Synthesis, Structure and Optoelectronic Properties of Rigid 3D Tetraindeno-Fused Spirofluorene with Thioxanthene or dioxothioxanthene Substitutes

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Table of Contents

General experimental methods

^{1}H NMR and ^{13}C NMR spectra were recorded in $C_2D_2Cl_4$ or $CDCl_3$ using a Bruker DPX 400 or 500 spectrometer. High-resolution MALDI mass spectrometry measurements were performed on a Solarix ESI-/MALDI-ICR (9.4 T) system. UV–vis absorption spectra were recorded using a Shimadu and SPECORD S600 spectrophotometer. Photoluminescence performance was investigated by a steady-state fluorescence spectrometer FLS920 at room temperature with the scanning range between 200 nm to 800 nm. CV measurements were carried out on a computer-controlled GSTAT12 in a three-electrode cell in a DCM solution of Bu_4NPF_6 (0.1 M), using glassy carbon discs as the working electrode, Pt wire as the counter electrode, Ag/AgCl electrode as the reference electrode. Thermogravimetric analysis (TGA) was carried out on Shanghai Tian Mei Balance (Ltd ZRY-2P) at a heating rate of 10 ºC /min under nitrogen flow. Density functional theory (DFT) calculations were performed using the Gaussian 09 program, with the B3LYP hybrid functional and basis set 6-31G(d) for the ground-state geometry optimization. All reagents and starting materials were obtained from commercial suppliers and used without further purification. All reported yields are isolated yields.

Experimental Section

Spiro-4S: (2-Bromophenyl)(phenyl)sulfane (2.64 g, 10 mmol) was dissolved in 40 mL dry THF, which was dropwised to a flask equipped with iodine (10 mg, 0.04 mmol) and magnesium (0.29 g, 12 mmol) at the beginning to initiate the Grignard reaction at argon atmosphere. Then, the mixture was heated to 80 °C for 5 h. Thereafter, **Spiro-4O** (1.9 g, 2 mmol) was added to the mixture all at once and refluxed 12 h. After cooling to room temperature, the reaction was quenched by 1M HCl (50 mL) and then extracted with DCM (3 × 50 mL). The combined organic solvent was removed by rotary evaporator to obtain tertiary alcohol intermediate

Spiro-4OH, which was used directly in the next step without purification. The resulting **Spiro-4OH** was dissolved in 100 mL acetic acid and refluxed overnight. Then the acetic acid was removed by distillation under reduced pressure. The residue was subjected to column chromatography to obtain desired pure compound as white solid (2.6 g, 80%). ^{1}H NMR (500 MHz, $C_2D_2Cl_4$) δ 8.17 (s, 4H), 7.49 (d, *J* = 7.3 Hz, 8H), 7.44 (s, 4H), 7.22 (d, *J* = 7.3 Hz, 4H), 7.19 (t, *J* = 8.0 Hz, 8H), 7.12 (d, *J* = 8.1 Hz, 4H), 6.99 (s, 4H), 6.90 (t, *J* = 8.0 Hz, 8H), 6.58 (d, *J* = 7.6 Hz, 8H), 1.22 (s, 36H). ^{13}C NMR (126 MHz, $C_2D_2Cl_4$): δ 155.91, 151.47, 150.17, 149.36, 141.53, 140.70, 138.68, 138.09, 131.35, 128.73, 127.25, 126.21, 126.50, 126.07, 125.85, 116.85, 116.44, 115.60, 59.85, 34.88, 31.68.

HR-MS (MALDI) m/z calculated for $C_{117}H_{89}S_4$

[M^+] 1621.5847. Found 1621.5859. Crystallographic data (CCDC deposition number): CCDC 1564493.

Spiro-4SO2:

Spiro-4S (1.62 g, 1.0 mmol) was dissolved in CH_2Cl_2 (250 mL) and meta-chloroperbenzoic acid (1.73 g, 10 mmol) was added slowly. The mixture was stirred overnight. Then, the organic layer was washed with saturated $NaHCO_3$ solution (3×75 mL) and concentrated under reduced pressure. The crude product was purified by column chromatography to obtain target compound **Spiro-4SO2** with 30% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.8 Hz, 8H), 7.89 (s, 2H), 7.57 – 7.50 (m, 12H), 7.36 – 7.26 (m, 10H), 7.25 – 7.19 (m, 8H), 7.17 (d, *J* = 8.2 Hz, 4H), 6.70 (dd, *J* = 8.0, 3.2 Hz, 8H), 1.28 (s, 36H). ^{13}C NMR (100 MHz, $C_2D_2Cl_4$): δ 152.64, 152.21, 150.13, 149.70, 142.21, 141.14, 140.53, 140.24, 136.78, 133.12, 129.69, 128.49, 127.09, 125.26, 123.55, 117.78, 117.04, 116.60, 57.71, 35.02, 31.68.

HR-MS (MALDI) m/z calculated for $C_{117}H_{88}O_8NaS_4$

[M^+] 1771.5260. Found 1771.5273. Crystallographic data (CCDC deposition number): CCDC 1564494.

TGA curves

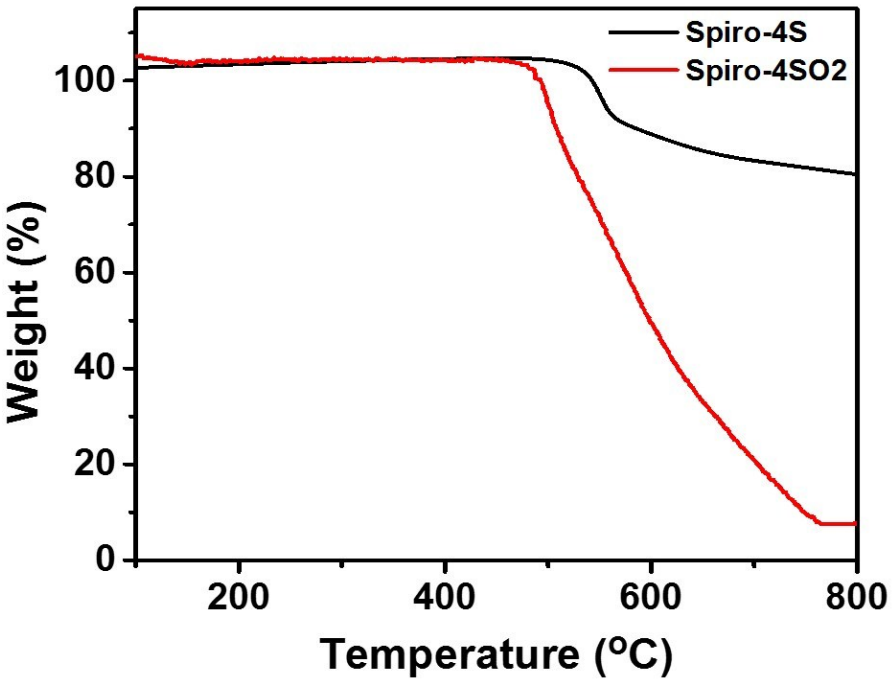


Figure S1. TGA curve for **Spiro-4S and Spiro-4SO2** measured under a nitrogen atmosphere at a heating rate of 10 ºC/min.

Absorption and emission spectra

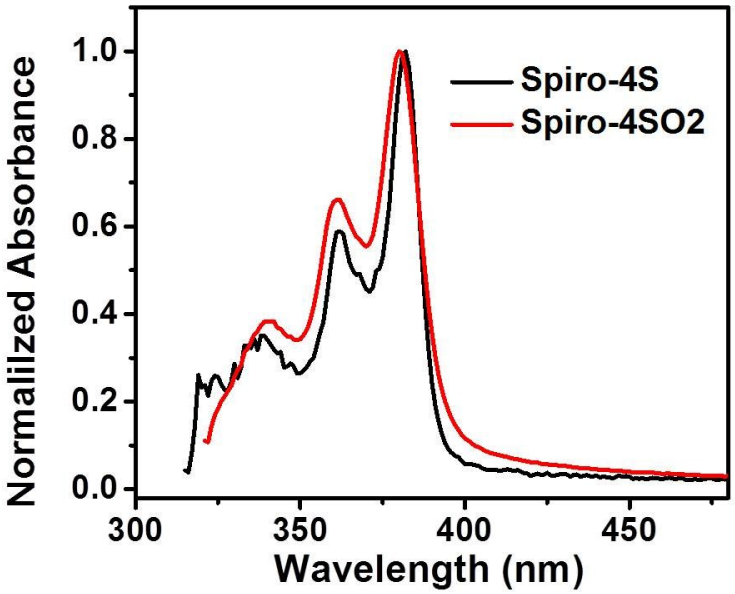


Figure S2. Absorption spectra of **Spiro-4S** film (black line) and **Spiro-4SO2** film (red line).

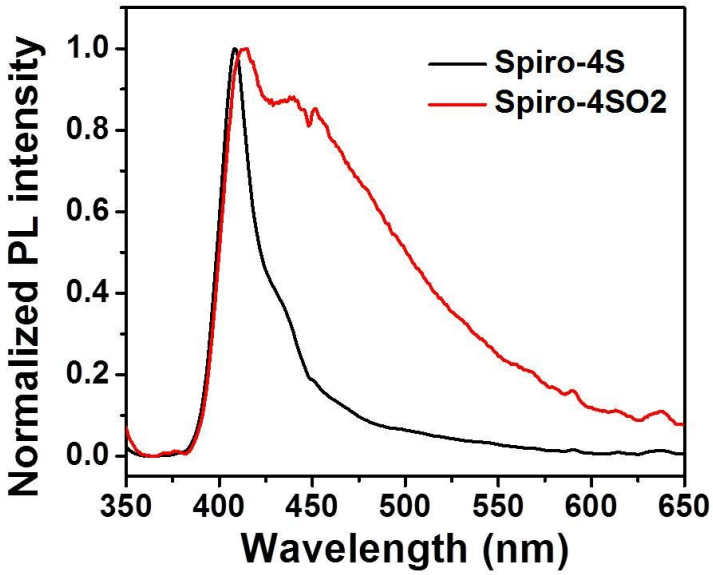


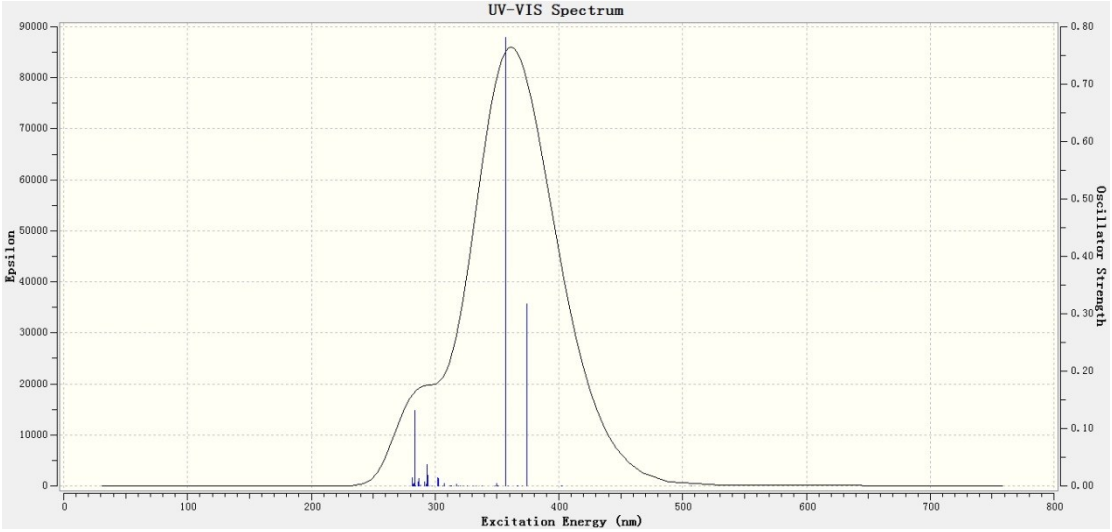
Figure S3. Photoluminescence spectra of **Spiro-4S** film (black line) and **Spiro-4SO2** film (red line) (λ_{Exc} = 337 nm).

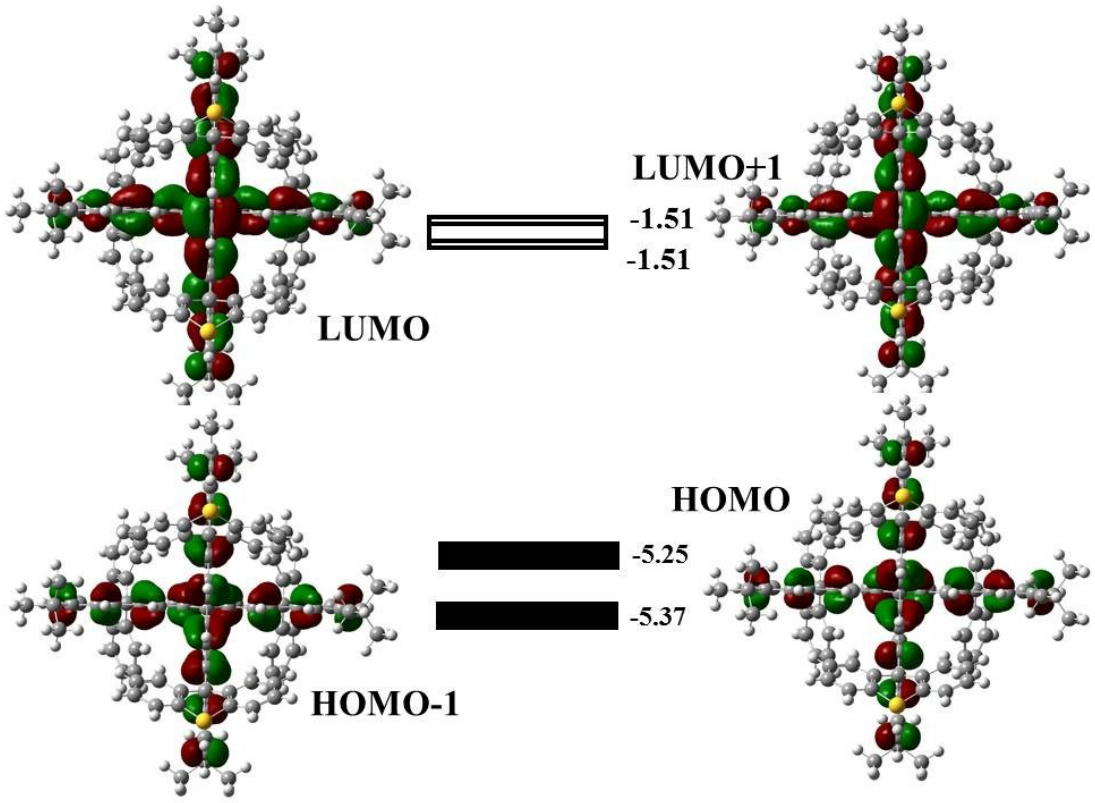
TD-DFT calculations

Table S1. Calculated energy levels, oscillator strengths (f), and orbital transition analyses of **Spiro-4S**.

	E_g (eV)	E_g (nm)	f	transition	coefficient	transition	coefficient
S_1	3.3105	374.52	0.3177	HOMO-1 -> LUMO+1	-0.12349	HOMO -> LUMO	0.69126
S_2	3.3119	374.36	0.3166	HOMO-1 -> LUMO	0.12800	HOMO -> LUMO+1	0.69044
S_3	3.4712	357.18	0.7812	HOMO-1 -> LUMO	0.68838	HOMO -> LUMO+1	-0.11914
S_4	3.4720	357.10	0.7640	HOMO-1 -> LUMO+1	0.68917	HOMO -> LUMO	-0.11456
S_5	3.5449	349.76	0.0031	HOMO-5 -> LUMO	-0.10653	HOMO-5 -> LUMO+1	-0.15771
				HOMO-4 -> LUMO	0.47567	HOMO-4 -> LUMO+1	-0.38504
				HOMO-3 -> LUMO	0.20193	HOMO-3 -> LUMO+1	-0.16611
S_6	3.5449	349.76	0.0041	HOMO-5 -> LUMO	0.37411	HOMO-5 -> LUMO+1	-0.15771
				HOMO-4 -> LUMO	0.47567	HOMO-4 -> LUMO+1	0.38504
				HOMO-2 -> LUMO	0.21190	HOMO-2 -> LUMO+1	0.25693
S_7	3.5462	349.62	0.0007	HOMO-5 -> LUMO	-0.22454	HOMO-5 -> LUMO+1	-0.26926
				HOMO-2 -> LUMO	0.38863	HOMO-2 -> LUMO+1	0.46660
S_8	3.5469	349.55	0.0014	HOMO-4 -> LUMO	-0.21301	HOMO-4 -> LUMO+1	-0.17509
				HOMO-3 -> LUMO	-0.49957	HOMO-3 -> LUMO+1	-0.40775
S_9	3.7180	333.47	0.0000	HOMO-2 -> LUMO	0.54324	HOMO-2 -> LUMO+1	-0.45241
S_{10}	3.7234	332.99	0.0000	HOMO-3 -> LUMO	0.44693	HOMO-3 -> LUMO+1	0.54505
T_1	2.4435	507.41	0.0000	HOMO-1 -> LUMO	0.17199	HOMO-1 -> LUMO+1	-0.39133
				HOMO -> LUMO	0.47352	HOMO-1 -> LUMO+1	-0.10830
T_2	2.4441	507.28	0.0000	HOMO-1 -> LUMO	-0.39260	HOMO-1 -> LUMO+1	-0.17229
				HOMO -> LUMO	0.10823	HOMO-1 -> LUMO+1	0.47232
T_3	3.0797	402.58	0.0000	HOMO-1 -> LUMO+12	0.12500	HOMO -> LUMO+11	-0.15695
				HOMO -> LUMO+7	-0.25890	HOMO-1 -> LUMO+6	0.25358
				HOMO-5 -> LUMO+1	0.11660	HOMO+7 -> LUMO+1	-0.11030
				HOMO-9 -> LUMO+1	-0.22035	HOMO-4 -> LUMO	0.19700
				HOMO-6 -> LUMO	-0.12317	HOMO-8 -> LUMO	0.20252

T_4	3.0868	401.66	0.0000	HOMO -> LUMO+12	-0.12501	HOMO -> LUMO+7	-0.13573
				HOMO-1 -> LUMO+11	0.15804	HOMO-1 -> LUMO+7	0.23518
				HOMO -> LUMO+6	-0.23913	HOMO-1 -> LUMO+6	-0.14456
				HOMO-4-> LUMO+1	0.17575	HOMO-6-> LUMO+1	-0.12211
				HOMO-8-> LUMO+1	0.19920	HOMO-5-> LUMO	0.12549
				HOMO-7-> LUMO	-0.11133	HOMO-9-> LUMO	-0.22235
T_5	3.3469	370.45	0.0000	HOMO-> LUMO+1	0.48402	HOMO-1-> LUMO+1	0.12993
				HOMO-> LUMO	0.47658		
T_6	3.3472	370.42	0.0000	HOMO-> LUMO+1	0.48402	HOMO-1-> LUMO+1	0.12993
				HOMO-1-> LUMO	0.47996		
T_7	3.3794	366.88	0.0000	HOMO-22-> LUMO+22	-0.12611	HOMO-> LUMO+3	-0.13338
				HOMO-16-> LUMO+16	0.12541	HOMO-1-> LUMO+3	0.10925
				HOMO-2-> LUMO+3	0.10145	HOMO-4-> LUMO+3	0.18698
				HOMO-5-> LUMO+3	0.22265	HOMO-6-> LUMO+3	0.18134
				HOMO-7-> LUMO+3	0.31151	HOMO-20-> LUMO+3	0.12045
				HOMO-22-> LUMO+3	-0.15345		
T_8	3.3799	366.82	0.0000	HOMO-13-> LUMO+26	0.10209	HOMO-22-> LUMO+23	-0.11022
				HOMO-23-> LUMO+23	0.14539	HOMO-17-> LUMO+17	-0.13034
				HOMO-> LUMO+2	0.11145	HOMO-1-> LUMO+2	0.13461
				HOMO-3-> LUMO+2	0.10226	HOMO-4-> LUMO+2	0.17166
				HOMO-5-> LUMO+2	-0.22416	HOMO-6-> LUMO+2	0.33338
				HOMO-7-> LUMO+2	-0.16043	HOMO-14-> LUMO+2	0.12196
				HOMO-15-> LUMO+2	-0.10138	HOMO-17-> LUMO+2	-0.14614
T_9	3.3828	366.52	0.0000	HOMO-21-> LUMO+23	0.16543	HOMO-17-> LUMO+18	0.10731
				HOMO-18-> LUMO+18	0.10271	HOMO-1-> LUMO+5	0.10279
				HOMO-4-> LUMO+5	-0.20299	HOMO-5-> LUMO+5	0.24414
				HOMO-6-> LUMO+5	0.17506	HOMO-7-> LUMO+5	-0.12076
				HOMO-8-> LUMO+5	0.24816	HOMO-9-> LUMO+5	0.16816
				HOMO-14-> LUMO+5	-0.11288	HOMO-17-> LUMO+5	-0.11834
				HOMO-18-> LUMO+5	-0.10023		
T_{10}	3.3842	366.36	0.0000	HOMO-20-> LUMO+23	-0.11720	HOMO-20-> LUMO+22	-0.1370
				HOMO-> LUMO+5	0.10338	HOMO-4-> LUMO+5	0.19693
				HOMO-5-> LUMO+5	0.23384	HOMO-7-> LUMO+5	-0.21037
				HOMO-8-> LUMO+5	-0.22916	HOMO-9-> LUMO+5	0.19038
				HOMO-14-> LUMO+5	0.11312	HOMO-16-> LUMO+5	0.10850





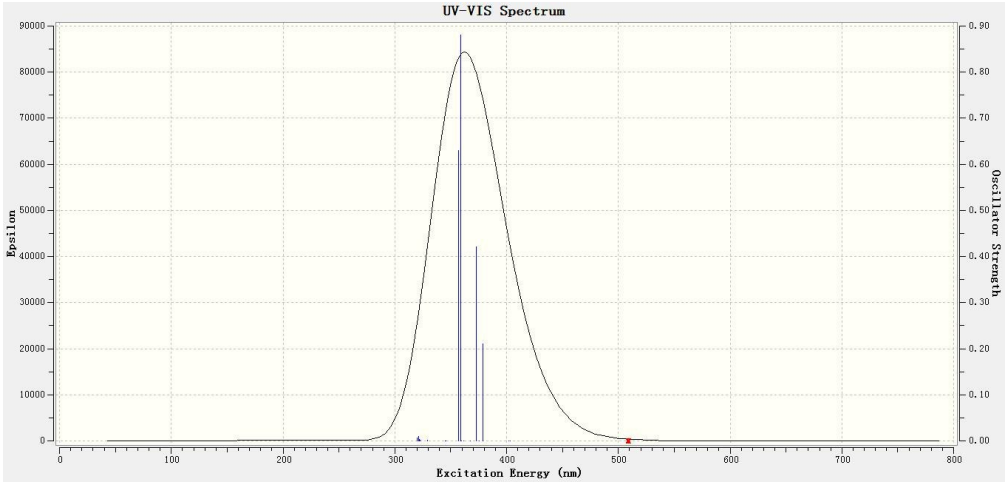
Excited State 1	**Excited State 2**	**Excited State 3**	**Excited State 4**
Energy: 3.31	Energy: 3.31	Energy: 3.47	Energy: 3.47
Wavelength: 374.52 nm	Wavelength: 374.36 nm	Wavelength: 357.18 nm	Wavelength: 357.10 nm
Oscillator strength: 0.32	Oscillator strength: 0.32	Oscillator strength: 0.78	Oscillator strength: 0.76
Configurations:	Configurations:	Configurations:	Configurations:
HOMO-1→LUMO+1	HOMO-1→LUMO	HOMO-1→LUMO	HOMO-1→LUMO+1
HOMO→LUMO	HOMO→LUMO+1	HOMO→LUMO+1	HOMO→LUMO

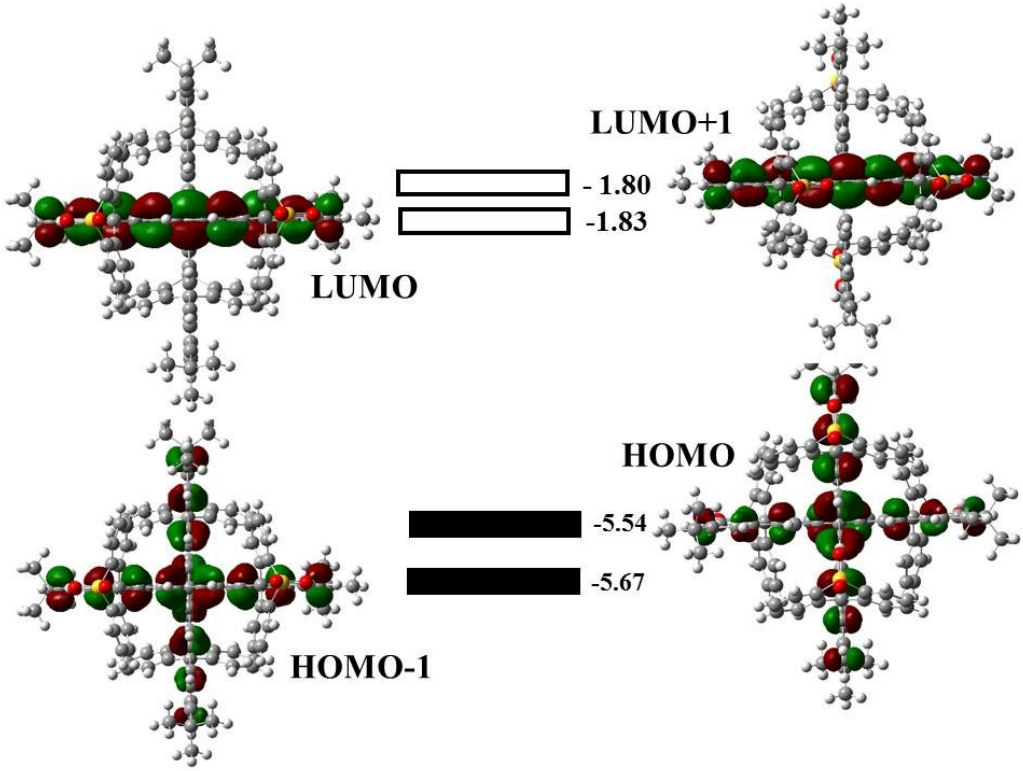
Figure S4. Calculated absorption spectrum of **Spiro-4S** (up); molecular orbitals and their energy levels (in eV) of **Spiro-4S**, as well as some major excitations calculated by TD-DFT at the B3LYP6-31G(d) level.

Table S2. Calculated energy levels, oscillator strengths (f), and orbital transition analyses of **Spiro-SO2**.

	E_g (eV)	E_g (nm)	f	transition	coefficient	transition	coefficient
S_1	3.2731	378.80	0.2110	HOMO-1 -> LUMO	-0.10058	HOMO -> LUMO	0.69620
S_2	3.3260	372.77	0.4215	HOMO-1 -> LUMO+1	0.15199	HOMO -> LUMO+1	0.68587
S_3	3.4537	358.99	0.8813	HOMO-1 -> LUMO	0.69492		
S_4	3.4753	356.76	0.6292	HOMO-1 -> LUMO+1	0.68740	HOMO -> LUMO+1	-0.14767
S_5	3.7653	329.28	0.0012	HOMO-1 -> LUMO+2	-0.23373	HOMO -> LUMO+2	0.65792
S_6	3.8453	322.43	0.0010	HOMO-1 -> LUMO+3 HOMO -> LUMO+3	0.31705 0.52692	HOMO-> LUMO+6	0.28315
S_7	3.8503	322.01	0.0026	HOMO-1 -> LUMO+3 HOMO-1 -> LUMO+4 HOMO -> LUMO+6	-0.17119 0.28926 0.29175	HOMO -> LUMO+3 HOMO -> LUMO+4	-0.17360 0.48481

S_8	3.8593	321.26	0.0098	HOMO-1 -> LUMO+3 HOMO-1 -> LUMO+6 HOMO-> LUMO+3 HOMO -> LUMO+5 HOMO -> LUMO+7	-0.15760 -0.13143 -0.12863 0.10577 0.25743	HOMO-1 -> LUMO+4 HOMO-1 -> LUMO+7 HOMO -> LUMO+4 HOMO -> LUMO+6	-0.22194 0.12850 -0.27049 0.41713
S_9	3.8729	320.13	0.0063	HOMO-7 -> LUMO HOMO-1 -> LUMO+7 HOMO -> LUMO+5 HOMO -> LUMO+7	-0.10595 0.24276 0.21974 0.49135	HOMO-1 -> LUMO+4 HOMO -> LUMO+4 HOMO -> LUMO+6	0.12814 0.16084 -0.19395
S_{10}	3.8741	320.04	0.0010	HOMO-1-> LUMO+5 HOMO-1 -> LUMO+5	-0.30653 0.59463	HOMO-> LUMO+7	-0.18818
T_1	2.4341	509.37	0.0000	HOMO-1 -> LUMO+1	-0.34805	HOMO -> LUMO+1	0.54171
T_2	2.4386	508.43	0.0000	HOMO-1 -> LUMO	0.49452	HOMO -> LUMO	0.41717
T_3	3.0739	403.34	0.0000	HOMO-6 -> LUMO HOMO-1 -> LUMO+9 HOMO-1 -> LUMO+15 HOMO-1 -> LUMO+19 HOMO -> LUMO+15	0.18189 -0.13963 0.18113 -0.10340 0.14998	HOMO-3 -> LUMO+1 HOMO-2 -> LUMO HOMO-1 -> LUMO+16 HOMO -> LUMO+9	-0.13613 0.37266 0.11506 -0.19080
T_4	3.0851	401.88	0.0000	HOMO-8 -> LUMO+1 HOMO-3 -> LUMO+1 HOMO-1 -> LUMO+9 HOMO-1 -> LUMO+14 HOMO -> LUMO+14	0.13579 0.34547 -0.15643 -0.10733 0.16766	HOMO-5 -> LUMO+1 HOMO-2 -> LUMO HOMO-1 -> LUMO+12 HOMO -> LUMO+12 HOMO-> LUMO+19	0.16244 0.15266 0.14227 -0.20387 -0.11279
T_5	3.2989	375.83	0.0000	HOMO-1 -> LUMO	-0.42943	HOMO -> LUMO	0.54762
T_6	3.3744	367.43	0.0000	HOMO-1 -> LUMO+1	0.56690	HOMO-> LUMO+1	0.38652
T_7	3.4291	361.56	0.0000	HOMO-1 -> LUMO+5 HOMO-1 -> LUMO+7 HOMO-> LUMO	0.11827 0.41830 0.10204	HOMO-1 -> LUMO+5 HOMO-1 -> LUMO+7	0.13436 0.45851
T_8	3.4465	359.74	0.0000	HOMO-1 -> LUMO+6 HOMO-1 -> LUMO+6	-0.25969 0.52518	HOMO-> LUMO+1 HOMO -> LUMO+14	0.15028 0.13957
T_9	3.5862	345.73	0.0000	HOMO-19 -> LUMO+10 HOMO-22 -> LUMO+21 HOMO-18 -> LUMO+3 HOMO-16 -> LUMO+3 HOMO-14 -> LUMO+21 HOMO-4 -> LUMO+10 HOMO-12 -> LUMO+10	-0.12617 0.14117 -0.19923 -0.18421 0.12858 0.11135 0.12729	HOMO-22 -> LUMO+15 HOMO-22 -> LUMO+22 HOMO-17 -> LUMO+3 HOMO-14 -> LUMO+9 HOMO-14 -> LUMO+22 HOMO-14 -> LUMO+10	-0.10062 0.11423 -0.23961 0.13427 0.11135 0.10062
T_{10}	3.5902	345.34	0.0000	HOMO-28 -> LUMO+8 HOMO-23 -> LUMO+20 HOMO-19 -> LUMO+6 HOMO-19 -> LUMO+20 HOMO-8 -> LUMO+8 HOMO-3 -> LUMO+8 HOMO -> LUMO+8	-0.15926 0.16556 -0.12538 0.18020 -0.16665 0.12214 -0.11749	HOMO-23 -> LUMO+14 HOMO-20 -> LUMO+2 HOMO-19 -> LUMO+12 HOMO-18 -> LUMO+2 HOMO-5 -> LUMO+8 HOMO -> LUMO+2	-0.12712 -0.31544 0.10589 -0.18641 0.11757 -0.11399

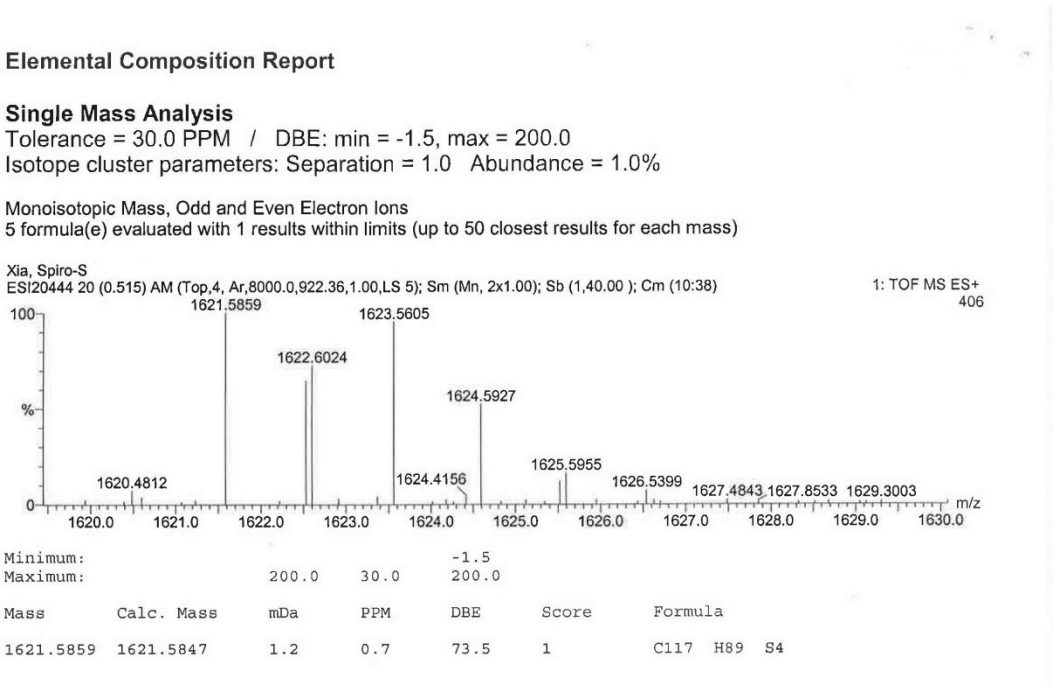




Excited State 1	**Excited State 2**	**Excited State 3**	**Excited State 4**
Energy: 3.27 eV	Energy: 3.33 eV	Energy: 3.45 eV	Energy: 3.47 eV
Wavelength: 378.80 nm	Wavelength: 372.77 nm	Wavelength: 358.99 nm	Wavelength: 356.76 nm
Oscillator strength: 0.21	Oscillator strength: 0.42	Oscillator strength: 0.88	Oscillator strength: 0.63
Configurations:	Configurations:	Configurations:	Configurations:
HOMO-1→LUMO	HOMO-1→LUMO+1	HOMO-1→LUMO	HOMO-1→LUMO+1
HOMO→LUMO	HOMO→LUMO+1		HOMO→LUMO+1

Figure S5. Calculated absorption spectrum of **Spiro-4SO2** (up).Molecular orbitals and their energy levels (in eV) of **Spiro-4SO2**, as well as some major excitations calculated by TD-DFT at the B3LYP6-31G(d) level.

HR-Mass spectra



Elemental Composition Report

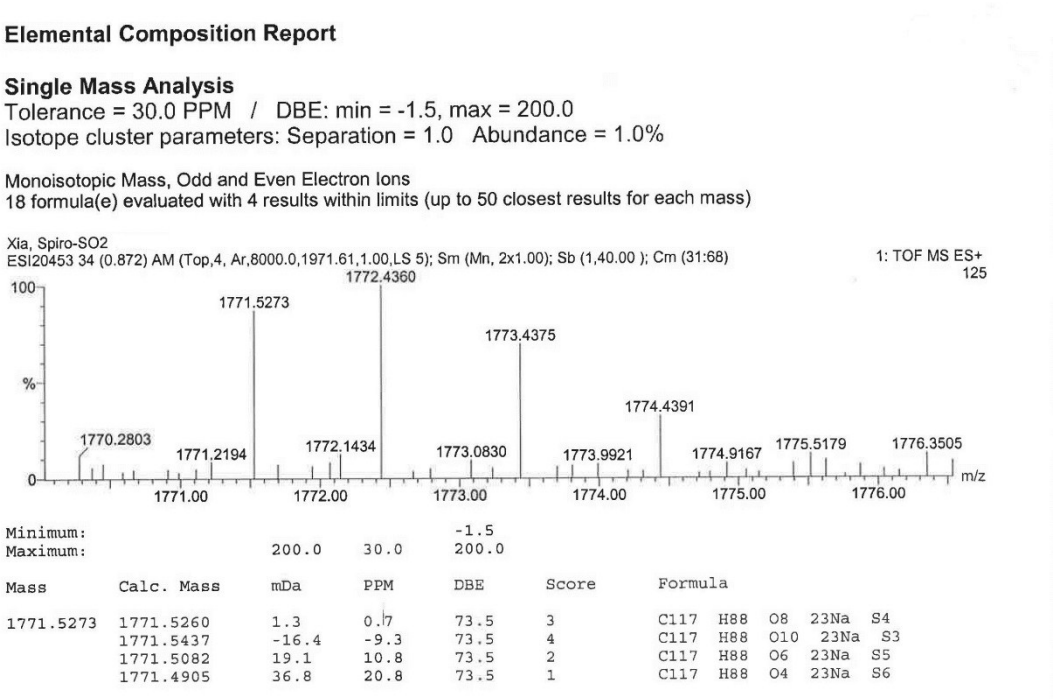
Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions
5 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Xia, Spiro-S
ESI20444 20 (0.515) AM (Top,4, Ar,8000.0,922.36,1.00,LS 5); Sm (Mn, 2x1.00); Sb (1,40.00); Cm (10:38) 1: TOF MS ES+ 406

Minimum:				-1.5		
Maximum:		200.0	30.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
1621.5859	1621.5847	1.2	0.7	73.5	1	C117 H89 S4

Figure S6. High-resolution MALDI mass spectrum of **Spiro-4S.**



Elemental Composition Report

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 200.0
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

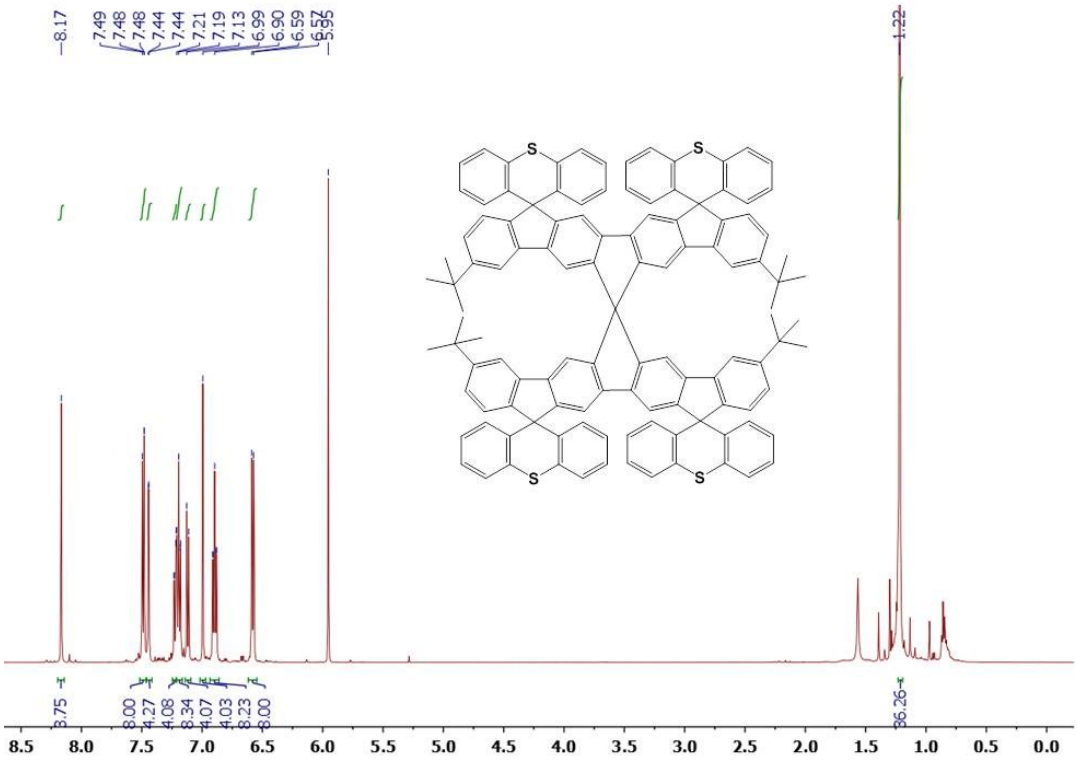
Monoisotopic Mass, Odd and Even Electron Ions
18 formula(e) evaluated with 4 results within limits (up to 50 closest results for each mass)

Xia, Spiro-SO2
ESI20453 34 (0.872) AM (Top,4, Ar,8000.0,1971.61,1.00,LS 5); Sm (Mn, 2x1.00); Sb (1,40.00); Cm (31:68) 1: TOF MS ES+ 125

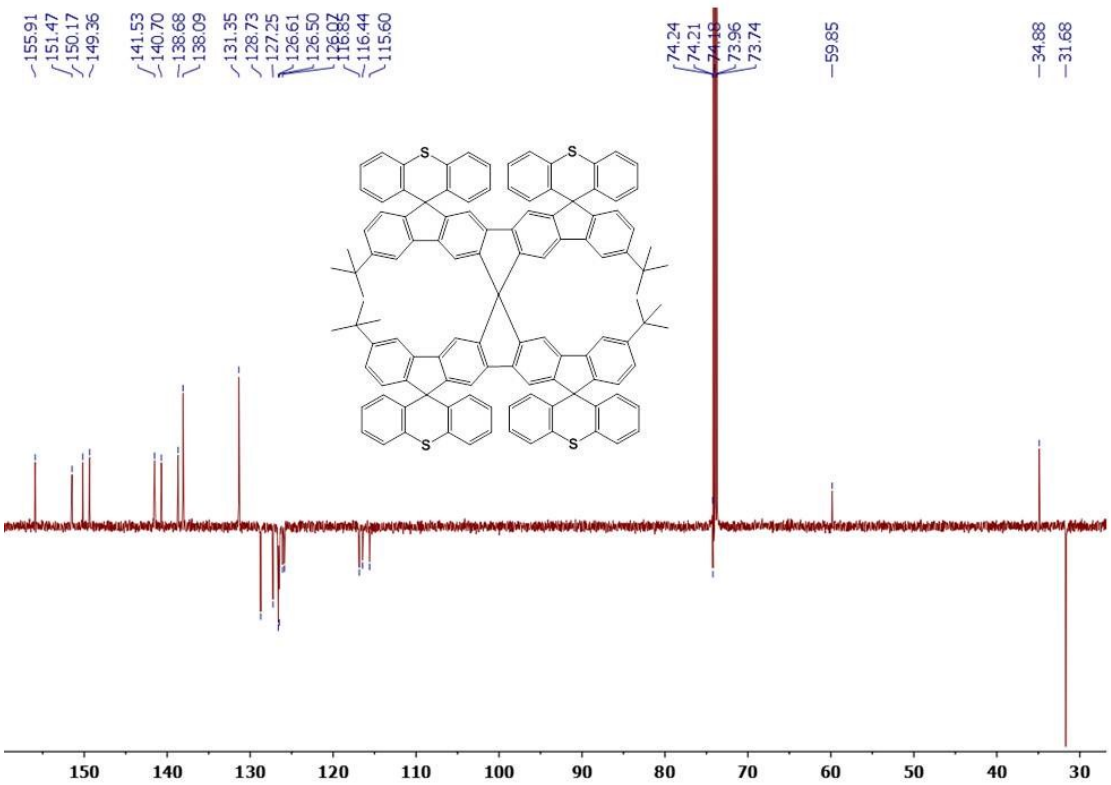
Minimum:				-1.5		
Maximum:		200.0	30.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
1771.5273	1771.5260	1.3	0.7	73.5	3	C117 H88 O8 23Na S4
	1771.5437	-16.4	-9.3	73.5	4	C117 H88 O10 23Na S3
	1771.5082	19.1	10.8	73.5	2	C117 H88 O6 23Na S5
	1771.4905	36.8	20.8	73.5	1	C117 H88 O4 23Na S6

Figure S7. High-resolution MALDI mass spectrum of **Spiro-4SO2.**

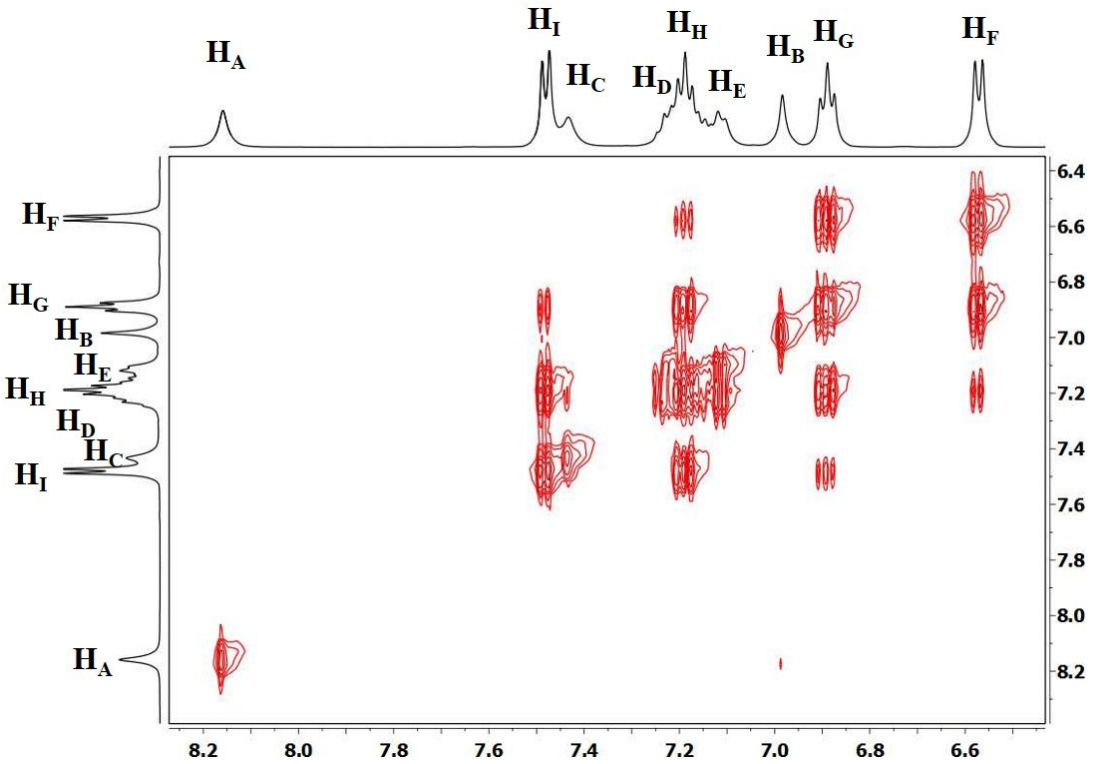
^{1}H−NMR and ^{13}C−NMR Spectra



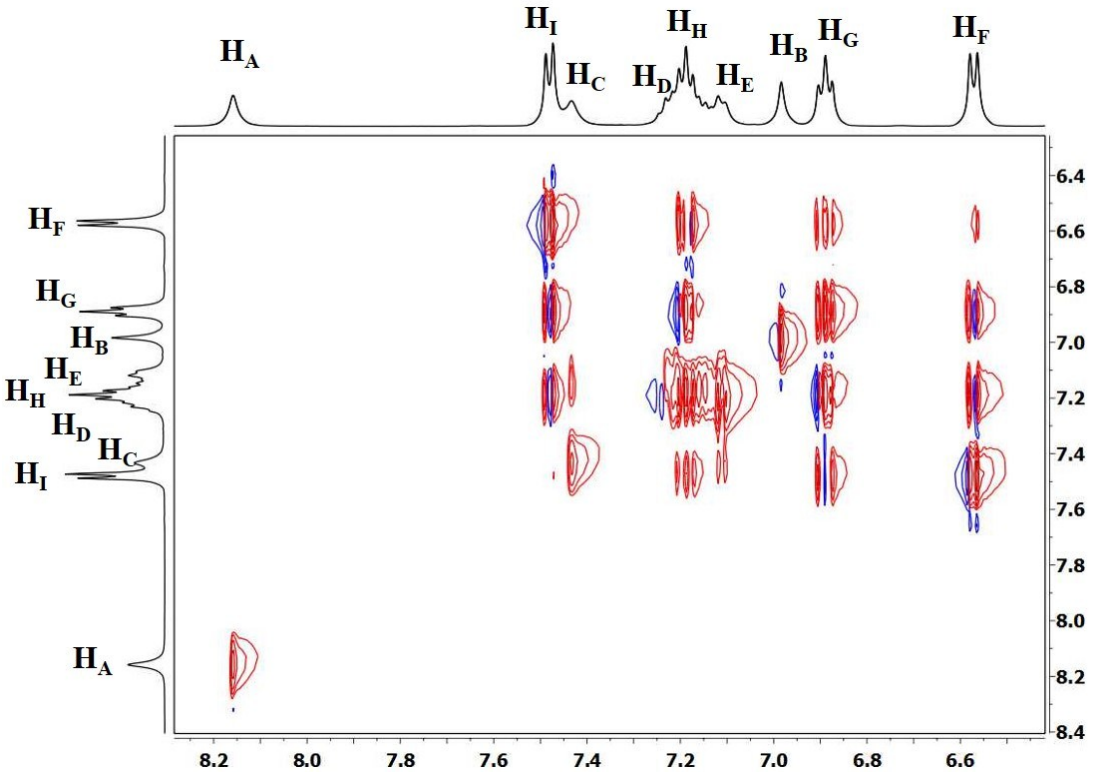
^{1}H-NMR spectrum of **Spiro-4S** (298K, $C_2D_2Cl_4$, 500 MHz).



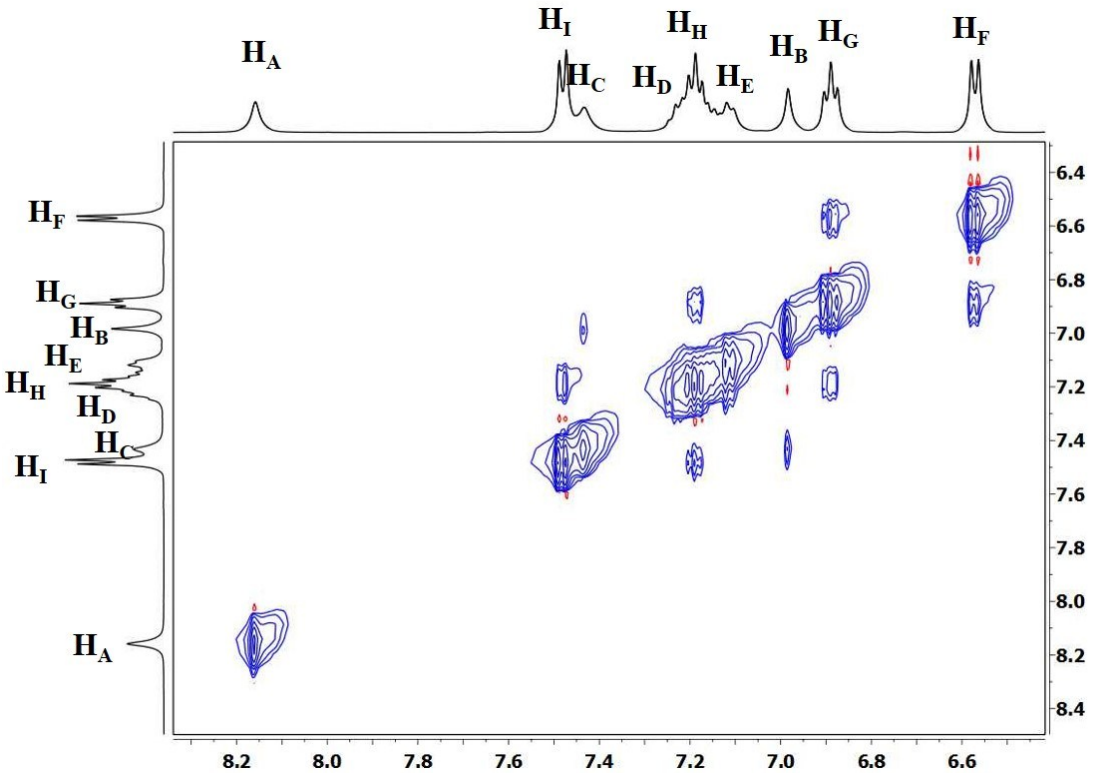
^{13}C-NMR spectrum of **Spiro-4S** (298K, $C_2D_2Cl_4$, 126 MHz).



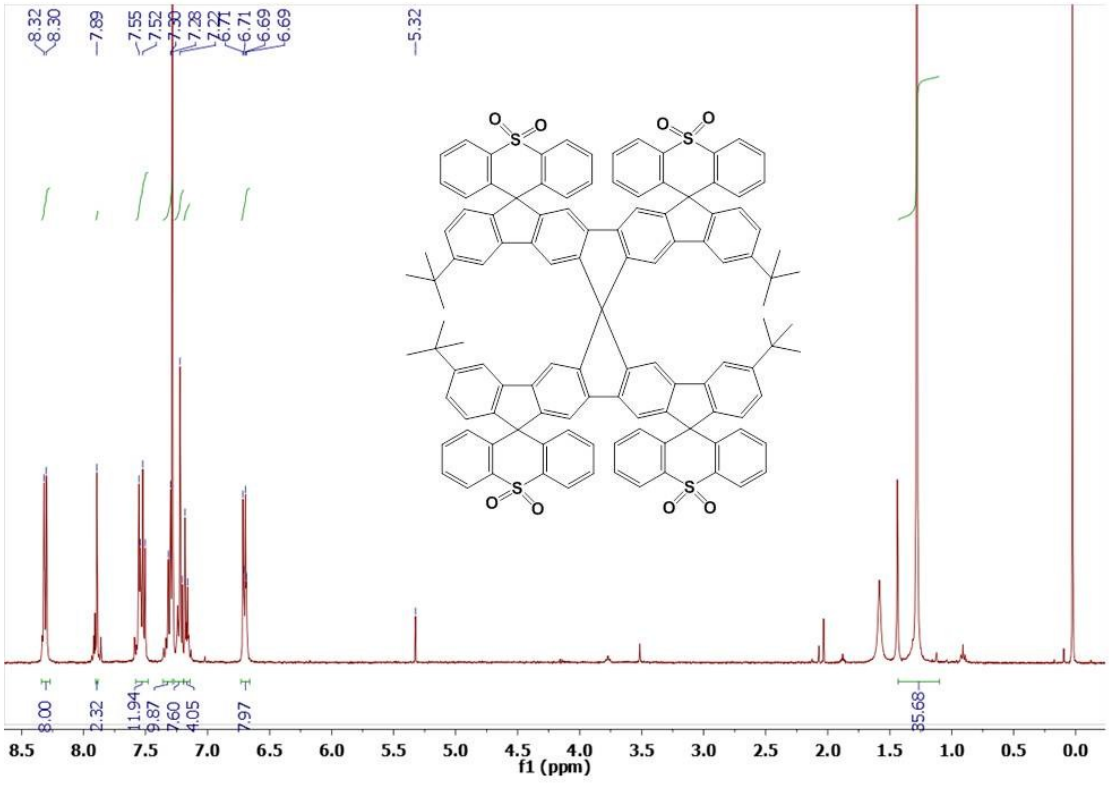
Aromatic region of H-H COSY spectrum of **Spiro-4S** (298K, $C_2D_2Cl_4$, 500 MHz).



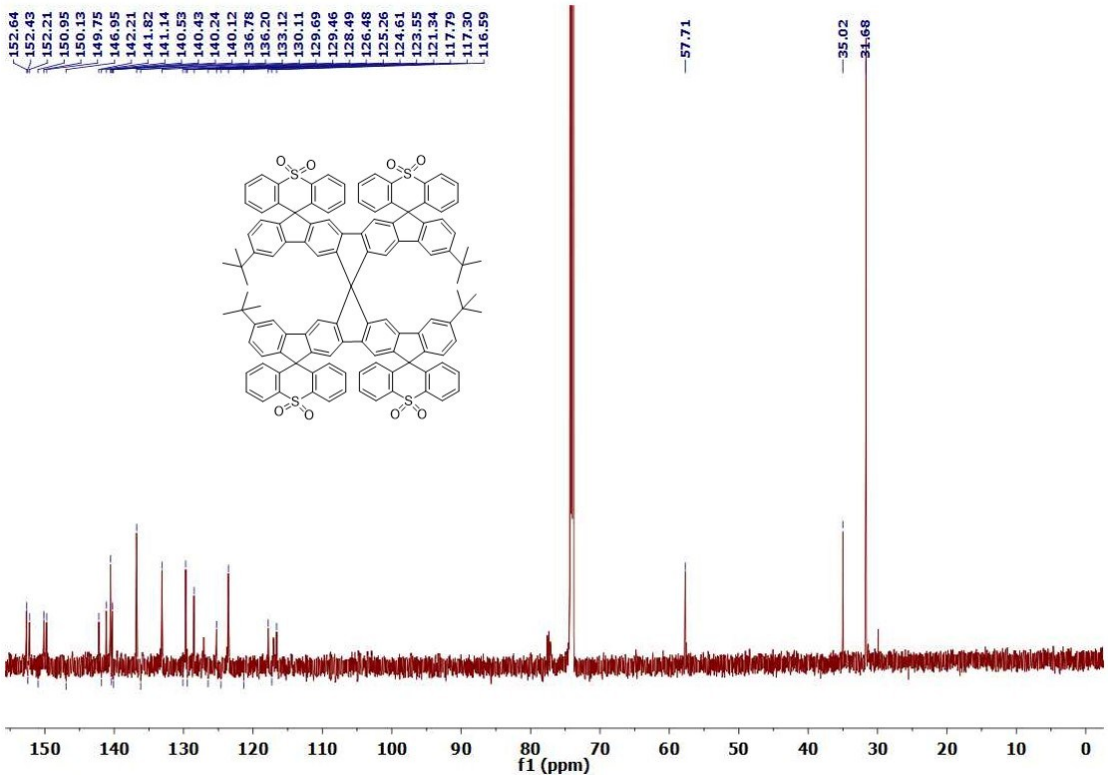
Aromatic region of H-H TOCSY spectrum of **Spiro-4S** (298K, $C_2D_2Cl_4$, 500 MHz).



Aromatic region of H-H NOESY spectrum of **Spiro-4S** (298K, $C_2D_2Cl_4$, 500 MHz).



^{1}H-NMR spectrum of **Spiro-4SO2** (298K, $CDCl_3$, 400 MHz).



^{13}C-NMR spectrum of **Spiro-4SO2** (298K, $C_2D_2Cl_4$, 151 MHz).

Single crystal structure

Crystal structure of Spiro-4S

Cambridge Crystallographic Data Centre deposition number: CCDC 1564493

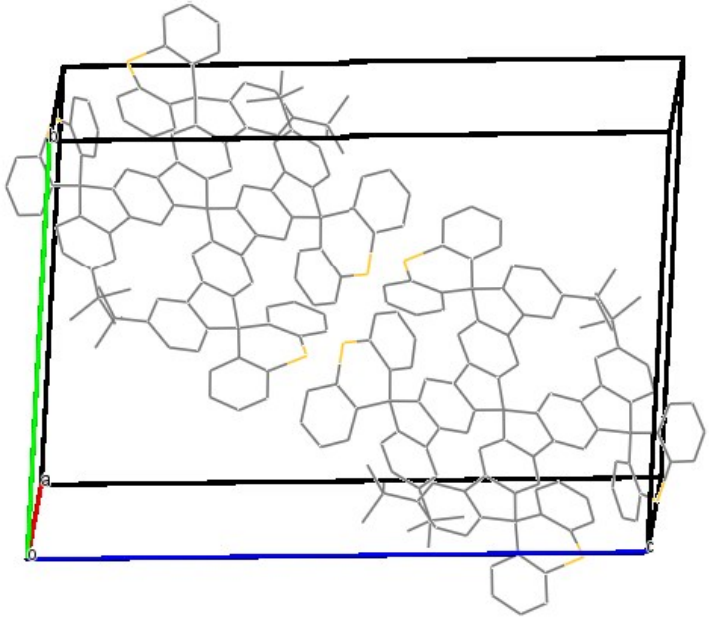


Table S3. Crystallographic table.

Compound	**Spiro-4S**
Molecular formula	$C_{157}H_{168}O_{10}S_4$
Formula weight	2343.14 $gmol^{-1}$
Absorption coefficient	$\mu = 0.135\ mm^{-1}$
Crystal size	
Space group	P-1 (triclinic)
Lattice parameters	a = 15.9701(10) Å alpha = 86.261(4) deg. b = 17.8188(8) Å beta = 87.234(4) deg. c = 25.3977(11) Å gamma = 63.893(5) deg.
Volume	6474.6(6) $Å^3$
Z value	2
F (000)	2508.0
Calculated density	$d_{xray} = 1.202 mg/m^3$
Temperature	173.0 K
Theta range for data collection	$2.9° < \theta < 25.3°$
Limiting indices	$-19 \leq h \leq 19$, $-21 \leq k \leq 21$, $-30 \leq l \leq 30$
Total number of reflections	63701
Unique number of reflections	23660 ($R_{int} = 0.0571$)
Refinement method	Full-matrix least-squares on F^2
Final R indices [I>2sigma(I)]	R1 = 0.1217, wR2 = 0.3276
R indices (all data)	R1 = 0.1912, wR2 = 0.3935
Goodness of fit	S = 1.206
Largest diff. peak and hole	2.135 and -0.551 $eÅ^{-3}$

Crystal structure of Spiro-4SO2

Cambridge Crystallographic Data Centre deposition number: CCDC 1564494

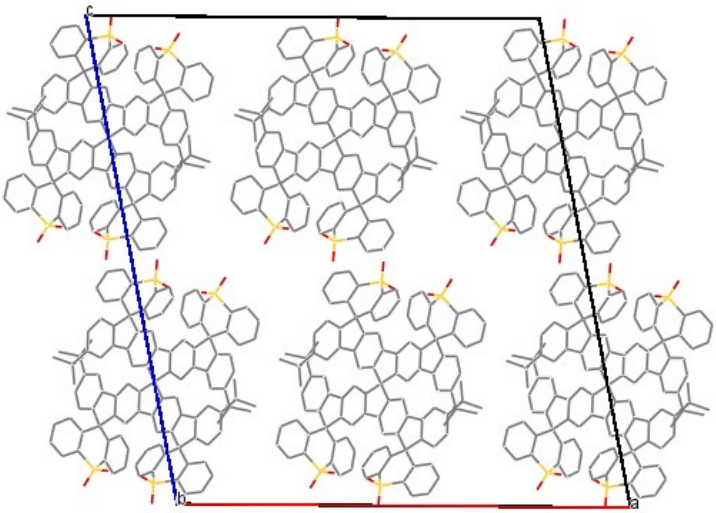


Table S4. Crystallographic table.

Compound	**Spiro-4SO2**
Molecular formula	$C_{133}H_{104}Cl_{32}O_8S_4$
Formula weight	3092.80 $gmol^{-1}$
Absorption coefficient	μ = 0.514 mm^{-1}
Space group	C 1 2/ c 1 (monoclinic)
Lattice parameters	a = 31.7737(8) Å alpha = 90 deg. b = 18.4299(6) Å beta = 101.028(2) deg. c = 34.7940(6) Å gamma = 90 deg.
Volume	19998.6(9) $Å^3$
Z value	4
F (000)	6296
Calculated density	d_{xray} = 1.027mg/m^3
Temperature	173.0 K
Theta range for data collection	$3.1° < \theta < 25.0°$
Limiting indices	$-37 \leq h \leq 34$, $-21 \leq k \leq 19$, $-41 \leq l \leq 41$
Total number of reflections	36447
Unique number of reflections	17507 (R_{int} = 0.0365)
Refinement method	Full-matrix least-squares on F^2
Final R indices [I>2sigma(I)]	R1 = 0.1438, wR2 = 0.4203
R indices (all data)	R1 = 0.1836, wR2 = 0.4561
Goodness of fit	S = 1.612
Largest diff. peak and hole	1.585 and -0.874 $eÅ^{-3}$