Supporting Information

A general approach to S-rhodamines from diaryl thioethers and its application for constructing pH probe

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CONTENTS

1. Experimental section

1.1 Materials and Instruments

Unless otherwise stated, all reagents and solvents for synthesis and detection were purchased from commercial suppliers and used without further purification. All water used was from Millipore water purification system with a minimum resistivity of 18.0 MΩ·cm. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 spectrometer. Mass spectrometry data were obtained with Waters Xevo G2-XS QTof. UV-Vis absorption spectra were collected on Shimadzu UV-1900i Spectrophotometer. Fluorescence measurements were performed on PerkinElmer LS55 and Zolix SFQY-9000 fluorescence spectrophotometers. The fluorescence imaging was performed by using Olympus FV1000 MPE confocal laser scanning microscope.

1.2 Synthesis

3,3'-thiobis(*N,N*-dimethylaniline): This compound was synthesized according to the literature with slight modification [1]. The mixture of 3-iodide-*N,N*-diethylaniline (3.95 g, 16 mmol), CuI (305 mg, 1.6 mmol), K_2CO_3 (2.21 g, 16 mmol), $Na_2S{\cdot}9H_2O$ (2.5 g, 10.4 mmol), and 15 mL DMF were stirred vigorously at 120 °C for 15 h under N_2. The resulting mixture was cooled to room temperature and diluted with EtOAc (100 mL). After washing with water (2 × 50 mL) and brine (50 mL), the organic layers dried over Na_2SO_4 and then concentrated under vacuum. The residue was purified by column chromatography to give product (2.05 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, J = 8.0 Hz, 2H), 6.81 – 6.72 (m, 2H), 6.69 (d, J = 7.6 Hz, 2H), 6.59 (dd, J = 8.4, 2.5 Hz, 2H), 2.90 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.04, 136.44, 129.56, 119.05, 114.79, 111.20, 40.50.

SRho: 3,3'-thiobis(*N,N*-dimethylaniline) (109 mg, 0.4 mmol, 1.0 equiv.), 2-carboxybenzaldehyde (0.4-3.2 mmol, 1.0-8.0 equiv.), Lewis acid catalyst (0.04 mmol, 0.1 equiv.) were mixed in a sealable pressure tube. The tube was sealed tightly and heated at 100-140 °C for 1-8 h. The mixture gradually turned a deep purple. After cooling to room temperature, the reaction mixture was purified directly by column chromatography on silica gel (ethyl acetate : triethylamine = 200 : 1) to give the desired compounds as violet powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 7.8 Hz, 1H), 7.61 (dd, J = 25.5, 7.0 Hz, 3H), 6.87 (d, J = 8.9 Hz, 2H), 6.75 (d, J = 2.7 Hz, 2H), 6.47 (dd, J = 8.9, 2.7 Hz, 2H), 2.97 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

170.24, 153.63, 150.09, 134.30, 133.36, 129.28, 127.93, 126.21, 125.52, 124.00, 119.80, 110.67, 108.46, 40.22. MS (ESI) m/z: calcd. for $C_{24}H_{23}N_2O_2S$ $[M+H]^+$ 403.1480, observed 403.1477.

General procedure for synthesis of **R-SRho**: To a sealable pressure tube added 3,3'-thiobis(*N,N*-dimethylaniline) (109 mg, 0.4 mmol, 1.0 equiv.), substituted 2-carboxybenzaldehyde (2 mmol, 5.0 equiv.), copper(II) bromide (9 mg, 0.04 mmol, 0.1 equiv.) and 200 μL nitrobenzene. The tube was sealed tightly and heated at 120 °C for 5 h. The mixture gradually turned a deep purple. After cooling to room temperature, the reaction mixture was purified directly by column chromatography on silica gel (ethyl acetate : triethylamine = 200 : 1) to give the desired compounds as violet powder. **6-Br-SRho**: 58 mg, 30%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.2 Hz, 1H), 7.73 (s, 1H), 7.65 (dt, J = 8.1, 1.3 Hz, 1H), 6.92 (d, J = 8.9 Hz, 2H), 6.72 (d, J = 2.5 Hz, 2H), 6.49 (dd, J = 9.0, 2.6 Hz, 2H), 2.96 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.43, 155.76, 150.20, 132.96, 132.89, 129.55, 127.71, 126.97, 126.89, 124.49, 119.13, 110.86, 108.41, 40.23; MS (ESI) m/z: calcd. for $C_{24}H_{22}N_2O_2SBr$ $[M+H]^+$ 481.0585, observed 481.0588. **6-CO_2Me-SRho**: 35 mg, 19%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.15 (m, 2H), 8.01 (d, J = 7.9 Hz, 1H), 6.81 (d, J = 9.0 Hz, 2H), 6.73 (d, J = 2.5 Hz, 2H), 6.44 (dd, J = 8.9, 2.6 Hz, 2H), 3.90 (s, 3H), 2.95 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.26, 165.81, 153.61, 150.18, 135.59, 133.50, 130.61, 129.87, 127.99, 125.63, 125.34, 118.99, 110.72, 108.41, 52.67, 40.22; MS (ESI) m/z: calcd. for $C_{26}H_{25}N_2O_4S$ $[M+H]^+$ 461.1535, observed 461.1534. **5-NO_2-SRho**: 50 mg, 28%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J = 2.0 Hz, 1H), 8.47 – 8.39 (m, 1H), 7.77 (d, J = 8.4 Hz, 1H), 6.88 (d, J = 8.9 Hz, 2H), 6.72 (d, J = 2.4 Hz, 2H), 6.47 (dd, J = 9.0, 2.5 Hz, 2H), 2.96 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.05, 159.55, 150.31, 148.93, 132.70, 129.35, 127.43, 126.87, 124.92, 121.35, 118.15, 110.85, 108.45, 40.20; MS (ESI) m/z: calcd. for $C_{24}H_{22}N_3O_4S$ $[M+H]^+$ 448.1331, observed 448.1334.

SRho-pH: **SRho** (81 mg, 0.2 mmol), 4-(2-aminoethyl) morpholine (78 mg, 0.6 mmol) and benzotriazol-1-yl-oxytripyrrolidinophosphonium hexafluorophosphate (PyBop) (104 mg, 0.2 mmol) were dissolved in 15 mL CH_2Cl_2. The mixture was stirred for 24 h at room temperature before evaporated under reduced pressure. The crude product was purified by column chromatography to afford pure product (55 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 5.9, 2.8 Hz, 1H), 7.53 – 7.39 (m, 2H), 7.15 (dd, J = 5.8, 2.7 Hz, 1H), 6.62 – 6.48 (m, 4H), 6.39 (dd, J = 9.0, 2.7 Hz, 2H), 3.62 (t, J = 4.7 Hz, 4H), 3.37 (t, J = 7.6 Hz, 2H), 2.95 (s, 12H), 2.33 (s, 4H),

2.21 (t, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.17, 154.54, 149.58, 132.53, 132.34, 130.81, 130.17, 128.04, 123.52, 122.96, 117.86, 111.27, 106.89, 69.20, 66.90, 55.87, 53.19, 40.17, 37.88; MS (ESI) m/z: calcd. for $C_{30}H_{35}N_4O_2S$ $[M+H]^+$ 515.2481, observed 515.2478.

1.3 Sample preparation

All compounds were dissolved in DMSO to afford 2 mM stock solution. The stock solutions of **SRho** and **R-SRhos** were diluted to 2 μM with PBS buffer solution (pH 7.40) for absorbance and fluorescence measurements. The stock solution of **SRho-pH** was diluted to 5 μM with different pH BR buffer solution for fluorescence measurements.

1.4 Determination of Φ and pK_a.

The fluorescence quantum yields (Φ) were determined using **SRho** (Φ = 0.47 in methanol) [2] as the standard and calculated using the following equation:

$$\Phi_s = \Phi_r \times \frac{A_r F_s n_s^2}{A_s F_r n_r^2}$$

where, the subscripts "s" and "r" stand for sample and reference, respectively. A is the absorbance. F is the integrated fluorescence intensity and n is the refractive index of the solvent.

pK_a of **SRho-pH** was determined by non-linear regression using the following equation:

$$F = \frac{F_{max} + F_{min} \times 10^{pH - pK_a}}{1 + 10^{pH - pK_a}}$$

1.5 Computational details

All the calculations were carried out at the ORCA 5.0.0 [3-5] program package using density functional theory (DFT) or time-dependent density functional theory (TD-DFT). The ground states geometries of dyes were optimized at r^{2}SCAN-3c [6] composite method. Single point energies of the optimized structures were further calculated at RI-ωB97M-V/def2-TZVP level. The excited states were calculated at RI-PBE0/def2-SV(P) level. All the calculations were conducted in conductor-like polarizable continuum model (CPCM) of water. The corresponding molecular orbital composition, absorption and emission were analyzed by Multiwfn [7]. Molecular representations were conducted by Avogadro [8] and VMD [9].

1.6 Cell culture and imaging experiments

About 2 × 10^4 HuH-7 cells were seeded into confocal dish (35 mm, NEST) and cultured in

Dulbecco's modified Eagle's medium (DMEM, Gibco) supplied with 10% fetal bovine serum (FBS, Gibco) under standard culture conditions (atmosphere of 5% CO_2 and 95% air at 37 ^oC) for 48 h. The cells were then rinsed twice with PBS and incubated with FBS-free DMEM containing **SRho-pH** (5 μM) and commercial dye (1 μM) for 15 min. After incubation, cells were rinsed with PBS twice again for imaging.

2. NMR spectra of the compounds

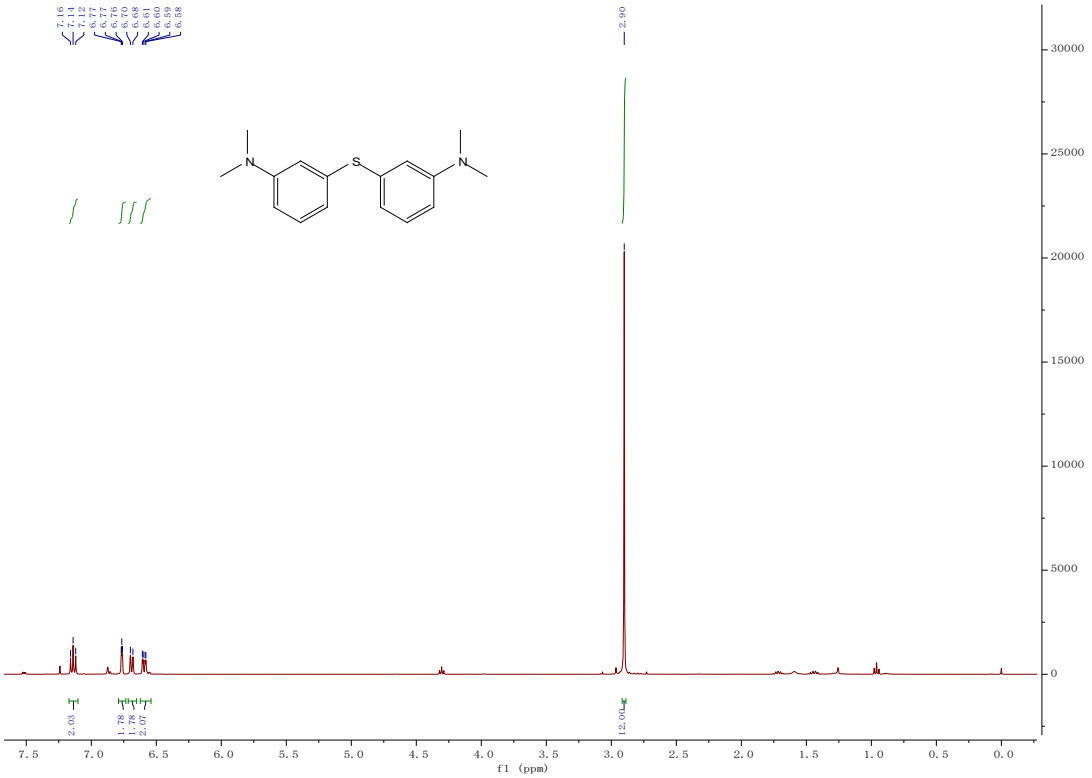


Fig. S1. ^{1}H NMR spectrum of **3,3'-thiobis(*N*,*N*-dimethylaniline)** in $CDCl_3$.

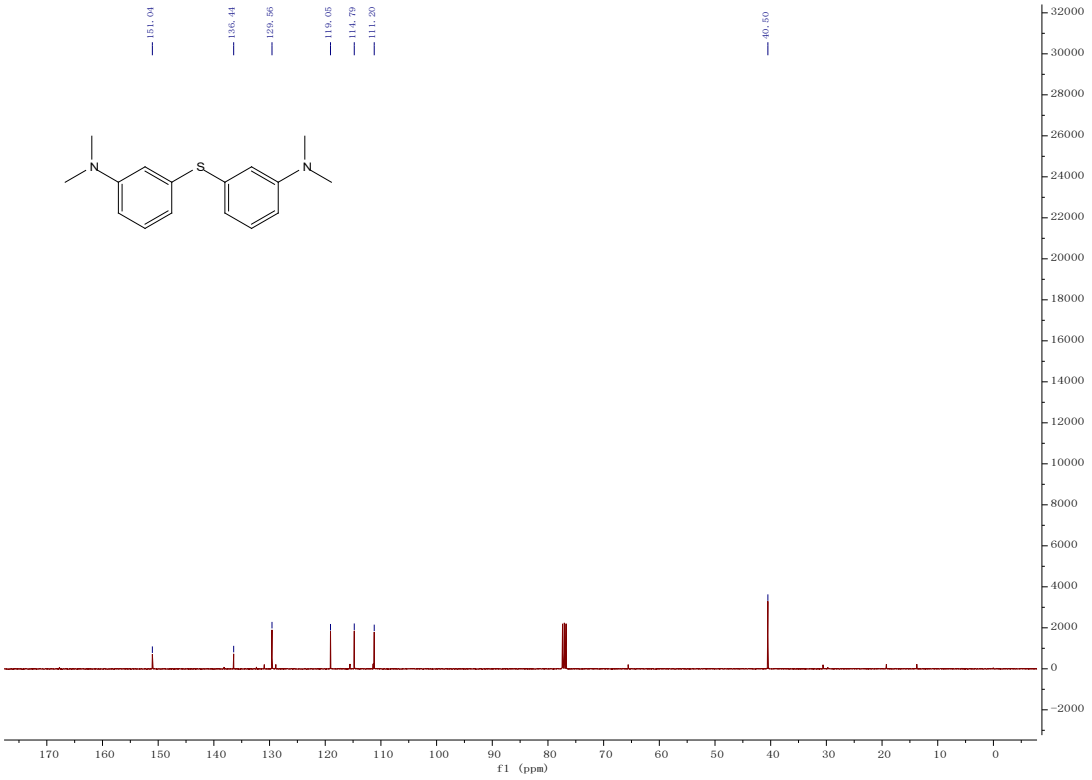


Fig. S2. ^{13}C NMR spectrum of **3,3'-thiobis(*N*,*N*-dimethylaniline)** in $CDCl_3$.

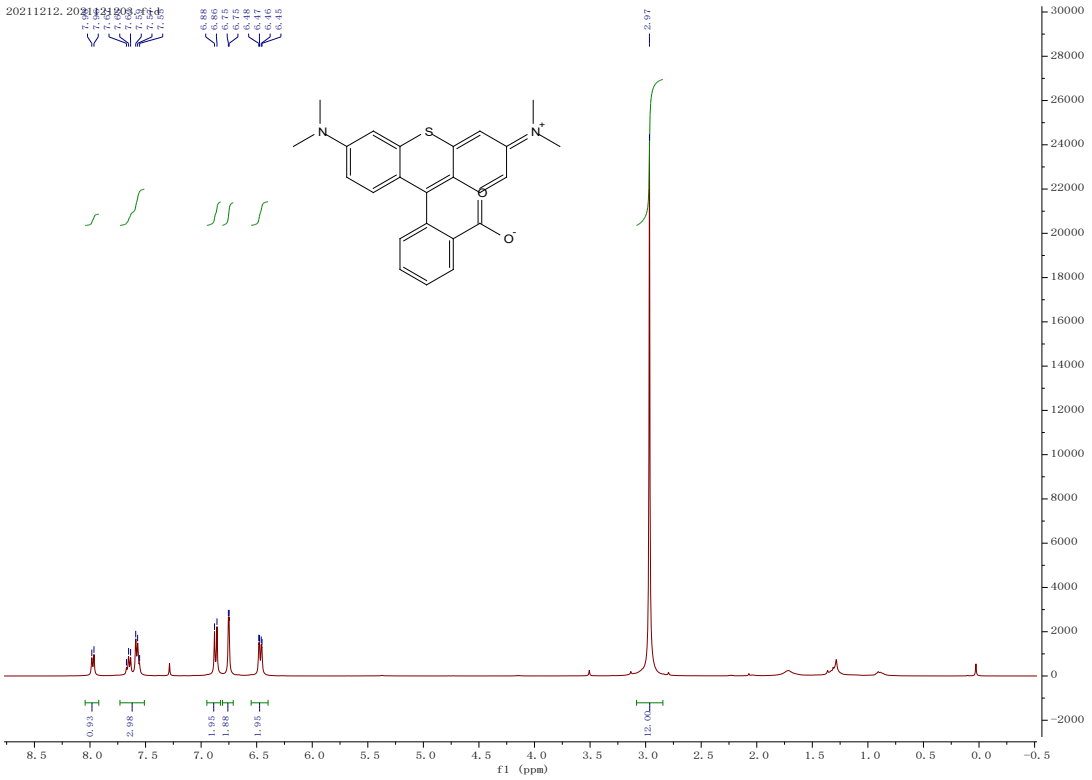


Fig. S3. ^{1}H NMR spectrum of **SRho** in $CDCl_3$.

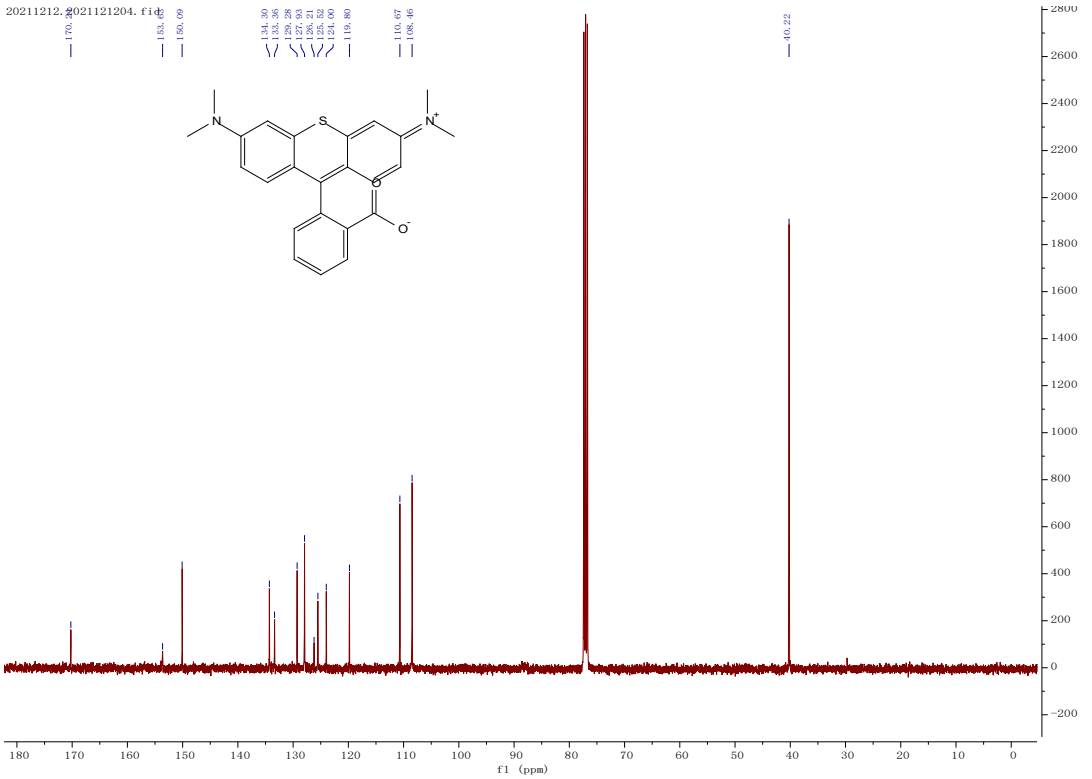


Fig. S4. ^{13}C NMR spectrum of **SRho** in $CDCl_3$.

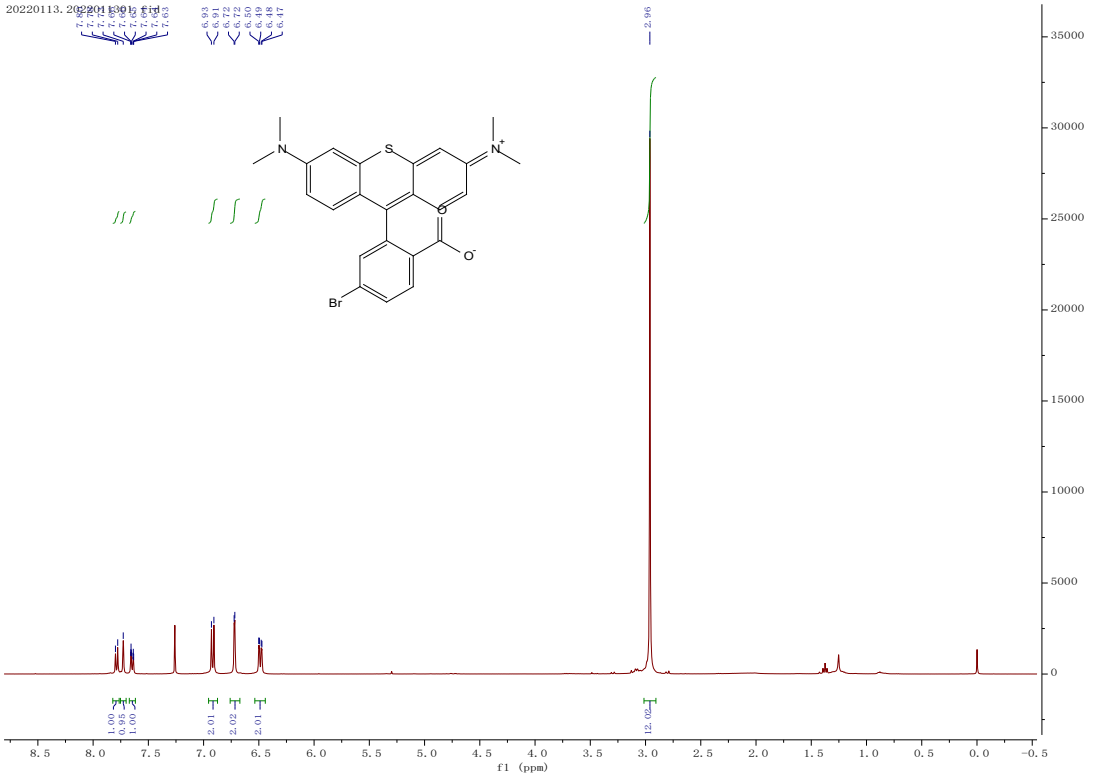


Fig. S5. ^{1}H NMR spectrum of **6-Br-SRho** in $CDCl_3$.

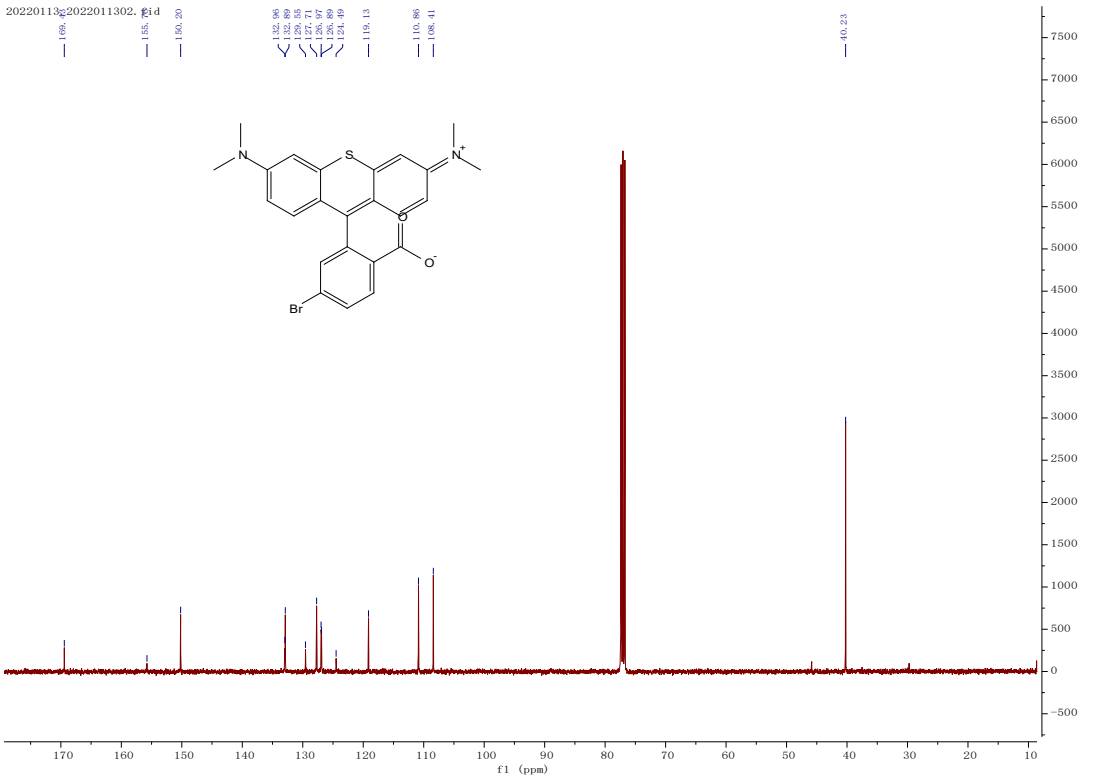


Fig. S6. ^{13}C NMR spectrum of **6-Br-SRho** in $CDCl_3$.

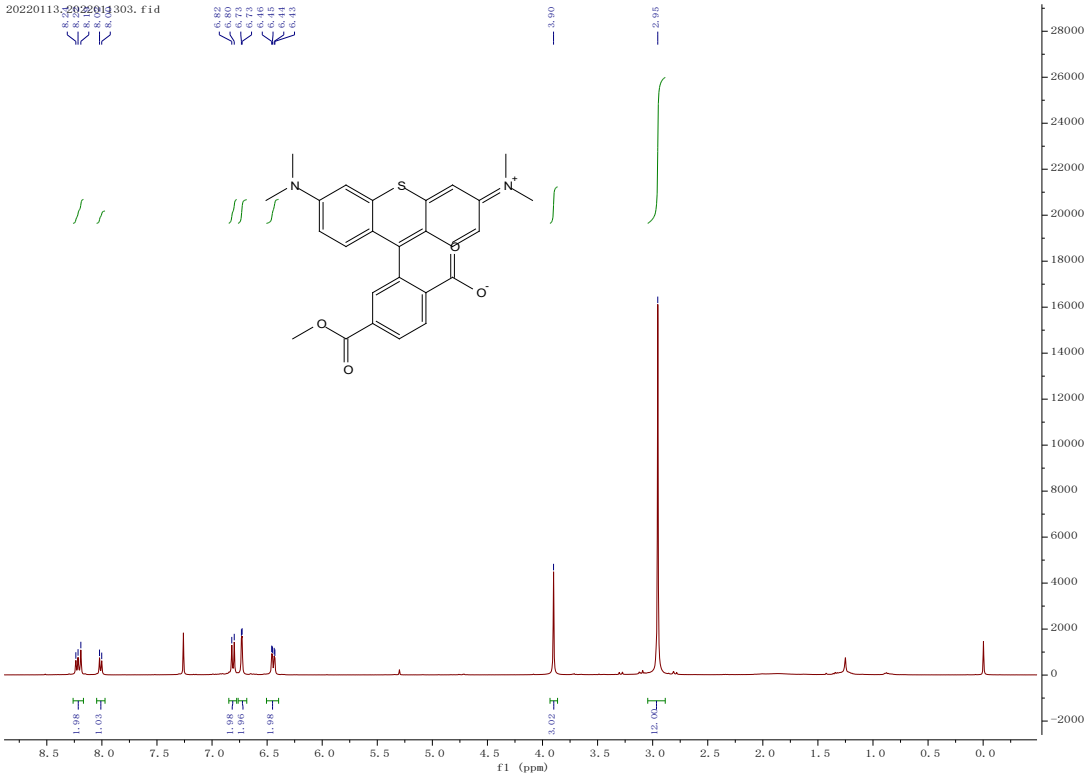


Fig. S7. ^{1}H NMR spectrum of **6-CO_2Me-SRho** in $CDCl_3$.

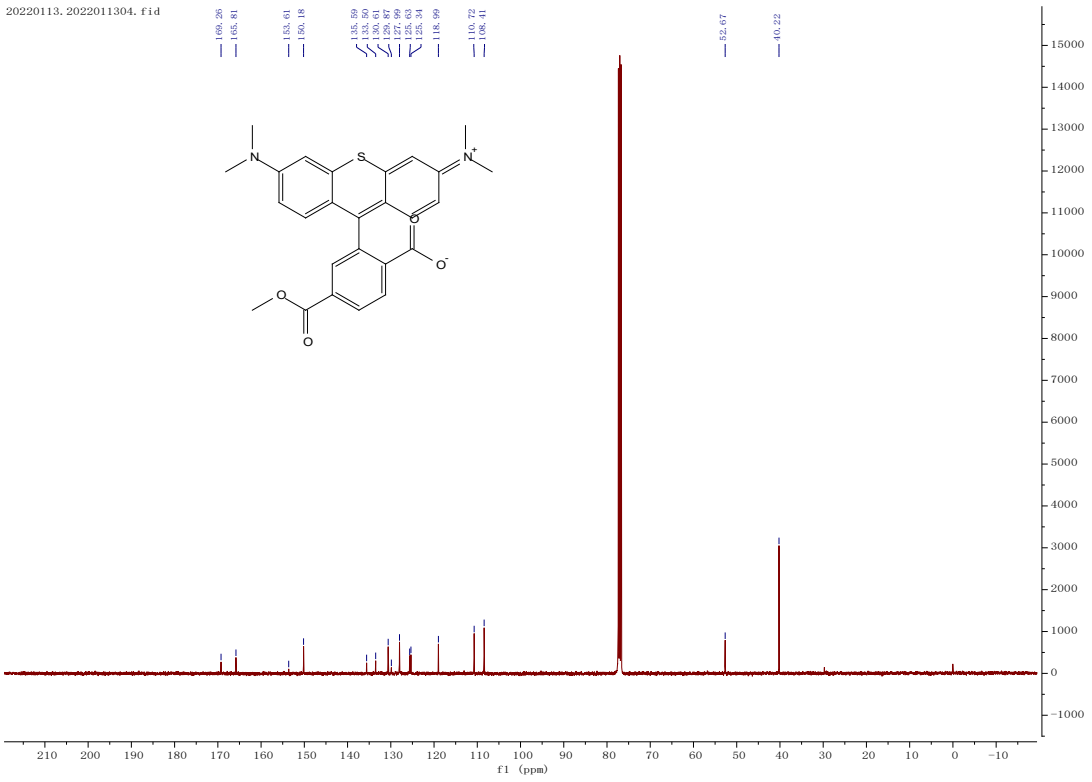


Fig. S8. ^{13}C NMR spectrum of **6-CO_2Me-SRho** in $CDCl_3$.

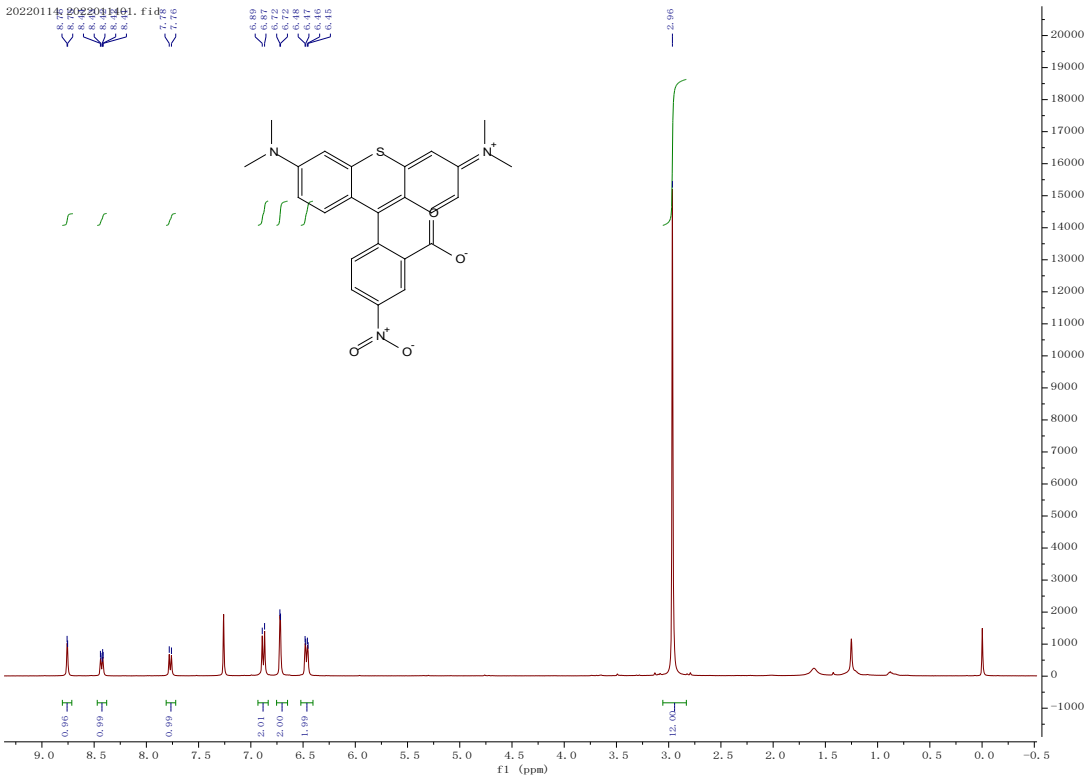


Fig. S9. ^{1}H NMR spectrum of **5-NO$_2$-SRho** in $CDCl_3$.

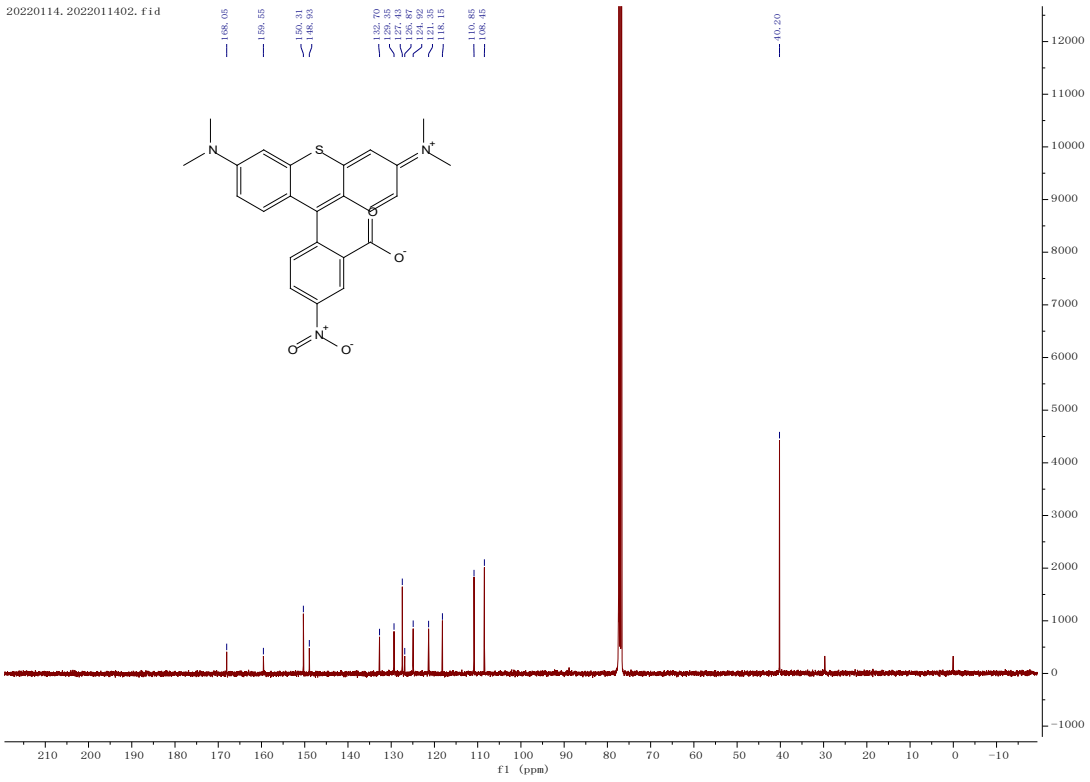


Fig. S10. ^{13}C NMR spectrum of **5-NO$_2$-SRho** in $CDCl_3$.

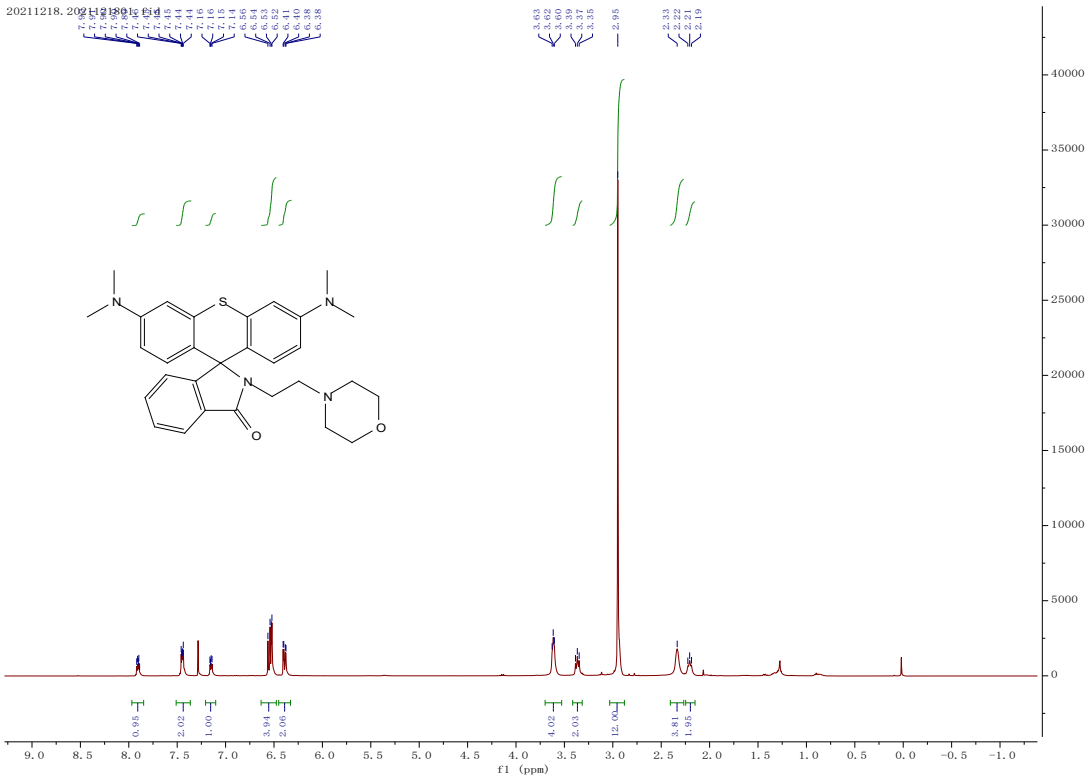


Fig. S11. ^{1}H NMR spectrum of **SRho-pH** in $CDCl_3$.

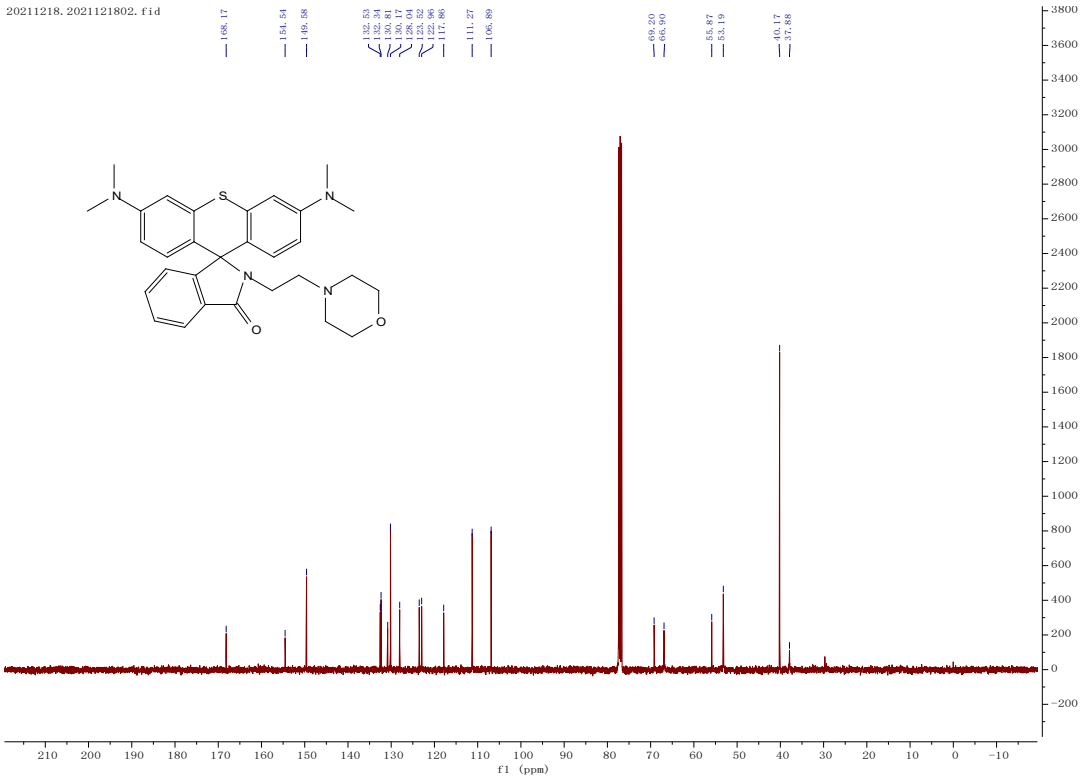


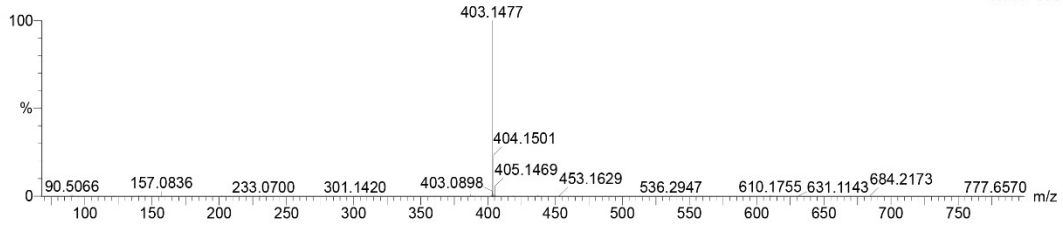
Fig. S12. ^{13}C NMR spectrum of **SRho-pH** in $CDCl_3$.

3. HRMS data of the compounds

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
70 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 1-40 H: 0-70 N: 1-5 O: 1-3 S: 1-1
A
1228-2-2 79 (0.455) 1: TOF MS ES+ 8.90e+006



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
403.1477	403.1480	-0.3	-0.7	14.5	1379.6	n/a	n/a	C24 H23 N2 O2 S

Fig. S13. HRMS data of **SRho**.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
214 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
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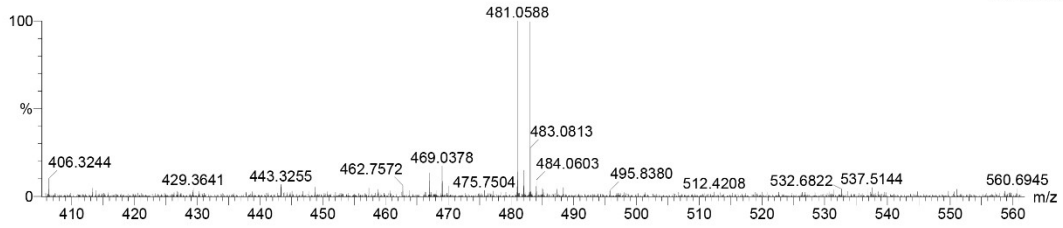
0315-1-1 131 (0.744) 1: TOF MS ES+ 1.17e+004



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
481.0588	481.0585	0.3	0.6	14.5	560.9	n/a	n/a	C24 H22 N2 O2 S Br

Fig. S14. HRMS data of **6-Br-SRho**.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
25 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
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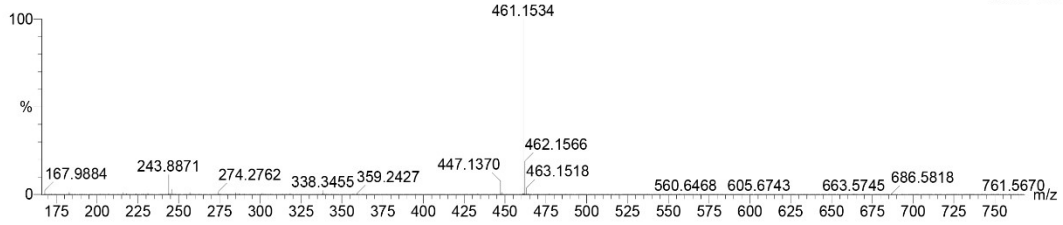


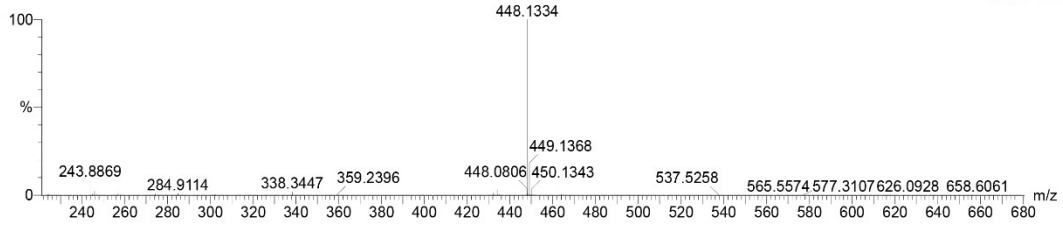
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
461.1534	461.1535	-0.1	-0.2	15.5	682.6	n/a	n/a	C26 H25 N2 O4 S

Fig. S15. HRMS data of **6-CO_2Me-SRho**.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
34 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 24-24 H: 22-22 N: 0-5 O: 0-5 S: 0-1
1
0315-1-3 159 (0.899) 1: TOF MS ES+ 9.81e+005



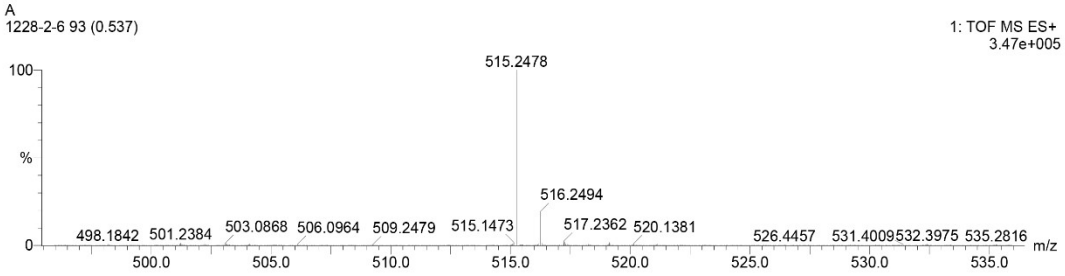
Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
448.1334	448.1331	0.3	0.7	15.5	825.6	n/a	n/a	C24 H22 N3 O4 S

Fig. S16. HRMS data of **6-NO_2-SRho**.

Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
201 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 1-41 H: 0-70 N: 1-5 O: 1-7 S: 1-1
A
1228-2-6 93 (0.537)



Minimum:				-1.5				
Maximum:		5.0	5.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
515.2478	515.2481	-0.3	-0.6	15.5	780.1	n/a	n/a	C30 H35 N4 O2 S

Fig. S17. HRMS data of **SRho-pH**.

4. Results of theoretical calculations

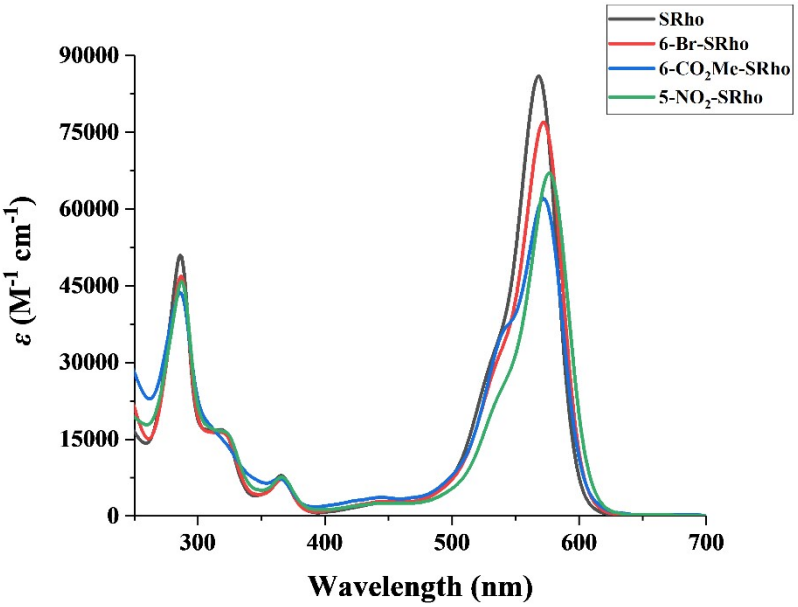


Fig. S18. Molar extinction coefficient spectra of **SRhos**.

5. Results of theoretical calculations

5.1 Geometry optimization

Table S1. Calculated atomic coordinates of **ORho**

Atom#	Symbol	X	Y	Z
1	C	3.703485	0.645771	0.677536
2	C	3.022263	1.901777	0.778413
3	C	1.671818	1.983714	0.584166
4	C	0.888843	0.842964	0.277999
5	C	1.580259	-0.38971	0.18648
6	C	2.939534	-0.50536	0.373725
7	O	0.914393	-1.54594	-0.10047
8	C	-0.42896	-1.52774	-0.33975
9	C	-1.16433	-0.31949	-0.26139
10	C	-2.55552	-0.41061	-0.51659
11	C	-3.15621	-1.59801	-0.82802
12	C	-2.39321	-2.80764	-0.90928
13	C	-1.00339	-2.73876	-0.6549
14	N	-2.98714	-3.98013	-1.22246
15	C	-4.42795	-4.04822	-1.46636
16	C	-2.19499	-5.20478	-1.31158
17	N	5.039527	0.565923	0.86375
18	C	5.825559	1.759001	1.177701
19	C	5.721958	-0.72118	0.750831
20	C	-0.50873	0.873346	0.100877
21	C	-1.22744	2.172598	0.042186
22	C	-1.33146	2.795525	-1.20544
23	C	-1.97968	4.020302	-1.32759
24	C	-2.52631	4.632212	-0.2012
25	C	-2.42034	4.014469	1.039415
26	C	-1.7753	2.783447	1.177335
27	C	-1.67163	2.102477	2.533097
28	O	-1.14468	0.952702	2.522899
29	O	-2.10931	2.718798	3.536414
30	H	3.574355	2.804063	1.009737
31	H	1.175748	2.946074	0.667845
32	H	3.389766	-1.48542	0.279749
33	H	-3.1539	0.493622	-0.45685
34	H	-4.22274	-1.61387	-1.0139
35	H	-0.36752	-3.61393	-0.69745
36	H	-4.69868	-5.08059	-1.68527
37	H	-4.9962	-3.72172	-0.58682
38	H	-4.71735	-3.42641	-2.32256
39	H	-1.72325	-5.4432	-0.3495

40	H	-2.84746	-6.0316	-1.59052
41	H	-1.40891	-5.11183	-2.07166
42	H	5.753819	2.505717	0.377273
43	H	5.495338	2.218203	2.117687
44	H	6.871041	1.471911	1.285572
45	H	5.339505	-1.43858	1.488154
46	H	5.594647	-1.14995	-0.25148
47	H	6.786689	-0.57612	0.930832
48	H	-0.90028	2.314845	-2.0802
49	H	-2.05627	4.494454	-2.30209
50	H	-3.03412	5.588456	-0.29238
51	H	-2.84009	4.476424	1.927843

Table S2. Calculated atomic coordinates of **SRho**.

Atom#	Symbol	X	Y	Z
1	C	3.848983	0.823465	0.694387
2	C	3.031068	1.993271	0.755015
3	C	1.683985	1.912893	0.545778
4	C	1.018253	0.688362	0.261943
5	C	1.843763	-0.47021	0.219606
6	C	3.212129	-0.40865	0.423185
7	S	1.195851	-2.07099	-0.07654
8	C	-0.50869	-1.80046	-0.37853
9	C	-1.10258	-0.51055	-0.28452
10	C	-2.50143	-0.45323	-0.5362
11	C	-3.24331	-1.55461	-0.85481
12	C	-2.63135	-2.84189	-0.95234
13	C	-1.24283	-2.92856	-0.70402
14	N	-3.35639	-3.93596	-1.27385
15	C	-4.79117	-3.82929	-1.53745
16	C	-2.71654	-5.24663	-1.36073
17	N	5.184477	0.896118	0.887432
18	C	5.829261	2.179912	1.163253
19	C	6.006904	-0.30993	0.822218
20	C	-0.38507	0.654784	0.078102
21	C	-1.10868	1.958676	0.027471
22	C	-1.1597	2.624543	-1.20057
23	C	-1.81979	3.8437	-1.31358
24	C	-2.43503	4.406622	-0.1968
25	C	-2.385	3.74461	1.024167
26	C	-1.72542	2.519942	1.152386
27	C	-1.67384	1.800277	2.490931
28	O	-1.04528	0.702655	2.495756

29	O	-2.24868	2.338307	3.47009
30	H	3.471298	2.959609	0.967236
31	H	1.092715	2.820948	0.600443
32	H	3.790607	-1.32386	0.37033
33	H	-2.99881	0.508513	-0.46719
34	H	-4.30532	-1.43761	-1.03158
35	H	-0.73377	-3.88343	-0.76787
36	H	-5.17565	-4.81633	-1.79262
37	H	-5.33299	-3.46459	-0.65589
38	H	-4.9921	-3.15354	-2.37786
39	H	-2.25987	-5.52874	-0.40353
40	H	-3.46864	-5.99241	-1.61624
41	H	-1.93907	-5.25832	-2.13547
42	H	5.676611	2.887259	0.338662
43	H	5.444057	2.628944	2.087081
44	H	6.900038	2.017122	1.281662
45	H	5.700889	-1.04038	1.582081
46	H	5.937744	-0.78386	-0.16533
47	H	7.047125	-0.04086	1.002824
48	H	-0.67808	2.180662	-2.06858
49	H	-1.85261	4.351876	-2.27332
50	H	-2.95151	5.358925	-0.28027
51	H	-2.85787	4.166409	1.905937

Table S3. Calculated atomic coordinates of **6-Br-SRho**.

Atom#	Symbol	X	Y	Z
1	C	3.823651	0.862222	0.738119
2	C	2.992991	2.024196	0.77916
3	C	1.649571	1.928315	0.556087
4	C	0.999858	0.693747	0.276565
5	C	1.838517	-0.45664	0.249659
6	C	3.203247	-0.37874	0.467963
7	C	-0.39946	0.640636	0.079169
8	C	-1.10379	-0.5321	-0.27855
9	C	-0.49384	-1.81589	-0.36355
10	S	1.211112	-2.06498	-0.04767
11	C	-2.50281	-0.4922	-0.53523
12	C	-3.22934	-1.60331	-0.8537
13	C	-2.60077	-2.88333	-0.94644
14	C	-1.21259	-2.95299	-0.68971
15	N	-3.31015	-3.98614	-1.27027
16	C	-4.74621	-3.89922	-1.53567
17	C	-2.65207	-5.28789	-1.35915

18	N	5.155146	0.950445	0.947261
19	C	5.783619	2.24348	1.218709
20	C	5.991685	-0.24692	0.898797
21	C	-1.13861	1.936511	0.022587
22	C	-1.20998	2.570782	-1.22077
23	C	-1.88225	3.779699	-1.32202
24	C	-2.48526	4.380036	-0.22355
25	C	-2.40153	3.735975	1.004297
26	C	-1.73573	2.517167	1.147677
27	Br	-1.97853	4.643353	-3.03131
28	C	-1.66102	1.830054	2.503784
29	O	-1.07463	0.710973	2.515832
30	O	-2.17984	2.420191	3.483596
31	H	3.421109	2.996896	0.986877
32	H	1.050124	2.831722	0.596323
33	H	3.792298	-1.28778	0.427062
34	H	-3.01394	0.462629	-0.47052
35	H	-4.29201	-1.49983	-1.03474
36	H	-0.69225	-3.90218	-0.74606
37	H	-5.2924	-3.53499	-0.65681
38	H	-4.9547	-3.2319	-2.38094
39	H	-5.11818	-4.89288	-1.78348
40	H	-2.20155	-5.57047	-0.39919
41	H	-3.3915	-6.04156	-1.6278
42	H	-1.86688	-5.28317	-2.12593
43	H	5.636652	2.940277	0.384203
44	H	5.379994	2.698122	2.131696
45	H	6.853879	2.092187	1.355191
46	H	5.682452	-0.97711	1.657447
47	H	5.941608	-0.72547	-0.08764
48	H	7.02611	0.034356	1.093264
49	H	-0.74374	2.118128	-2.09069
50	H	-3.00697	5.326217	-0.32226
51	H	-2.8608	4.179275	1.882339

Table S4. Calculated atomic coordinates of **6-CO_2Me-SRho**.

Atom#	Symbol	X	Y	Z
1	C	4.05191	0.174284	1.130117
2	C	3.2322	1.342959	1.193743
3	C	1.88827	1.264332	0.966758
4	C	1.227249	0.042213	0.66005
5	C	2.054862	-1.11553	0.613151
6	C	3.419908	-1.05515	0.83538

7	C	-0.17218	0.006948	0.458852
8	C	-0.88658	-1.15263	0.077862
9	C	-0.28962	-2.44113	-0.02613
10	S	1.412283	-2.71228	0.28755
11	C	-2.28382	-1.09416	-0.18485
12	C	-3.0208	-2.19276	-0.52236
13	C	-2.40598	-3.4782	-0.62943
14	C	-1.01924	-3.56593	-0.37068
15	N	-3.12667	-4.56909	-0.96843
16	C	-4.55918	-4.46114	-1.24494
17	C	-2.48364	-5.87753	-1.06839
18	N	5.383957	0.245489	1.342506
19	C	6.024247	1.526461	1.641982
20	C	6.208011	-0.95974	1.27775
21	C	-0.89973	1.310203	0.427083
22	C	-0.94267	1.991287	-0.78699
23	C	-1.60367	3.216287	-0.89199
24	C	-2.2292	3.763181	0.233854
25	C	-2.18495	3.080902	1.439963
26	C	-1.52586	1.855166	1.556408
27	C	-1.6114	3.893299	-2.21549
28	O	-2.27077	5.062252	-2.18667
29	O	-1.08134	3.444539	-3.21688
30	C	-2.32518	5.787731	-3.43932
31	C	-1.48827	1.12064	2.89168
32	O	-0.86014	0.025125	2.891552
33	O	-2.07561	1.655068	3.8641
34	H	3.668878	2.306904	1.423307
35	H	1.297368	2.172301	1.025524
36	H	4.0002	-1.96899	0.779045
37	H	-2.78528	-0.13503	-0.10968
38	H	-4.0814	-2.07526	-0.70686
39	H	-0.5084	-4.5194	-0.44063
40	H	-5.10894	-4.10316	-0.3657
41	H	-4.75226	-3.7793	-2.08225
42	H	-4.94056	-5.44659	-1.5105
43	H	-2.03243	-6.1707	-0.11202
44	H	-3.2328	-6.62128	-1.33785
45	H	-1.70149	-5.87737	-1.83843
46	H	5.880023	2.24369	0.824582
47	H	5.627988	1.963147	2.567011
48	H	7.093767	1.36314	1.770237
49	H	5.889697	-1.69798	2.024817
50	H	6.155036	-1.42288	0.284172

51	H	7.244947	-0.69222	1.478189
52	H	-0.45842	1.570157	-1.66357
53	H	-2.74562	4.714152	0.164329
54	H	-2.66485	3.490179	2.323266
55	H	-2.8914	6.692998	-3.22237
56	H	-1.3151	6.035978	-3.77525
57	H	-2.83245	5.188811	-4.20005

Table S5. Calculated atomic coordinates of **5-NO_2-SRho**.

Atom#	Symbol	X	Y	Z
1	C	3.959457	0.636126	0.72709
2	C	3.125569	1.795306	0.786781
3	C	1.781891	1.698588	0.568005
4	C	1.134868	0.465426	0.274516
5	C	1.976724	-0.68271	0.229308
6	C	3.341563	-0.60334	0.443563
7	C	-0.26356	0.408765	0.081559
8	C	-0.96943	-0.76066	-0.27891
9	C	-0.35601	-2.04195	-0.38275
10	S	1.352856	-2.28811	-0.08857
11	C	-2.37148	-0.72209	-0.52089
12	C	-3.09761	-1.83206	-0.84262
13	C	-2.4659	-3.10928	-0.95467
14	C	-1.07477	-3.17739	-0.71279
15	N	-3.17499	-4.21053	-1.28204
16	C	-4.61473	-4.12632	-1.52902
17	C	-2.51288	-5.50848	-1.39619
18	N	5.290884	0.725555	0.932347
19	C	5.917126	2.017024	1.217294
20	C	6.130311	-0.46939	0.869761
21	C	-1.00563	1.703156	0.038195
22	C	-1.08177	2.355679	-1.19818
23	C	-1.74963	3.562988	-1.32282
24	C	-2.34068	4.106612	-0.18623
25	C	-2.27803	3.481335	1.049726
26	C	-1.60641	2.268155	1.171435
27	C	-1.53599	1.573426	2.529217
28	O	-0.93713	0.463897	2.53874
29	O	-2.07333	2.158755	3.499998
30	N	-3.05474	5.385465	-0.30113
31	O	-3.59137	5.84174	0.704284
32	O	-3.07972	5.935701	-1.39895
33	H	3.551515	2.766255	1.006591

34	H	1.181913	2.600885	0.624079
35	H	3.933143	-1.51	0.389208
36	H	-2.88696	0.229427	-0.442
37	H	-4.16233	-1.73011	-1.01189
38	H	-0.55258	-4.12462	-0.78292
39	H	-5.15014	-3.7676	-0.64148
40	H	-4.83554	-3.45573	-2.36856
41	H	-4.98721	-5.11992	-1.77627
42	H	-2.05286	-5.80347	-0.44453
43	H	-3.25194	-6.26069	-1.66965
44	H	-1.73479	-5.48877	-2.16979
45	H	5.761042	2.724494	0.393656
46	H	5.51894	2.457179	2.139713
47	H	6.988913	1.867532	1.343037
48	H	5.823314	-1.20829	1.620742
49	H	6.080113	-0.93691	-0.12187
50	H	7.164211	-0.18778	1.066271
51	H	-0.61116	1.908241	-2.06917
52	H	-1.81221	4.071146	-2.2776
53	H	-2.74084	3.91755	1.926583

5.2 Major MO transitions in excited states

ORho

1 2.7790 eV 446.15 nm f= 0.90403 Spin multiplicity= 1:

H -> L 97.2%

2 2.9830 eV 415.64 nm f= 0.13762 Spin multiplicity= 1:

H-1 -> L 96.1%

3 3.2600 eV 380.32 nm f= 0.05895 Spin multiplicity= 1:

H-2 -> L 91.7%

4 3.3470 eV 370.43 nm f= 0.06289 Spin multiplicity= 1:

H-4 -> L 88.6%, H-3 -> L 7.5%

5 3.4480 eV 359.58 nm f= 0.00557 Spin multiplicity= 1:

H-3 -> L 83.4%, H-4 -> L 8.2%

6 3.8010 eV 326.19 nm f= 0.00464 Spin multiplicity= 1:

H-5 -> L 81.8%, H-7 -> L 8.9%, H-6 -> L 7.4%

7 3.9390 eV 314.76 nm f= 0.00582 Spin multiplicity= 1:

H-6 -> L 66.8%, H-7 -> L 17.7%, H-5 -> L 14.5%

8 4.1650 eV 297.68 nm f= 0.01806 Spin multiplicity= 1:

H-7 -> L 53.6%, H-6 -> L 17.1%, H -> L+1 12.2%, H -> L+2 7.9%

9 4.2230 eV 293.59 nm f= 0.00067 Spin multiplicity= 1:

H-1 -> L+1 69.9%, H-1 -> L+2 16.8%

10 4.4230 eV 280.32 nm f= 0.14835 Spin multiplicity= 1:

H -> L+1 83.9%, H-7 -> L 7.8%

11 4.5080 eV 275.03 nm f= 0.00322 Spin multiplicity= 1:

H-8 -> L 72.0%, H -> L+5 9.6%, H-2 -> L+1 7.9%

12 4.5510 eV 272.43 nm f= 0.00044 Spin multiplicity= 1:

H-2 -> L+1 49.2%, H-2 -> L+2 15.9%, H-3 -> L+1 13.5%, H-8 -> L 8.4%

13 4.6250 eV 268.07 nm f= 0.12021 Spin multiplicity= 1:

H -> L+2 83.2%

14 4.7760 eV 259.60 nm f= 0.01937 Spin multiplicity= 1:

H-1 -> L+2 58.8%, H-1 -> L+1 13.6%, H-8 -> L 10.0%, H -> L+5 9.1%

15 4.8910 eV 253.49 nm f= 0.01178 Spin multiplicity= 1:

H -> L+5 31.2%, H -> L+3 21.1%, H-1 -> L+2 12.3%, H -> L+4 11.9%, H-1 -> L+3 5.7%, H-8 -> L 5.3%

16 4.9310 eV 251.44 nm f= 0.03778 Spin multiplicity= 1:

H -> L+3 62.5%, H -> L+5 23.7%

17 5.0360 eV 246.20 nm f= 0.01345 Spin multiplicity= 1:

H-1 -> L+3 80.2%, H -> L+5 6.3%

18 5.0910 eV 243.54 nm f= 0.13288 Spin multiplicity= 1:

H -> L+4 67.3%, H -> L+3 10.0%

19 5.1590 eV 240.33 nm f= 0.01330 Spin multiplicity= 1:

H-2 -> L+2 43.9%, H-2 -> L+3 25.2%, H-2 -> L+1 11.4%, H-3 -> L+3 6.7%

20 5.2400 eV 236.61 nm f= 0.04266 Spin multiplicity= 1:

H-4 -> L+1 49.3%, H-3 -> L+1 16.4%, H-1 -> L+5 7.9%

SRho

1 2.6930 eV 460.39 nm f= 0.84123 Spin multiplicity= 1:

H -> L 96.6%

2 2.8970 eV 427.97 nm f= 0.12824 Spin multiplicity= 1:

H-1 -> L 95.6%

3 3.0740 eV 403.33 nm f= 0.00366 Spin multiplicity= 1:

H-2 -> L 95.5%

4 3.1800 eV 389.89 nm f= 0.06216 Spin multiplicity= 1:

H-3 -> L 96.8%

5 3.2600 eV 380.32 nm f= 0.06269 Spin multiplicity= 1:

H-4 -> L 96.6%

6 3.6900 eV 336.00 nm f= 0.00008 Spin multiplicity= 1:

H-5 -> L 82.3%, H-7 -> L 15.9%

7 3.8360 eV 323.21 nm f= 0.00438 Spin multiplicity= 1:

H-7 -> L 82.0%, H-5 -> L 15.6%

8 4.0420 eV 306.74 nm f= 0.00796 Spin multiplicity= 1:

H-6 -> L 69.7%, H -> L+1 22.2%

9 4.1880 eV 296.05 nm f= 0.00004 Spin multiplicity= 1:

H-1 -> L+1 46.4%, H-1 -> L+2 42.2%

10 4.3190 eV 287.07 nm f= 0.23375 Spin multiplicity= 1:

H -> L+1 72.9%, H-6 -> L 18.7%

11 4.4050 eV 281.46 nm f= 0.01649 Spin multiplicity= 1:

H-8 -> L 49.1%, H -> L+3 25.7%, H-2 -> L+1 7.8%, H-1 -> L+2 6.4%, H-1 -> L+1 5.1%

12 4.5210 eV 274.24 nm f= 0.00324 Spin multiplicity= 1:

H-3 -> L+2 38.8%, H-3 -> L+1 35.0%, H-1 -> L+1 10.0%, H-8 -> L 7.4%

13 4.5910 eV 270.06 nm f= 0.05404 Spin multiplicity= 1:

H -> L+2 90.1%

14 4.6030 eV 269.36 nm f= 0.00039 Spin multiplicity= 1:

H-1 -> L+2 36.5%, H-1 -> L+1 28.8%, H-8 -> L 13.6%, H-3 -> L+2 12.7%

15 4.6650 eV 265.78 nm f= 0.10984 Spin multiplicity= 1:

H -> L+3 33.2%, H-8 -> L 28.4%, H-2 -> L+1 23.9%

16 4.8220 eV 257.12 nm f= 0.84781 Spin multiplicity= 1:

H-2 -> L+1 52.5%, H -> L+3 34.4%

17 4.9120 eV 252.41 nm f= 0.03772 Spin multiplicity= 1:

H -> L+4 90.4%

18 4.9690 eV 249.52 nm f= 0.00667 Spin multiplicity= 1:

H-1 -> L+4 87.0%

19 4.9830 eV 248.81 nm f= 0.00018 Spin multiplicity= 1:

H-1 -> L+3 73.5%, H -> L+5 15.0%

20 5.0480 eV 245.61 nm f= 0.00448 Spin multiplicity= 1:

H-3 -> L+1 46.7%, H-3 -> L+2 31.0%, H-3 -> L+4 11.2%

6-Br-SRho

1 2.6680 eV 464.71 nm f= 0.85311 Spin multiplicity= 1:

H -> L 96.8%

2 2.8790 eV 430.65 nm f= 0.12245 Spin multiplicity= 1:

H-1 -> L 95.7%

3 3.0390 eV 407.98 nm f= 0.00519 Spin multiplicity= 1:

H-2 -> L 95.5%

4 3.1820 eV 389.64 nm f= 0.05405 Spin multiplicity= 1:

H-3 -> L 97.1%

5 3.2490 eV 381.61 nm f= 0.05414 Spin multiplicity= 1:

H-4 -> L 95.5%

6 3.5670 eV 347.59 nm f= 0.00177 Spin multiplicity= 1:

H-5 -> L 95.7%

7 4.0010 eV 309.88 nm f= 0.00752 Spin multiplicity= 1:

H-7 -> L 55.6%, H-6 -> L 31.8%, H -> L+1 6.9%

8 4.0190 eV 308.50 nm f= 0.00486 Spin multiplicity= 1:

H-7 -> L 41.7%, H-6 -> L 37.4%, H -> L+1 12.2%

9 4.0580 eV 305.53 nm f= 0.00019 Spin multiplicity= 1:

H-1 -> L+1 67.3%, H-1 -> L+2 19.4%

10 4.2220 eV 293.66 nm f= 0.15688 Spin multiplicity= 1:

H -> L+1 78.1%, H-6 -> L 15.7%

11 4.3800 eV 283.07 nm f= 0.00839 Spin multiplicity= 1:

H-3 -> L+1 29.4%, H-8 -> L 28.0%, H -> L+4 12.9%, H-3 -> L+2 9.9%, H-2 -> L+1 5.1%, H-1 -> L+1 5.1%

12 4.4100 eV 281.14 nm f= 0.01367 Spin multiplicity= 1:

H-3 -> L+1 36.4%, H-8 -> L 28.1%, H-3 -> L+2 13.6%, H -> L+4 9.8%

13 4.4440 eV 278.99 nm f= 0.10977 Spin multiplicity= 1:

H -> L+2 83.2%, H-6 -> L 6.2%

14 4.5650 eV 271.60 nm f= 0.00050 Spin multiplicity= 1:

H-1 -> L+2 59.9%, H-1 -> L+1 16.2%, H-8 -> L 13.7%

15 4.6420 eV 267.09 nm f= 0.13310 Spin multiplicity= 1:

H -> L+4 31.1%, H-8 -> L 26.5%, H-2 -> L+1 21.7%, H-2 -> L+2 9.2%

16 4.7010 eV 263.74 nm f= 0.06003 Spin multiplicity= 1:

H -> L+3 89.7%

17 4.7820 eV 259.27 nm f= 0.48993 Spin multiplicity= 1:

H-2 -> L+1 42.0%, H -> L+4 22.5%, H-1 -> L+3 22.2%

18 4.8050 eV 258.03 nm f= 0.15712 Spin multiplicity= 1:

H-1 -> L+3 63.4%, H -> L+4 14.6%, H-2 -> L+1 9.5%, H-1 -> L+1 5.3%

19 4.9370 eV 251.13 nm f= 0.00005 Spin multiplicity= 1:

H-3 -> L+2 43.6%, H-3 -> L+3 34.7%, H-3 -> L+1 13.3%

20 4.9760 eV 249.16 nm f= 0.22990 Spin multiplicity= 1:

H-2 -> L+2 69.6%, H-2 -> L+1 12.5%

6-CO_2Me-SRho

1 2.6760 eV 463.32 nm f= 0.85779 Spin multiplicity= 1:

H -> L 96.8%

2 2.9070 eV 426.50 nm f= 0.12675 Spin multiplicity= 1:

H-1 -> L 95.2%

3 3.0480 eV 406.77 nm f= 0.00689 Spin multiplicity= 1:

H-2 -> L 95.2%

4 3.2080 eV 386.48 nm f= 0.04811 Spin multiplicity= 1:

H-3 -> L 97.1%

5 3.2830 eV 377.66 nm f= 0.05072 Spin multiplicity= 1:

H-4 -> L 97.5%

6 3.5810 eV 346.23 nm f= 0.00008 Spin multiplicity= 1:

H-1 -> L+1 87.5%, H-2 -> L+1 6.7%

7 3.6190 eV 342.59 nm f= 0.02435 Spin multiplicity= 1:

H -> L+1 98.8%

8 3.8830 eV 319.30 nm f= 0.00057 Spin multiplicity= 1:

H-6 -> L 65.4%, H-7 -> L 32.5%

9 3.9070 eV 317.34 nm f= 0.00020 Spin multiplicity= 1:

H-3 -> L+1 90.5%

10 4.0150 eV 308.80 nm f= 0.00223 Spin multiplicity= 1:

H-7 -> L 66.4%, H-6 -> L 32.2%

11 4.0320 eV 307.50 nm f= 0.02260 Spin multiplicity= 1:

H-5 -> L 75.8%, H -> L+2 18.3%

12 4.2310 eV 293.04 nm f= 0.05127 Spin multiplicity= 1:

H-2 -> L+1 88.8%, H-1 -> L+1 6.0%

13 4.4000 eV 281.78 nm f= 0.26460 Spin multiplicity= 1:

H -> L+2 74.5%, H-5 -> L 15.4%

14 4.4060 eV 281.40 nm f= 0.00519 Spin multiplicity= 1:

H-8 -> L 58.3%, H -> L+4 23.6%, H-1 -> L+2 8.6%

15 4.4820 eV 276.63 nm f= 0.00303 Spin multiplicity= 1:

H-4 -> L+1 97.5%

16 4.5970 eV 269.71 nm f= 0.00239 Spin multiplicity= 1:

H-1 -> L+2 66.9%, H-8 -> L 21.7%, H -> L+4 5.4%

17 4.6710 eV 265.43 nm f= 0.05766 Spin multiplicity= 1:

H -> L+4 38.1%, H-2 -> L+2 25.2%, H-8 -> L 18.0%, H-1 -> L+2 12.9%

18 4.7570 eV 260.64 nm f= 0.03418 Spin multiplicity= 1:

H -> L+3 92.1%

19 4.8500 eV 255.64 nm f= 0.91754 Spin multiplicity= 1:

H-2 -> L+2 59.7%, H -> L+4 27.2%

20 4.8730 eV 254.43 nm f= 0.03388 Spin multiplicity= 1:

H-7 -> L+1 75.1%, H-6 -> L+3 12.8%

5-NO_2-SRho

1 2.6580 eV 466.46 nm f= 0.87492 Spin multiplicity= 1:

H -> L 97.0%

2 2.8210 eV 439.50 nm f= 0.00323 Spin multiplicity= 1:

H -> L+1 99.4%

3 2.9140 eV 425.48 nm f= 0.12441 Spin multiplicity= 1:

H-1 -> L 94.7%

4 3.0200 eV 410.54 nm f= 0.01229 Spin multiplicity= 1:

H-2 -> L 95.0%

5 3.0420 eV 407.57 nm f= 0.00081 Spin multiplicity= 1:

H-1 -> L+1 88.9%, H-2 -> L+1 9.1%

6 3.2320 eV 383.61 nm f= 0.04358 Spin multiplicity= 1:

H-3 -> L 97.5%

7 3.2920 eV 376.62 nm f= 0.04296 Spin multiplicity= 1:

H-4 -> L 98.0%

8 3.3390 eV 371.32 nm f= 0.00013 Spin multiplicity= 1:

H-3 -> L+1 89.4%, H-2 -> L+1 6.0%

9 3.4360 eV 360.84 nm f= 0.00040 Spin multiplicity= 1:

H-2 -> L+1 84.4%, H-3 -> L+1 7.7%, H-1 -> L+1 7.5%

10 3.6300 eV 341.55 nm f= 0.00568 Spin multiplicity= 1:

H-4 -> L+1 99.1%

11 3.8980 eV 318.07 nm f= 0.00009 Spin multiplicity= 1:

H-9 -> L+1 90.3%

12 3.9910 eV 310.66 nm f= 0.01655 Spin multiplicity= 1:

H-5 -> L 66.3%, H -> L+2 21.2%, H -> L+3 7.0%

13 4.0720 eV 304.48 nm f= 0.00016 Spin multiplicity= 1:

H-1 -> L+2 67.4%, H-1 -> L+3 10.7%, H-2 -> L+2 9.4%

14 4.1260 eV 300.49 nm f= 0.00254 Spin multiplicity= 1:

H-6 -> L 86.1%, H-7 -> L 8.2%

15 4.1710 eV 297.25 nm f= 0.19678 Spin multiplicity= 1:

H -> L+2 74.0%, H-5 -> L 17.5%

16 4.2180 eV 293.94 nm f= 0.00083 Spin multiplicity= 1:

H-5 -> L+1 88.1%

17 4.2500 eV 291.73 nm f= 0.02194 Spin multiplicity= 1:

H-6 -> L+1 73.4%, H-7 -> L 14.7%

18 4.2600 eV 291.04 nm f= 0.00399 Spin multiplicity= 1:

H-7 -> L 71.8%, H-6 -> L+1 14.0%, H-6 -> L 5.9%

19 4.3960 eV 282.04 nm f= 0.00558 Spin multiplicity= 1:

H-3 -> L+2 54.8%, H-3 -> L+3 12.2%, H-8 -> L 11.6%, H -> L+4 5.5%

20 4.4220 eV 280.38 nm f= 0.02536 Spin multiplicity= 1:

H-8 -> L 46.9%, H-3 -> L+2 18.5%, H -> L+4 16.1%

5.3 Molecular orbital composition analysis

Table S6. Composition of each shell in LUMO of **ORho**

Shell	6 Type: P	in atom	1(C) :	2.97516 %
Shell	7 Type: P	in atom	1(C) :	2.94663 %
Shell	8 Type: P	in atom	1(C) :	1.27982 %
Shell	17 Type: P	in atom	2(C) :	0.80211 %
Shell	18 Type: P	in atom	2(C) :	0.79743 %
Shell	19 Type: P	in atom	2(C) :	0.50568 %
Shell	21 Type: D	in atom	2(C) :	0.53532 %
Shell	28 Type: P	in atom	3(C) :	3.11049 %
Shell	29 Type: P	in atom	3(C) :	3.00385 %

Shell	30 Type: P	in atom	3(C) :	2.18759 %
Shell	43 Type: D	in atom	4(C) :	1.33192 %
Shell	50 Type: P	in atom	5(C) :	2.29655 %
Shell	51 Type: P	in atom	5(C) :	2.23401 %
Shell	52 Type: P	in atom	5(C) :	1.01104 %
Shell	72 Type: P	in atom	7(O) :	2.06075 %
Shell	73 Type: P	in atom	7(O) :	1.35463 %
Shell	83 Type: P	in atom	8(C) :	2.31200 %
Shell	84 Type: P	in atom	8(C) :	2.25022 %
Shell	85 Type: P	in atom	8(C) :	0.99980 %
Shell	98 Type: D	in atom	9(C) :	1.34222 %
Shell	105 Type: P	in atom	10(C) :	3.12806 %
Shell	106 Type: P	in atom	10(C) :	3.00787 %
Shell	107 Type: P	in atom	10(C) :	2.24284 %
Shell	116 Type: P	in atom	11(C) :	0.80950 %
Shell	117 Type: P	in atom	11(C) :	0.80176 %
Shell	118 Type: P	in atom	11(C) :	0.51313 %
Shell	120 Type: D	in atom	11(C) :	0.54040 %
Shell	127 Type: P	in atom	12(C) :	2.99418 %
Shell	128 Type: P	in atom	12(C) :	2.96570 %
Shell	129 Type: P	in atom	12(C) :	1.28716 %
Shell	149 Type: P	in atom	14(N) :	1.77011 %
Shell	150 Type: P	in atom	14(N) :	1.41279 %
Shell	182 Type: P	in atom	17(N) :	1.75450 %
Shell	183 Type: P	in atom	17(N) :	1.40068 %
Shell	215 Type: P	in atom	20(C) :	12.88617 %
Shell	216 Type: P	in atom	20(C) :	11.14608 %
Shell	217 Type: P	in atom	20(C) :	4.35832 %
Shell	230 Type: D	in atom	21(C) :	1.02886 %

Shell	303 Type: P	in atom	28(O) :	0.86472 %
Shell	304 Type: P	in atom	28(O) :	0.63175 %

Table S7. Composition of each atom in LUMO of **ORho**

Atom	1(C) :	7.34979 %
Atom	2(C) :	2.72816 %
Atom	3(C) :	8.35558 %
Atom	4(C) :	2.14851 %
Atom	5(C) :	5.72942 %
Atom	6(C) :	0.55015 %
Atom	7(O) :	3.23623 %
Atom	8(C) :	5.75120 %
Atom	9(C) :	2.16353 %
Atom	10(C) :	8.44939 %
Atom	11(C) :	2.74913 %
Atom	12(C) :	7.39724 %
Atom	13(C) :	0.54902 %
Atom	14(N) :	3.42856 %
Atom	15(C) :	0.08750 %
Atom	16(C) :	0.17370 %
Atom	17(N) :	3.39804 %
Atom	18(C) :	0.08688 %
Atom	19(C) :	0.17234 %
Atom	20(C) :	28.51252 %
Atom	21(C) :	1.17670 %
Atom	22(C) :	0.49597 %
Atom	23(C) :	0.18299 %
Atom	24(C) :	-0.01078 %
Atom	25(C) :	0.07673 %

Atom	26(C) :	0.81952 %
Atom	27(C) :	-0.21005 %
Atom	28(O) :	1.44875 %
Atom	29(O) :	0.02717 %
Atom	30(H) :	0.01922 %
Atom	31(H) :	0.06223 %
Atom	32(H) :	0.00034 %
Atom	33(H) :	0.06031 %
Atom	34(H) :	0.01952 %
Atom	35(H) :	0.00039 %
Atom	36(H) :	0.00035 %
Atom	37(H) :	0.39069 %
Atom	38(H) :	0.38837 %
Atom	39(H) :	0.28946 %
Atom	40(H) :	0.00014 %
Atom	41(H) :	0.28262 %
Atom	42(H) :	0.39012 %
Atom	43(H) :	0.38515 %
Atom	44(H) :	0.00020 %
Atom	45(H) :	0.28115 %
Atom	46(H) :	0.28663 %
Atom	47(H) :	0.00003 %
Atom	48(H) :	-0.00217 %
Atom	49(H) :	0.09271 %
Atom	50(H) :	0.01024 %
Atom	51(H) :	0.01838 %

Table S8. Composition of each shell in LUMO of **SRho**

Shell	6 Type: P	in atom	1(C) :	2.87182 %

Shell	7 Type: P	in atom	1(C) :	2.85166 %
Shell	8 Type: P	in atom	1(C) :	1.20066 %
Shell	28 Type: P	in atom	3(C) :	2.71372 %
Shell	29 Type: P	in atom	3(C) :	2.64450 %
Shell	30 Type: P	in atom	3(C) :	2.03596 %
Shell	43 Type: D	in atom	4(C) :	1.32264 %
Shell	50 Type: P	in atom	5(C) :	2.99777 %
Shell	51 Type: P	in atom	5(C) :	2.72613 %
Shell	52 Type: P	in atom	5(C) :	1.07040 %
Shell	74 Type: P	in atom	7(S) :	1.20776 %
Shell	75 Type: P	in atom	7(S) :	2.64887 %
Shell	76 Type: P	in atom	7(S) :	2.31104 %
Shell	85 Type: P	in atom	8(C) :	2.99180 %
Shell	86 Type: P	in atom	8(C) :	2.71990 %
Shell	87 Type: P	in atom	8(C) :	1.06894 %
Shell	100 Type: D	in atom	9(C) :	1.32298 %
Shell	107 Type: P	in atom	10(C) :	2.71016 %
Shell	108 Type: P	in atom	10(C) :	2.64224 %
Shell	109 Type: P	in atom	10(C) :	2.02901 %
Shell	129 Type: P	in atom	12(C) :	2.86640 %
Shell	130 Type: P	in atom	12(C) :	2.84632 %
Shell	131 Type: P	in atom	12(C) :	1.19744 %
Shell	151 Type: P	in atom	14(N) :	1.73517 %
Shell	152 Type: P	in atom	14(N) :	1.38498 %
Shell	184 Type: P	in atom	17(N) :	1.73924 %
Shell	185 Type: P	in atom	17(N) :	1.38817 %
Shell	217 Type: P	in atom	20(C) :	12.78481 %
Shell	218 Type: P	in atom	20(C) :	11.43928 %
Shell	219 Type: P	in atom	20(C) :	3.84905 %

Shell	232 Type: D	in atom	21(C) :	0.96317 %
Shell	305 Type: P	in atom	28(O) :	0.91374 %
Shell	306 Type: P	in atom	28(O) :	0.66833 %

Table S9. Composition of each atom in LUMO of **SRho**

Atom	1(C) :	7.03883 %
Atom	2(C) :	1.85565 %
Atom	3(C) :	7.42066 %
Atom	4(C) :	1.78860 %
Atom	5(C) :	6.86433 %
Atom	6(C) :	0.51811 %
Atom	7(S) :	6.61578 %
Atom	8(C) :	6.85038 %
Atom	9(C) :	1.78726 %
Atom	10(C) :	7.40711 %
Atom	11(C) :	1.85402 %
Atom	12(C) :	7.02465 %
Atom	13(C) :	0.51711 %
Atom	14(N) :	3.36020 %
Atom	15(C) :	0.11023 %
Atom	16(C) :	0.14633 %
Atom	17(N) :	3.36841 %
Atom	18(C) :	0.11030 %
Atom	19(C) :	0.14653 %
Atom	20(C) :	28.17636 %
Atom	21(C) :	1.25799 %
Atom	22(C) :	0.45143 %
Atom	23(C) :	0.18564 %
Atom	24(C) :	-0.03561 %

Atom	25(C) :	0.04552 %
Atom	26(C) :	0.88200 %
Atom	27(C) :	-0.18813 %
Atom	28(O) :	1.54468 %
Atom	29(O) :	0.03218 %
Atom	30(H) :	0.01170 %
Atom	31(H) :	0.05150 %
Atom	32(H) :	0.00260 %
Atom	33(H) :	0.05171 %
Atom	34(H) :	0.01156 %
Atom	35(H) :	0.00229 %
Atom	36(H) :	0.00018 %
Atom	37(H) :	0.34077 %
Atom	38(H) :	0.34232 %
Atom	39(H) :	0.30047 %
Atom	40(H) :	0.00015 %
Atom	41(H) :	0.31050 %
Atom	42(H) :	0.34433 %
Atom	43(H) :	0.33978 %
Atom	44(H) :	0.00014 %
Atom	45(H) :	0.30120 %
Atom	46(H) :	0.31089 %
Atom	47(H) :	0.00007 %
Atom	48(H) :	0.02375 %
Atom	49(H) :	0.09588 %
Atom	50(H) :	0.01066 %
Atom	51(H) :	0.01102 %

5.4 Spectra calculation

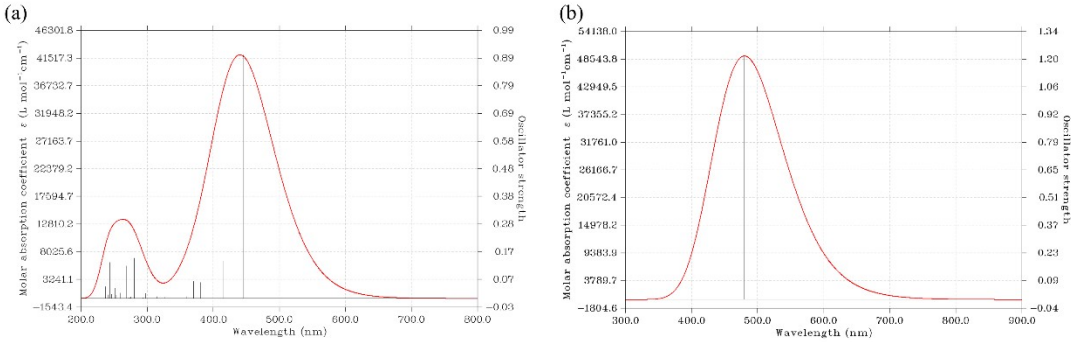


Fig. S19. Calculated absorption and emission spectra of **ORho**.

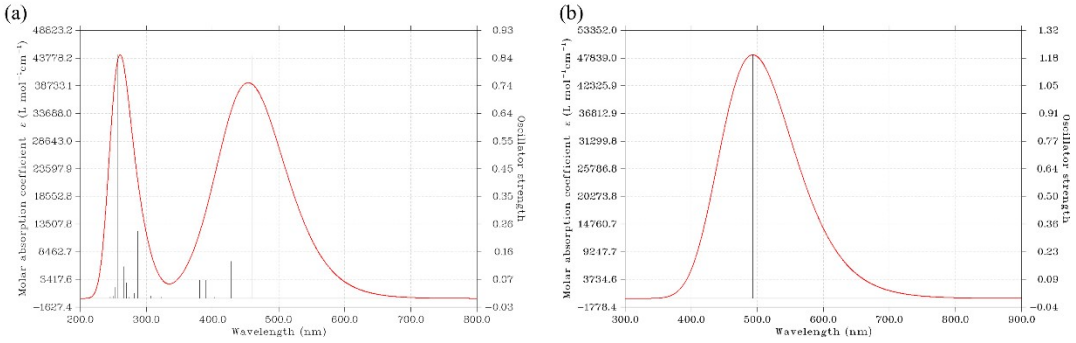


Fig. S20. Calculated absorption and emission spectra of **SRho**.

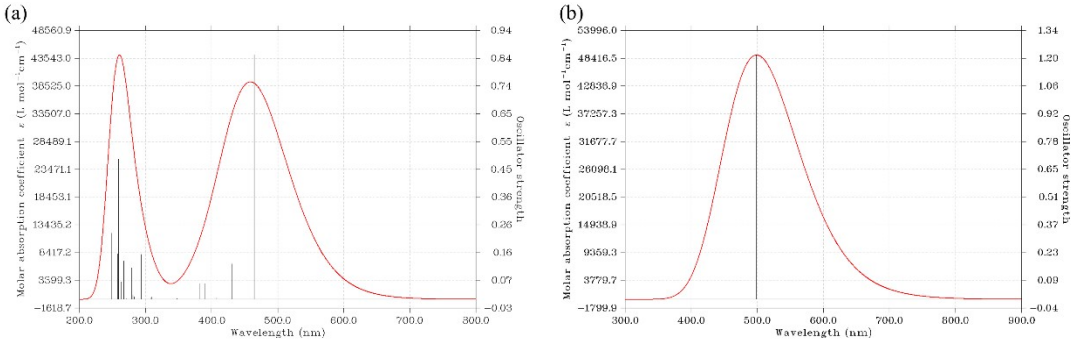


Fig. S21. Calculated absorption and emission spectra of **6-Br-SRho**.

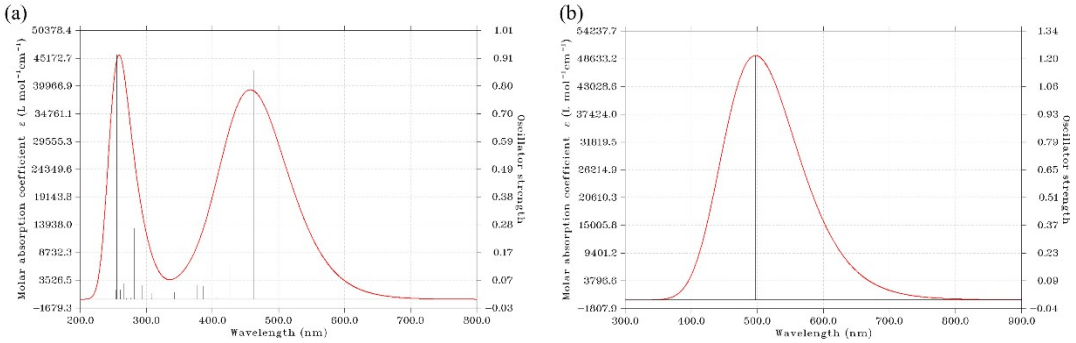


Fig. S22. Calculated absorption and emission spectra of **6-CO_2Me-SRho**.

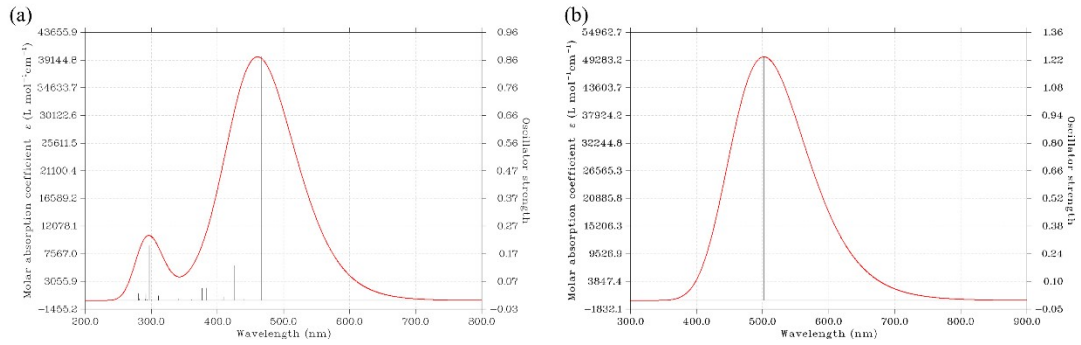


Fig. S23. Calculated absorption and emission spectra of **5-NO_2-SRho**.

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