	1.09964100	-0.49583700
H	-6.20632000	1.95589900	-0.91145300
H	-6.40495700	0.29803800	-0.79398300
N	5.89661400	-1.09976700	-0.76709800
H	6.35226400	-1.86386700	-0.28893700
H	6.18925200	-1.04015500	-1.73193800
H	-2.80606100	-4.85250700	0.83876300
H	2.58901200	5.03890900	1.03209000

Cyclic isomer (H)

C	-2.74483100	3.03795300	-0.05663100
C	-1.30193600	2.95838500	-0.31940500
C	-3.35095200	4.24081800	0.12911300
C	-4.75617400	4.36253200	0.48446600
C	-2.54161200	5.52082400	0.14421300
C	-5.38742400	5.54824300	0.43977900
H	-5.30282300	3.46910100	0.76132500
C	-3.37094100	6.73439700	-0.20569800
H	-2.18641900	5.63383000	1.19006200
C	-4.70201000	6.75609100	-0.02760600

C	-0.59529500	4.08369700	-0.61338700
C	-1.29439600	5.42373500	-0.73433500
C	0.81038100	4.04870400	-0.98798800
C	-0.35274200	6.57838800	-0.48369600
H	-1.63153800	5.50211700	-1.78864200
C	1.54443300	5.17694300	-1.04941600
H	1.26694700	3.08718400	-1.18989300
C	0.96519100	6.46097800	-0.67140500
H	-0.77803600	7.52874400	-0.18110500
C	-3.52657600	1.77127800	0.05239100
C	-4.49292900	1.45198500	-0.90281900
C	-3.29542900	0.87867000	1.10283200
C	-5.20927900	0.26112500	-0.81649900
H	-4.67375000	2.14028800	-1.72154300
C	-4.01197100	-0.30815600	1.19248100
H	-2.54152300	1.11577200	1.84542100
C	-4.96847600	-0.62256300	0.22985800
H	-5.95266600	0.02439100	-1.56862500
C	-0.63665600	1.62492000	-0.29630700
C	0.32266900	1.32213900	0.67121900
C	-0.96165300	0.63222500	-1.22534400
C	0.93259800	0.07568300	0.72043600
H	0.58995500	2.07659600	1.40386800
C	-0.35590100	-0.61362700	-1.19067900
H	-1.70573400	0.83880100	-1.98724200
C	0.60087800	-0.91513500	-0.21107700
H	1.66966300	-0.13901900	1.48684900
H	-2.86296300	7.62512700	-0.55971500
H	-6.44047300	5.61983200	0.69185700
H	2.59194500	5.13239900	-1.32353300
H	-3.82201300	-0.99077800	2.01233000
H	-0.62387500	-1.36797600	-1.92275200
N	-5.52684600	7.83890300	-0.35482500
H	-6.32960400	7.93346900	0.25320000
H	-5.03348600	8.71862700	-0.42719100
N	1.15899300	-2.18750100	-0.12878200
H	1.16593200	-2.70303600	-0.99730100
H	2.05730400	-2.22534400	0.33150500
H	1.62262400	7.31046600	-0.52559300
H	-5.52253600	-1.55135000	0.29661000

TS of S-2Cl-2NH_2-TPE

C	0.26286800	1.43342300	-0.94907900

C	1.64801900	1.57232100	-1.23668800
C	2.18875600	2.72930300	-1.77193300
C	1.37435500	3.82584000	-2.01979700
C	0.02986000	3.77393600	-1.68552300
C	-0.50486900	2.61104800	-1.15237600
H	2.33215100	0.75893900	-1.03517600
H	3.24840200	2.78000500	-1.99113600
H	-0.59808100	4.64675000	-1.81820600
H	-1.53392400	2.64257900	-0.82608000
C	-0.30948800	0.24873500	-0.33042200
C	0.62258400	-0.62362500	0.40437500
C	0.70694000	-0.49463800	1.85086400
C	-0.35717500	0.04038400	2.61956800
C	1.93350800	-0.67578200	2.53175100
C	-0.24576300	0.25213400	3.97003400
H	-1.29624100	0.27279800	2.13564400
C	2.07190100	-0.42309400	3.88125600
H	2.82145800	-0.94140800	1.97435300
C	0.97537900	0.01465700	4.64243900
H	-1.09329300	0.62979500	4.53070600
H	3.03902400	-0.53849300	4.35663700
C	1.44757200	-1.54214200	-0.31998700
C	1.44409400	-1.53212600	-1.74597600
C	2.13756000	-2.62977000	0.28954700
C	2.17256600	-2.41881900	-2.48723900
H	0.84754800	-0.78618900	-2.25572700
C	2.84324200	-3.54991700	-0.44144400
H	2.05837500	-2.78723400	1.35562600
C	2.91377500	-3.44765800	-1.85080600
H	2.16096200	-2.36899800	-3.56969900
H	3.33019500	-4.38194300	0.05327300
C	-1.69656800	-0.13544400	-0.35478800
C	-2.15148900	-1.28934800	0.35085600
C	-2.67494900	0.45912000	-1.20228000
C	-3.46426800	-1.72275900	0.31776600
H	-1.45100700	-1.87332100	0.93605100
C	-3.98587000	0.01392300	-1.25568800
H	-2.39754200	1.25227400	-1.87963700
C	-4.39233800	-1.05713100	-0.47307100
H	-3.76199800	-2.59437300	0.88813800
H	-4.69122400	0.49684800	-1.92135900
N	1.07732800	0.20385600	5.98594300
H	1.99264300	0.23567700	6.40580300
H	0.36006700	0.72801000	6.46121000

Cl	-6.06039100	-1.60383800	-0.52333000
N	3.62591500	-4.32767400	-2.57387300
H	4.11685600	-5.08788800	-2.13260400
H	3.64190400	-4.28166000	-3.57955800
Cl	2.05544200	5.28730800	-2.71439100

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