Unveiling a New Aspect of Oxocarbons: Open-Shell Character of 4- and 5-Membered Oxocarbon Derivatives Showing Near-Infrared Absorption

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1. Experimental Section

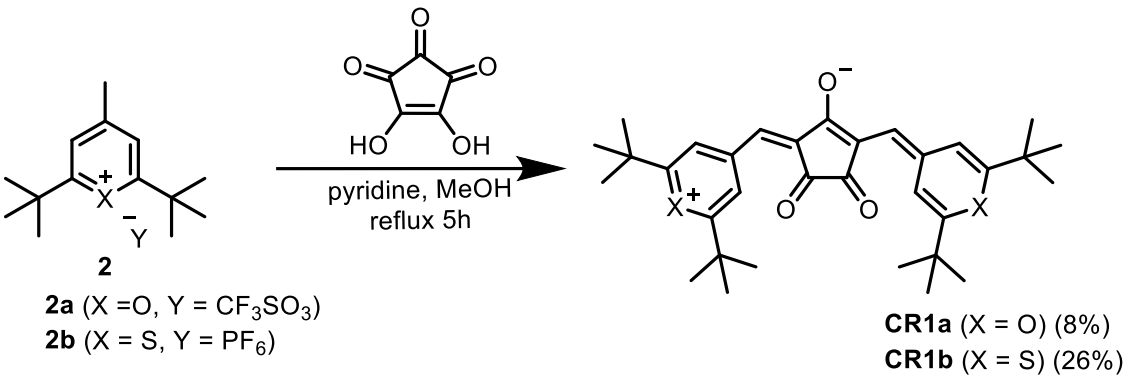
1-1. Materials and Instruments

Preparative HPLC was performed on Japan Analytical Industry Co., Ltd. LC-9130NEXT equipped with size-exclusion colomns of JAIGEL-2H-40 and JALGEL-1H-40 using $CHCl_3$ as an eluent. ^{1}H-NMR spectra were obtained using JEOL ECX-400 or ECS-400 spectrometers operating at 400 MHz. Variable-temperature ESR spectra were recorded with a JEOL JES-TE-200 X-band spectrometer with a JEOL DVT2 variable-temperature unit. The magnetic susceptibilities were measured on Quantum Design MPMS-3 SQUID magnetometers. The electrospray ionization mass spectra (ESI-MS) were recorded on a JEOL JMS-T100CS spectrometer using methanol-dichloromethane (1/1, v/v) as eluents. The elemental analyses were performed on a Yanako CHN CORDER JM-10 analyzer. The absorption spectra were measured in a 1.0 or 0.10 cm quartz cell on a Shimadzu UV-3600 spectrophotometer. The oxidation potential of the dye was measured on Hokuto Denko HZ-5000 electrochemical measurement system at a scanning rate of 100 mV s^{-1}, equipped with a normal one-compartment cell with a glassy carbon working electrode, a Pt counter electrode, and a nonaqueous $Ag/AgNO_3$ reference electrode. The measurement was performed in a dichloromethane solution including 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte.

All solvents and reagents were purchased from commercial sources and used as received without further purification. Silica gel (SiO_2, spherically-shaped, neutral) for the flash chromatography was purchased from Kanto chemical (Tokyo, Japan). Spectroscopic-grade solvents were purchased from Wako Pure Chemicals (Osaka, Japan) and used immediately after opening for all spectroscopic measurements. Crononic acid, squaric acid, and 2,6-Di-*tert*-butyl-4-methylpyrylium trifluoromethanesulfonate (**2a**) were purchased from Tokyo Chemical Industry (Tokyo, Japan). 2,6-Di-*tert*-butyl-4-methylthiopyrylium hexafluorophosphate (**2b**) and were prepared according to the literature.[1]

1-2. Synthesis and characterization

Synthesis of croconaine dyes



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2a (X =O, Y = CF_3SO_3)
2b (X = S, Y = PF_6)

CR1a (X = O) (8%)
CR1b (X = S) (26%)

Preparation of CR1a

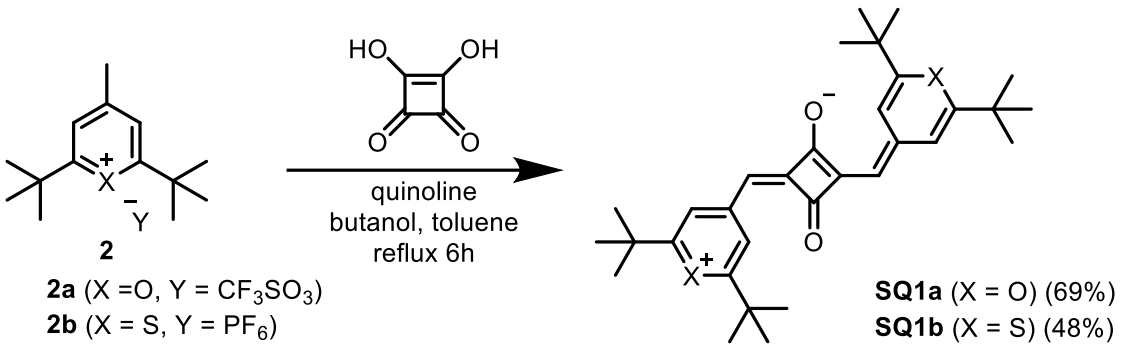
2,6-Di-*tert*-butyl-4-methylpyrylium trifluoromethanesulfonate (**2a**) (0.40 g, 1.1 mmol) and 4,5-dihydroxycyclopent-4-ene-1,2,3-trione (croconic acid) (0.080 g, 0.56 mmol) were dissolved in methanol (15 mL). Pyridine was added, and then the solution was heated under reflux for 5 hours. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent: $CHCl_3$). The crude product was further purified by preparative HPLC (JALGEL-2H-40:JALGEL-1H-40) to give **CR1a** (0.022 g, 0.043 mmol) as a black solid in 8% yield. m.p. 145 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 213K): δ 9.32 (s, 0.5H, *trans*-isomer, Ar-H), 9.26 (s, 0.1H, *cis*-isomer, Ar-H), 9.21 (s, 0.5H, *trans*-isomer, Ar-H), 9.17 (s, 0.9H, *cis*-isomer, Ar-H), 6.76–6.61 (m, 2H, Ar-H), 6.54 (s, 0.5H, *trans*-isomer, CH), 6.48 (s, 0.1H, *cis*-isomer, CH), 6.46 (s, 0.9H, *cis*-isomer, CH), 6.43 (s, 0.5H, *trans*-isomer, CH), 1.61–1.28 (m, 36H, CH_3). UV/Vis/NIR ($CHCl_3$): λ_{max} (ε)=845 (181000 $mol^{-1}dm^3cm^{-1}$). HRMS (ESI): *m/z* calcd for $C_{33}H_{42}O_5$+H^+: 519.3110, found 519.3088. Elemental analysis calcd (%) for $C_{33}H_{42}O_5$: C 76.42, H 8.16; found: C76.22, H 8.23.

Preparation of CR1b

2,6-Di-tert-butyl-4-methylthiopyrylium hexafluorophosphate (**2b**) (0.40 g, 1.0 mmol) and croconic acid (0.073 g, 0.52 mmol) were dissolved in a mixture of methanol (15 mL). Pyridine was added, and then the solution was heated under reflux for 5 hours. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent: $CHCl_3$). The crude

product was further purified by preparative HPLC (JALGEL-2H-40:JALGEL-1H-40) to give **CR1b** (0.074 g, 0.13 mmol) as a black solid in 26% yield. m.p.: 213 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$, 213K): δ 10.06 (s, 0.4H, *trans*-isomer, Ar-H), 9.94 (s, 0.4H, *trans*-isomer, Ar-H), 9.90 (s, 1.2H, *cis*-isomer, Ar-H), 7.46–7.35 (m, 2H, Ar-H), 7.34 (s, 0.1H, *cis*-isomer, Ar-H), 6.80 (s, 0.4H, *trans*-isomer, Ar-H), 6.75 (s, 0.1H, *cis*-isomer, Ar-H), 6.71 (s, 1.1H, *cis*-isomer, Ar-H), 6.70 (s, 0.4H, *trans*-isomer, Ar-H), 1.56–1.37 (m, 36H, CH_3). UV/Vis/NIR ($CHCl_3$): λ_{max} (ε)=954 (218000 $mol^{-1}dm^3cm^{-1}$). HRMS (ESI): *m/z* calcd for $C_{33}H_{42}O_3S_2+H^+$: 551.2654, found 551.2623. Elemental analysis calcd (%) for $C_{33}H_{42}O_3S_2$: C 71.96, H 7.69; found: C71.62, H 7.76.

Synthesis of squaraine dyes



Preparation of SQ1a

2,6-Di-tert-butyl-4-methylpyrylium trifluoromethanesulfonate (**2a**) (0.40 g, 1.1 mmol) and squaric acid (0.064 g, 0.56 mmol) were dissolved in a mixture of 1-butanol/benzene (1/1, 15 mL). A few drop of quinoline was added, and then the solution was heated under reflux for 6 hours. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent: ethyl acetate/DCM (1/1, v/v)) to give **SQ1a** (0.17 g, 0.34 mmol) as a green solid in 61% yield. m.p.: 205 °C (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz, 213 K): δ 8.68–8.63 (m ,2H, Ar-H), 6.24–6.19 (m, 2H, Ar-H), 5.82–5.80 (m, 2H, CH), 1.34–1.28 (m, 36H, CH_3). UV/Vis/NIR ($CHCl_3$): λ_{max} (ε)=710 (247000 $mol^{-1}dm^3cm^{-1}$). HRMS (ESI): *m/z* calcd for $C_{32}H_{42}O_4+H^+$: 491.3161, found 491.3133. Elemental analysis calcd (%) for $C_{32}H_{42}O_4$: C 78.33, H 8.63; found: C78.41, H 8.65.

Preparation of SQ1b 2,6-Di-tert-butyl-4-methylthiopyrylium hexafluorophosphate (**2b**) (0.40 g, 1.0 mmol) and squaric acid (0.059 g, 0.52 mmol) were dissolved in a mixture of 1-butanol/benzene (1/1, 15 mL). A few drop of quinoline was added, and then the solution was heated under reflux for 6 hours. After cooling, the solvent was removed on a rotary evaporator, and the residue was purified by silica gel column chromatography (eluent: ethyl acetate) to give **SQ1b** (0.13 g, 0.25 mmol) as a orange solid in 48% yield. m.p.: 253 °C (decomp.); ^{1}H NMR ($CDCl_3$, 400 MHz, 213 K): δ 9.28 (s, 0.3H, *cis*-isomer, Ar-H), 9.21 (s, 1.7H, *trans*-isomer, Ar-H), 6.95–6.88 (m, 2H, Ar-H), 6.08–6.00 (m, 2H, CH), 1.54–1.27 (m, 36H, CH_3). UV/Vis/NIR ($CHCl_3$): λ_{max} (ε)=810 (298000 $mol^{-1}dm^3cm^{-1}$). HRMS (ESI): *m/z* calcd for $C_{32}H_{42}O_2S_2+H^+$: 523.2704, found 523.2684. Elemental analysis calcd (%) for $C_{32}H_{42}O_2S_2$: C 73.52, H 8.10; found: C73.16, H 8.22.

2. Stability assessment

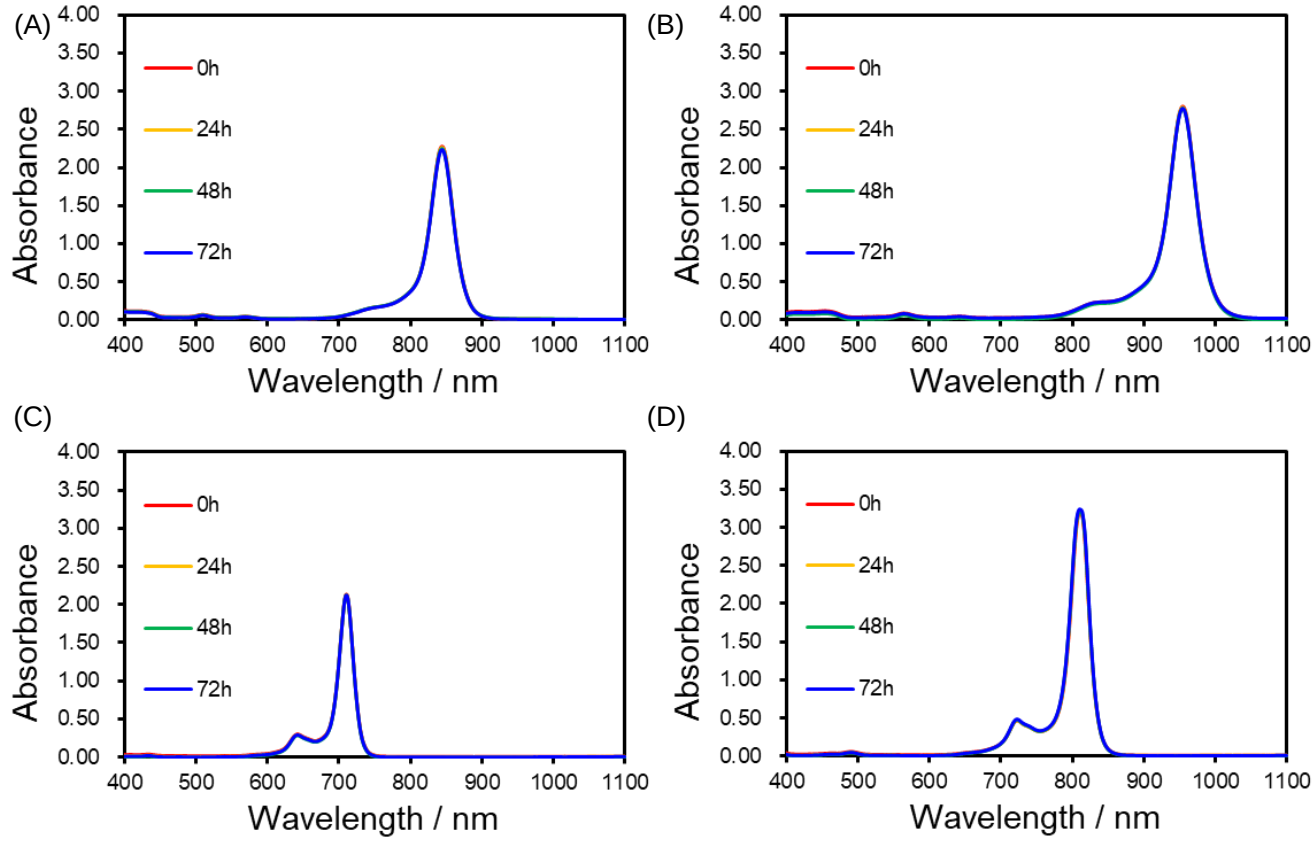


Fig. S1. Time dependent UV-vis-NIR absorption spectra (100 μM, $CHCl_3$) of **CR1a** (A), **CR1b** (B), **SQ1a** (C), and **SQ1b** (D) measured in a 1-mm-cuvette under dark and ambient air condition. No change in spectrum was observed for each compound within 72h.

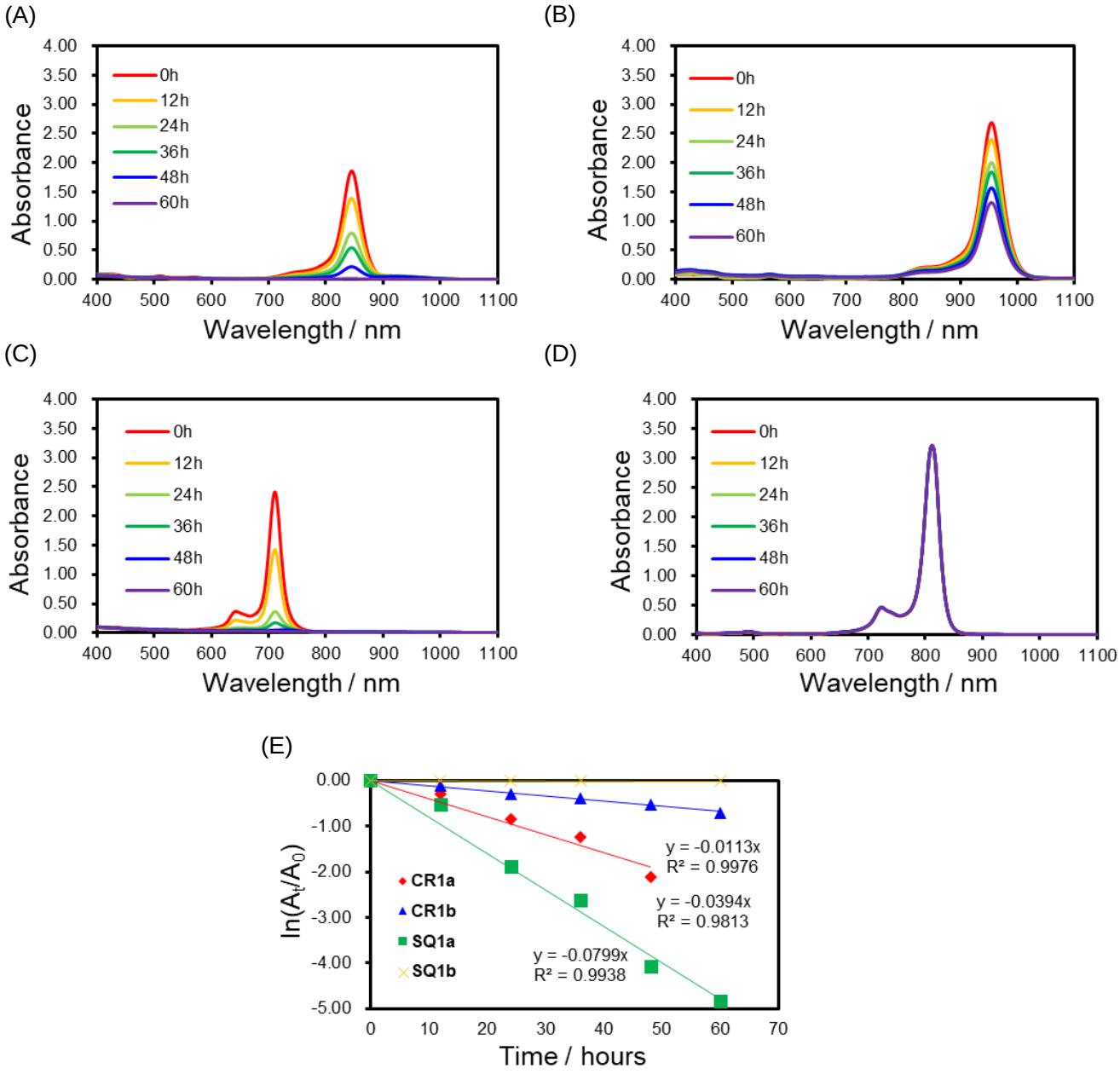


Fig. S2. Time dependent UV-vis-NIR absorption spectra (100 μM, $CHCl_3$) of **CR1a** (A), **CR1b** (B), **SQ1a** (C), and **SQ1b** (D) measured in a 1-mm-cuvette under ambient air and room light, and pseudo-first-order kinetics of the degradation when monitored at maximum absorption wavelength of **CR1a-b** and **SQ1a-b** (E). The half-life periods were estimated to be 37 h for **CR1a**, 61 h for **CR1b,** and 8.7h for **SQ1a**. **SQ1b** showed no change in the absorbance.

3. Variable temperature ^{1}H-NMR spectra

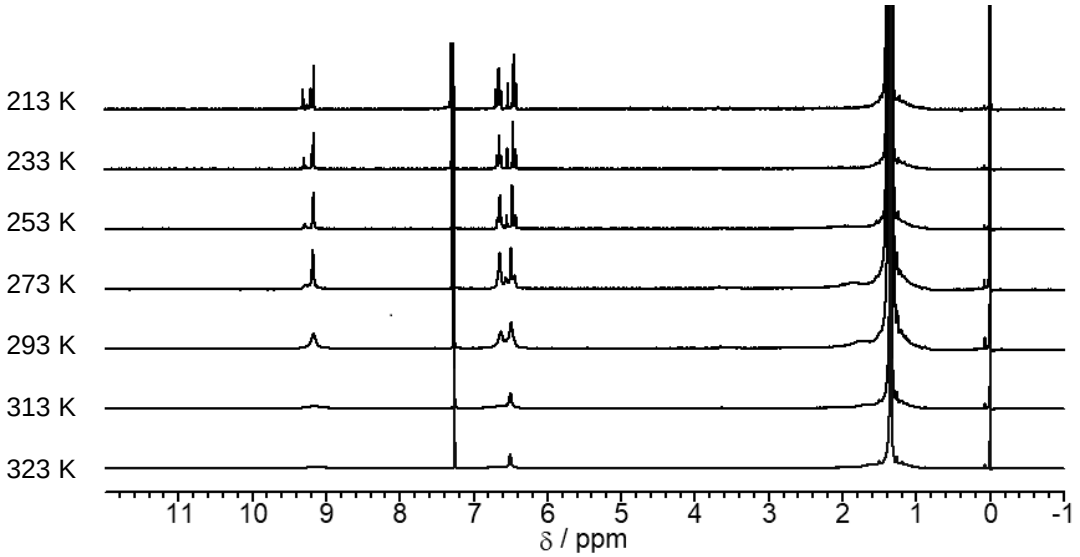


Fig. S3. Variable temperature ^{1}H-NMR spectra ($CDCl_3$, 213 K-323 K) of **CR1a.**

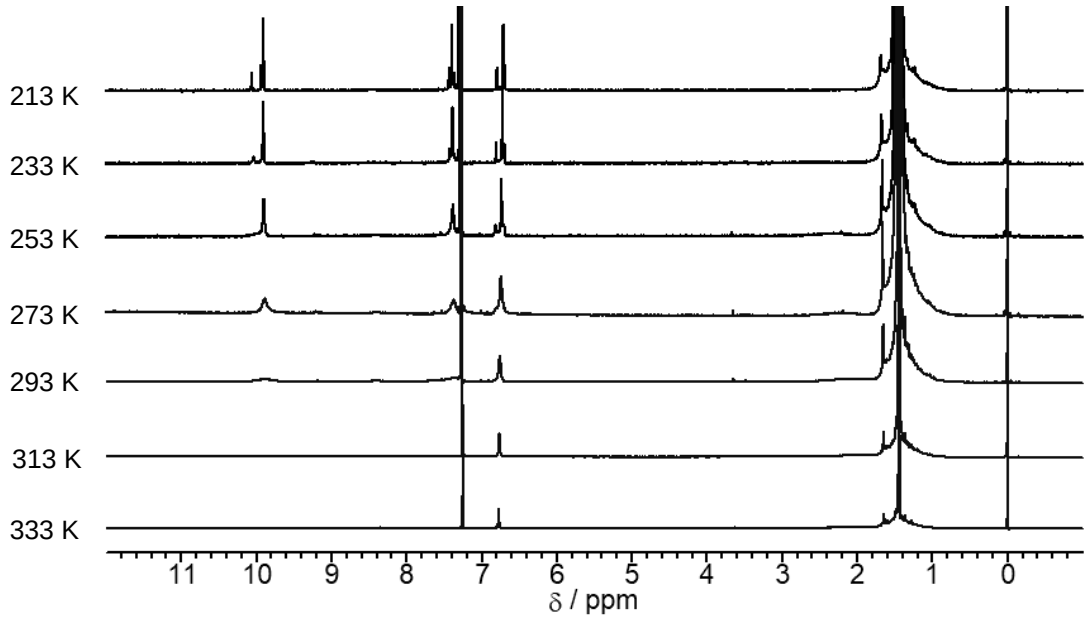


Fig. S4. Variable temperature ^{1}H-NMR spectra ($CDCl_3$, 213 K-323 K) of **CR1b**.

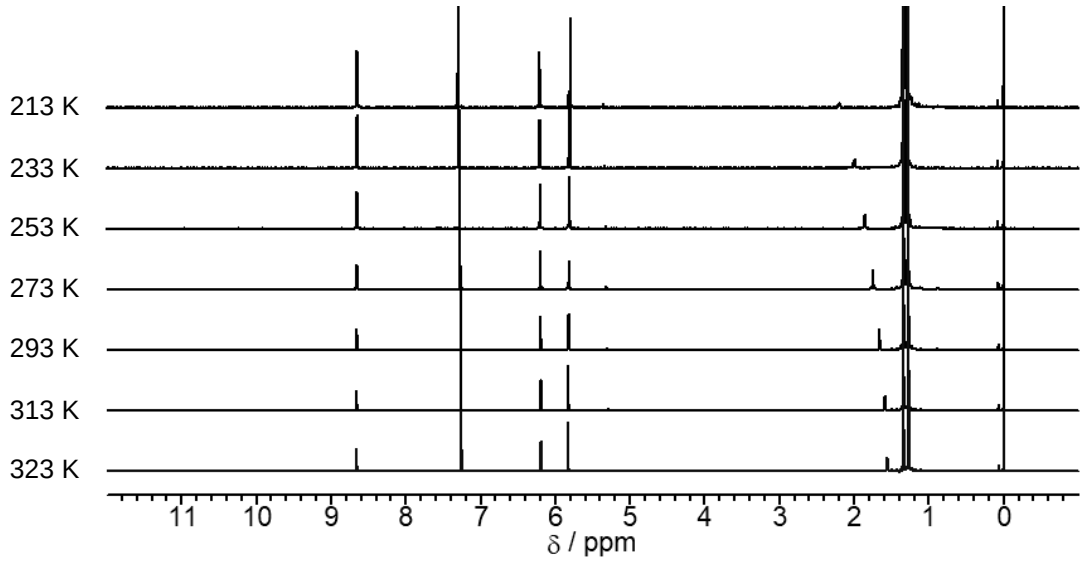


Fig. S5. Variable temperature ^{1}H-NMR spectra of **SQ1a** in $CDCl_3$ (213 K-323 K).

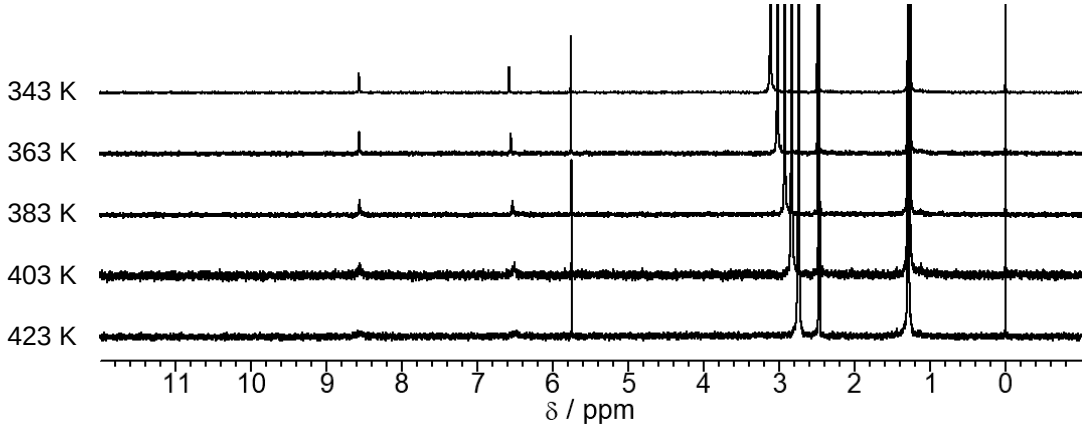


Fig. S6. Variable temperature ^{1}H-NMR spectra of **SQ1a** in DMSO-d_6 (343-423 K).

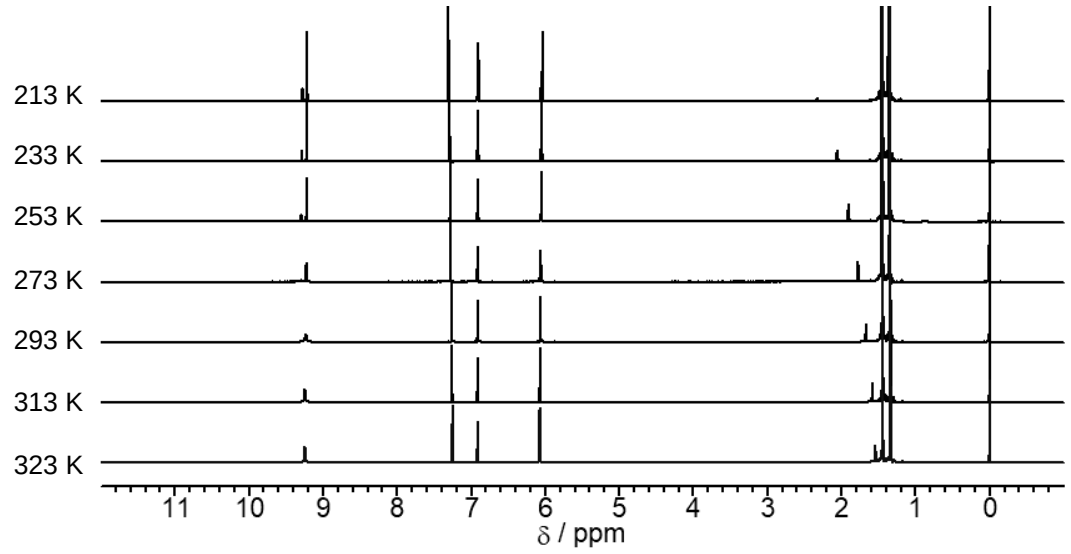


Fig. S7. Variable temperature ^{1}H-NMR spectra of **SQ1b** in $CDCl_3$ (213 K-323 K).

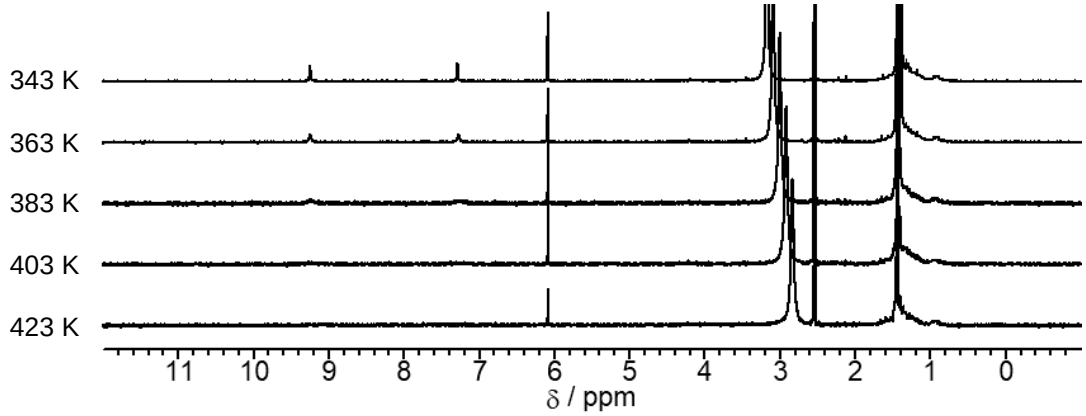


Fig. S8. Variable temperature ^{1}H-NMR spectra of **SQ1b** in DMSO-d_6 (343-423 K).

4. Variable temperature ESR spectra

The variable temperature (VT) ESR spectra were measured on a JEOL JES-TE-200 X-band spectrometer with a JEOL DVT2 variable-temperature unit. The temperature dependency of ESR intensities (I_{ESR}) of present dyes in the solid state was fitted by modified Bleaney-Bowers equation:

$$I_{ESR}T = \frac{C}{3+exp(-\Delta E_{S-T}/k_B T)}$$

Where I_{ESR} is the ESR intensity, T is the temperature, C is a constant, k_B is Boltzman's constant, and $\Delta E_{S\text{-}T}$ is an energy gap between the singlet ground state to the triplet excited state.

Although **CR1a-b** and **SQ1b** exhibited temperature-dependent ESR signals (Fig. 4), **SQ1a** showed very weak ESR signals above 383 K (Fig. S9).

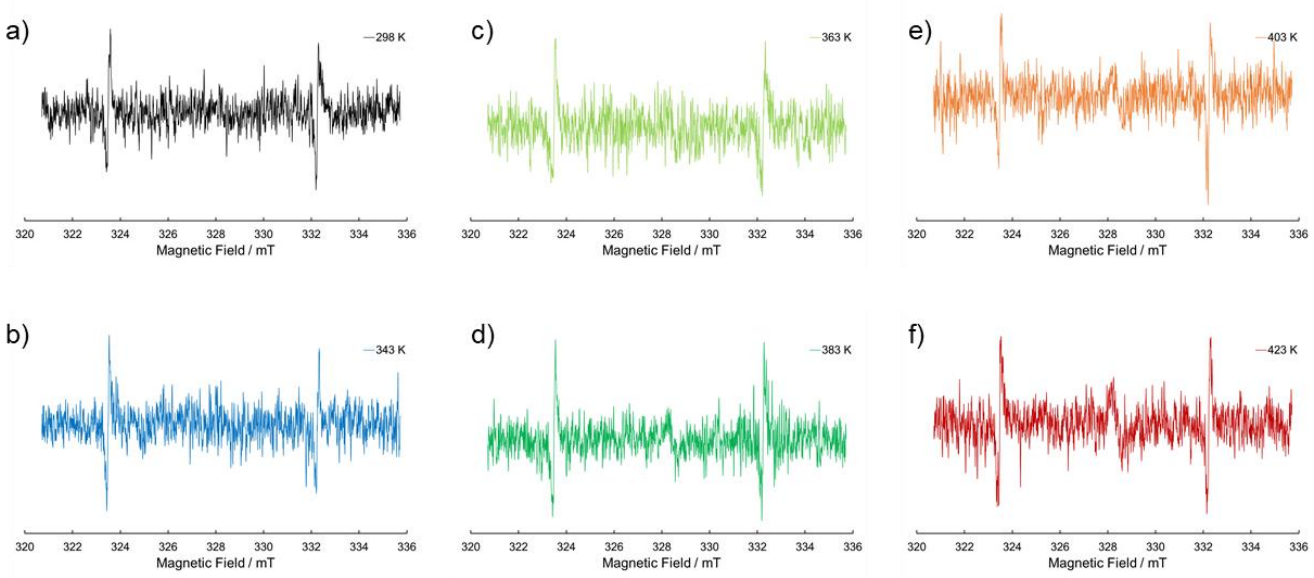


Fig. S9. ESR spectra of the powder samples of **SQ1a** measured at 298 K (a), 343 K (b), 368 K (c), 383 K (d), 403 K (e), and 423 K (f).

5. SQUID magnetometry

Magnetic susceptibility measurements were performed with an applied DC field of 1 T in the temperature range 10-340 K for all dyes. The samples were wrapped by aluminum foil (3.0×5.0 mm, 11.8 mg). The

susceptibility data for the samples were obtained by the deduction of the contribution of the aluminum foil for wrapping. The product of the molar magnetic susceptibility (χ) and temperature (T) for present dyes increased with an increase in temperature, and the data was fitted using the Bleaney-Bowers equation: [6]

$$\chi T = \frac{N_A g^2 {\mu_B}^2}{k_B} \frac{2}{3+exp(-2J/k_B T)}$$

Where χ is the molar magnetic susceptibility, T is the temperature, N_A is Avogadro constant, g is the magnetic field splitting factor, μ_B is the Bohr magneton, k_B is Boltzmann's constant, and $-2J$ is correlated to an energy gap between the singlet ground state to the triplet excited state ($\Delta E_{S\text{-}T}$).

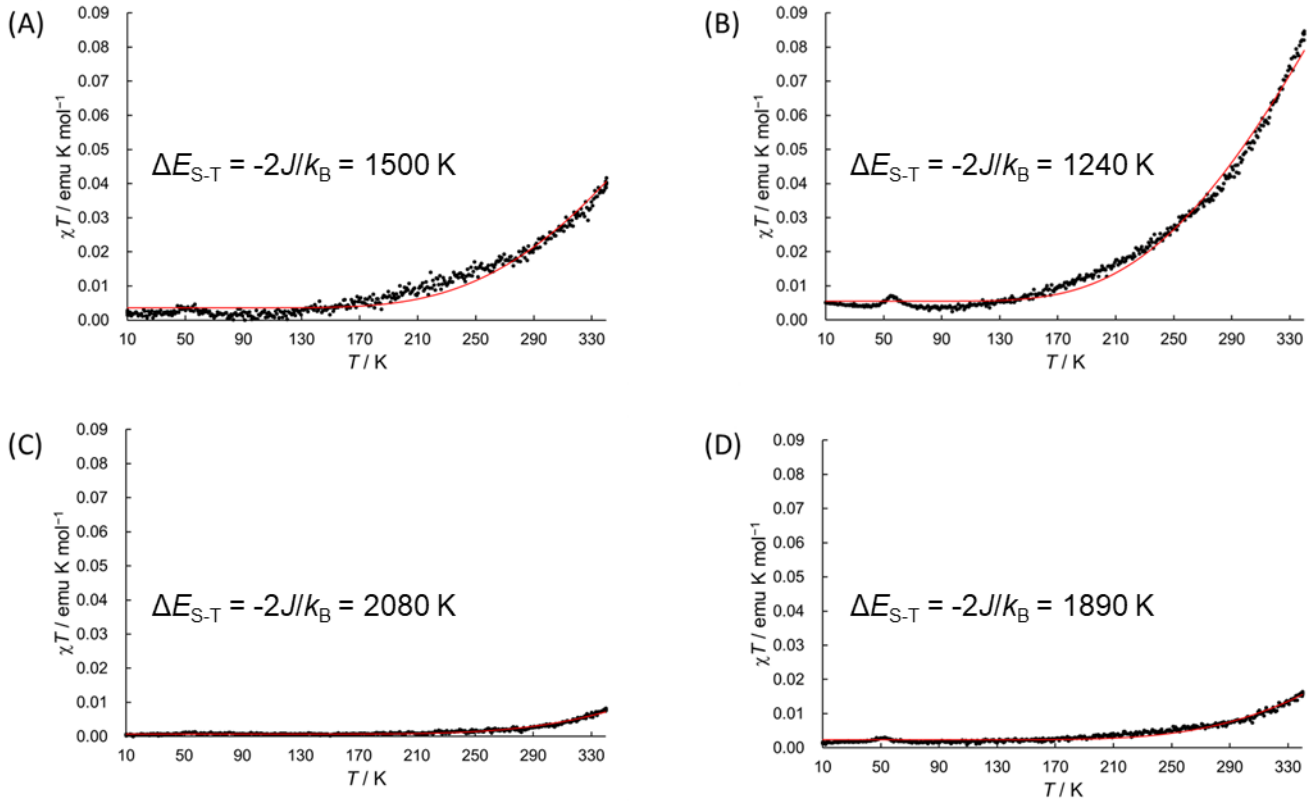


Fig. S10. χT–T plot in the SQUID of measurement for polycrystalline (solid) **CR1a** (A), **CR1b** (B), **SQ1a** (C) and **SQ1b** (D); the solid red line is the fitting curve according to Bleaney–Bowers equation.[6]

6. X-ray crystallographic analysis

Single crystals of **CR1b**, **SQ1a**, **SQ1b** were obtained by the slow diffusion of hexane into its chloroform solution. A black block crystal of **CR1b** having approximate dimensions of 0.400 x 0.200 x 0.150 mm, a bronze block crystal of **SQ1a** having approximate dimensions of 0.500 x 0.400 x 0.300 mm, a bronze platelet crystal of **SQ1b** having approximate dimensions of 0.450 x 0.400 x 0.050 mm were used for the measurements. Each crystal was mounted on a glass fiber. All measurements were made on a Rigaku R-AXIS RAPID diffractometer using graphite monochromated Mo-Kα radiation at 293 K. The structure was solved by a direct methods using the SIR92 program.[2] All the calculations were performed using the CrystalStructure 4.3 software package of the Molecular Structure Corporation.[3]

A summary of the crystallographic data and structure refinement for these two compounds is given in Table S1. Full crystallographic details excluding structure factors have been deposited at the Cambridge Crystallographic Data Centre (CCDC). CCDC- 2194627 for **CR1b**, CCDC- 2194625 for **SQ1a**, and CCDC- 2194626 for **SQ1b** contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystallographic data for **CR1b**, **SQ1a**, and **SQ1b** at 293 K.

	CR1b	**SQ1a**	**SQ1b**
Empirical Formula	$C_{34}H_{43}Cl_3O_3S_2$	$C_{32}H_{42}O_4$	$C_{48}H_{63}O_3S_3$
Formula Weight	670.19	490.68	784.20
T / K	293(2)	293(2)	298(2)
Color, habit	black, block	bronze,block	bronze, platelet
Size, mm	0.400 × 0.200 × 0.150	0.500 × 0.400 × 0.300	0.450 × 0.400 × 0.050
Crystal system	Triclinic	Monoclinic	Triclinic
Lattice Type	Primitive	Primitive	Primitive
Space group	P-1 (#2)	$P2_1/c$ (#14)	P-1 (#2)
a / Å	10.8829(10)	9.0911(8)	13.5881(12)
b / Å	11.8981(11)	15.1646(10)	14.1008(10)
c / Å	14.5843(12)	10.8715(8)	14.4563(12)
α / °	100.894(7)	-	89.576(6)
β / °	93.914(7)	90.782(6)	67.544(5)
γ / °	104.037(7)	-	67.336(5)
V/ Å^3	1786.1(3)	1498.63(19)	2330.2(4)
Z	2	2	2
*D*calc / g cm^{-3}	1.246	1.087	1.118
F_{000}	708	532	846
μ / cm^{-1}	MoKα, 4.041	MoKα, 0.699	MoKα, 1.960
2*θ*max / º	55	54.9	54.9
Total reflections	17414	13804	22351
Unique reflections	8104	3400	10470
Reflection/Parameter Ratio	9.28	11.73	8.77
R (*I* > 3.00σ(*I*)[a]	0.0897	0.0466	0.0746
*R*w (*I* > 3.00σ(*I*)[b]	0.0926	0.0548	0.0893
Goodness of Fit Indicator	1.151	1.13	1.113

[a]$R = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo|$, [b]$Rw = [\Sigma \, w \, (|Fo| - |Fc|)^2 \, / \, \Sigma \, w \, Fo^2]^{1/2}$

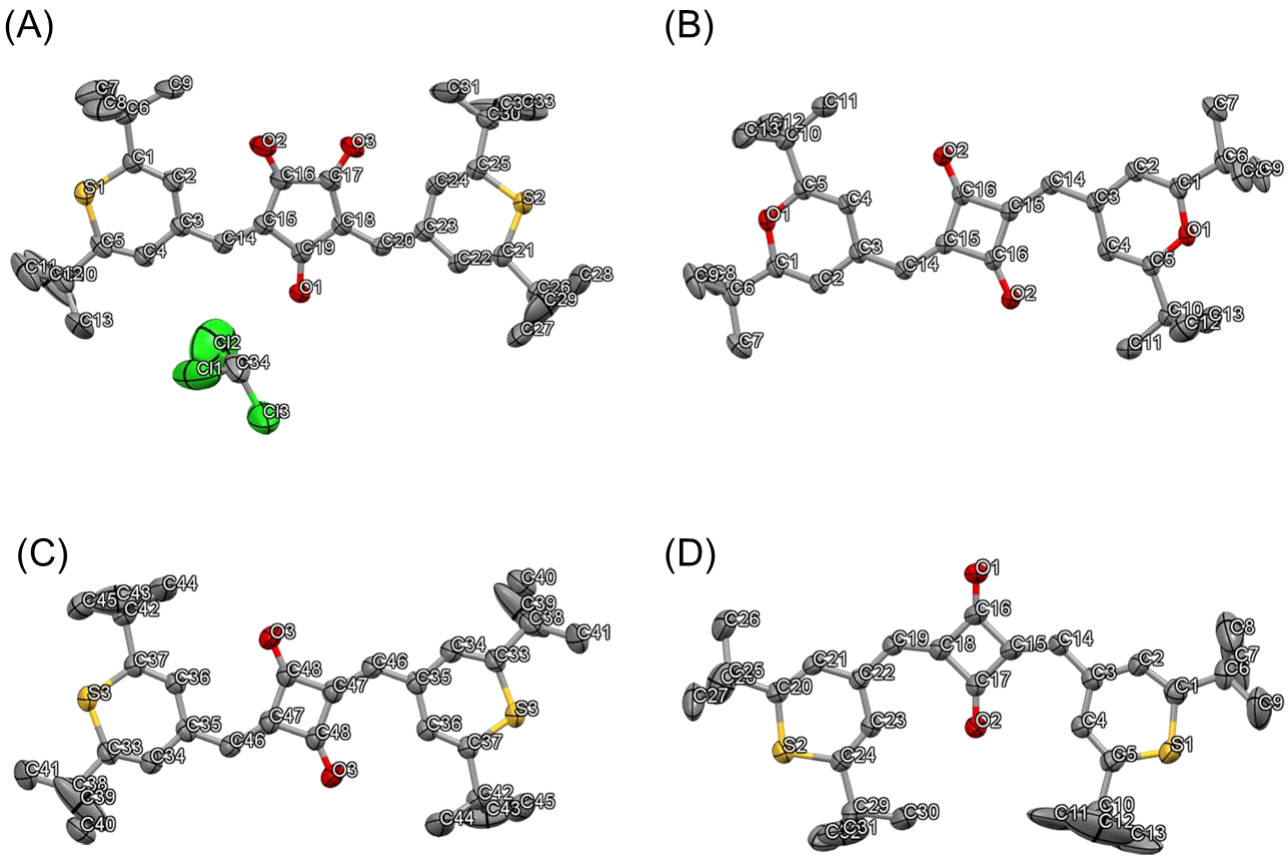


Fig. S11. Oak Ridge thermal ellipsoid program drawing of **CR1b** (A), **SQ1a** (B), transoid **SQ1b** (C), and cisoid **SQ1b** conformers in the crystal (D).

Table S2. Representative C-C bond lengths of the single cyratal of **CR1b**, **SQ1a** and **SQ1b** at 293 K.

CR1b		**SQ1a**		**SQ1b** (*trans*)		**SQ1b** (*cis*)	
bond	length (Å)	bond	length (Å)	bond	length (Å)	bond	length (Å)
S1-C1	1.720	O1-C1	1.367	S3-C33	1.722	S1-C1	1.744
S1-C5	1.714	O2-C16	1.230	S3-C37	1.737	S1-C5	1.742
S2-C21	1.720	C1-C2	1.353	O3-C48	1.222	S2-C20	1.744
S2-C25	1.725	C2-C3	1.436	C33-C34	1.345	S2-C24	1.736
O1-C19	1.234	C3-C4	1.436	C34-C35	1.431	O1-C16	1.222
O2-C16	1.203	C4-C5	1.348	C35-C36	1.432	O2-C17	1.224
O3-C17	1.223	C5-O1	1.371	C36-C37	1.340	C1-C2	1.344
C1-C2	1.354	C3-C14	1.397	C35-C46	1.396	C2-C3	1.435
C2-C3	1.419	C14-C15	1.395	C46-C47	1.377	C3-C4	1.429
C3-C4	1.427	C15-C16	1.469	C47-C48_a	1.487	C3-C14	1.397
C4-C5	1.341	C15-C15_a	1.481	C47-C48	1.463	C4-C5	1.338
C3-C14	1.414					C5-C10	1.338
C14-C15	1.366					C14-C15	1.397
C15-C16	1.457					C15-C16	1.466
C15-C19	1.471					C15-C17	1.474
C16-C17	1.509					C16-C18	1.463
C17-C18	1.424					C17-C18	1.485
C18- C19	1.473					C18-C19	1.464
C18-C20	1.392					C19-C22	1.474
C20-C23	1.394					C20-C21	1.344
C21-C22	1.350					C21-C22	1.435
C22-C23	1.415					C22-C23	1.434
C23-C24	1.429					C23-C24	1.340
C24-C25	1.343						

7. Resonance structures

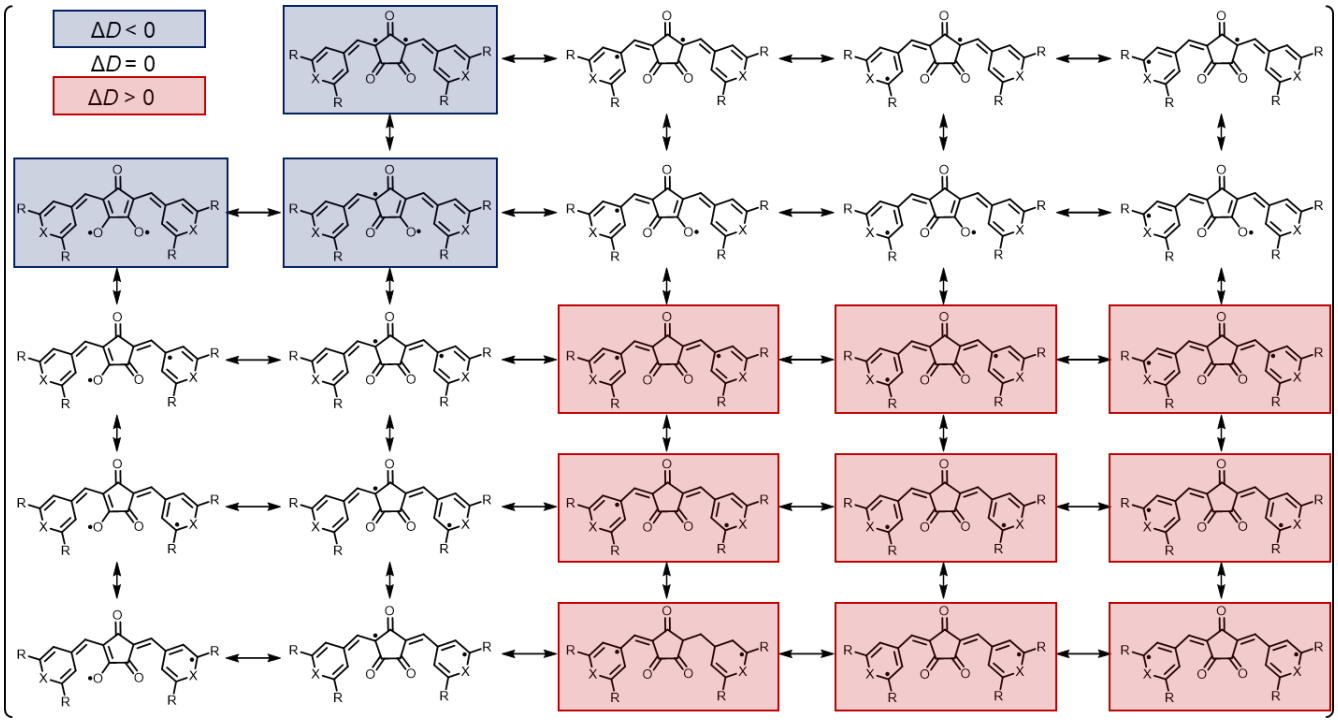


Fig. S12. A resonance structure for diradical form of **CR1a-b**. Glay and red backgrounds indicate resonance forms with $\Delta D < 0$ and $\Delta D > 0$, respectively. ΔD is defined as following equation: ΔD = ave. (***g***, ***p***) – ave. (***h***, ***q***).

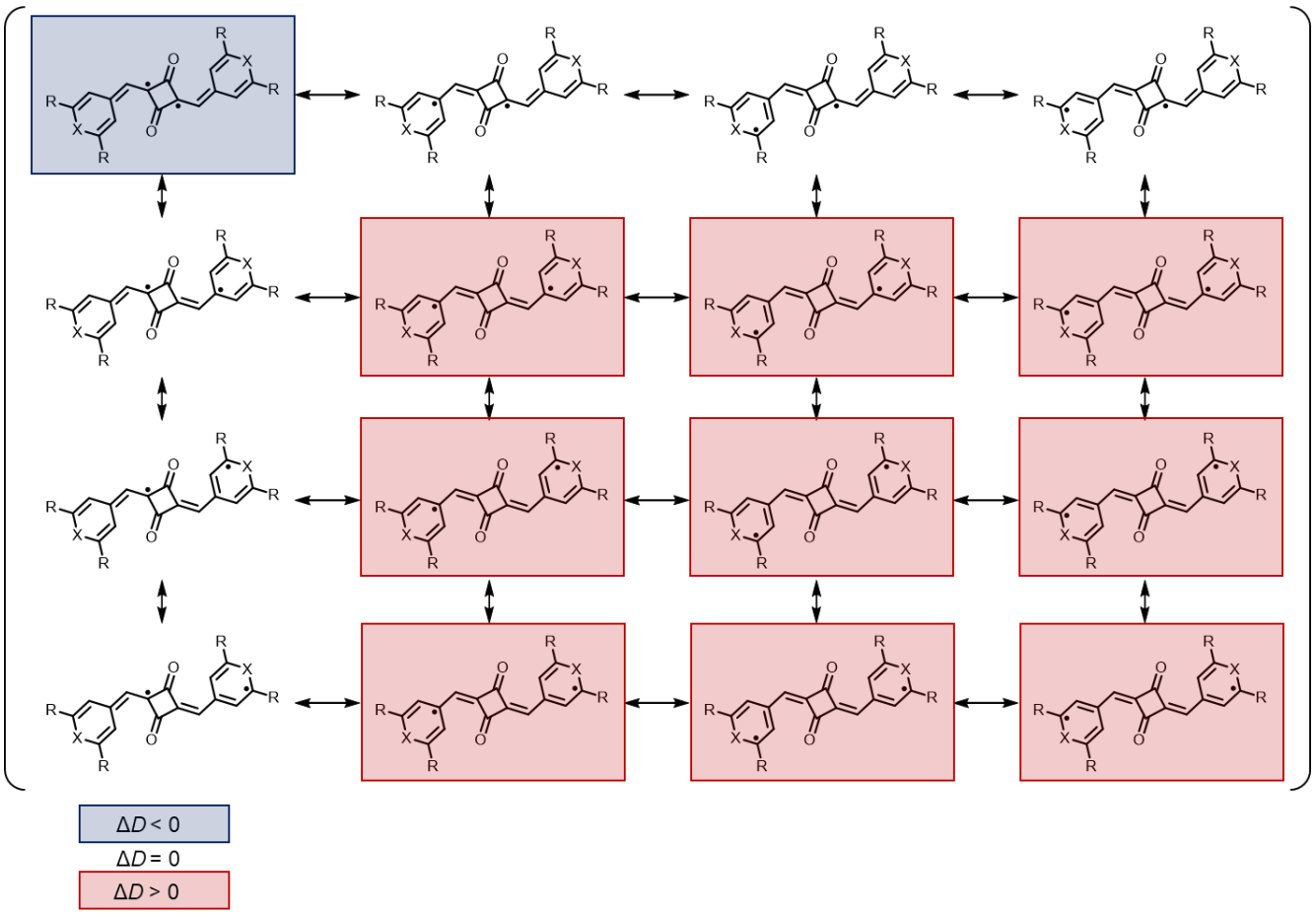
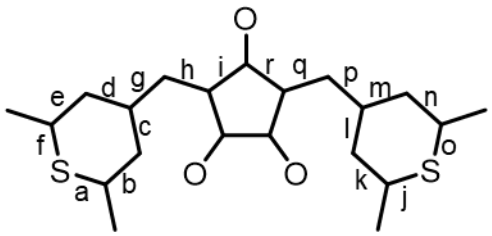


Fig. S13. A resonance structure for the diradical form of **CR1a-b**. Glay and red backgrounds indicate resonance forms with $\Delta D < 0$ and $\Delta D > 0$, respectively. ΔD is defined as following equation: ΔD = ave. (***g***, ***p***) – ave. (***h***, ***q***).

8. Bond length analysis

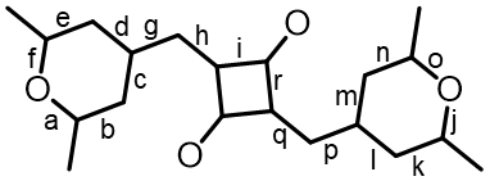
We examined the open shell character of the series of dyes in the aspect of geometric structures. Their structure can be described by the resonance between the mesomeric form with bond alternation (closed-shell) and the non-Kekuré form with singlet diradical character. The geometry optimizations were performed at CAM-RB3LYP/6-31G(d,p) level for singlet state, and at CAM-UB3LYP/6-31G(d,p) level for triplet states (Table S3-S6).[4] All calculations were performed on structures based on X-ray analysis. *t*-Butyl group on thiopyryliumu and pyrylium units in the X-ray structure was omitted for the calculations. Coordinates of the optimized geometries are shown in Tables S14-S28.

Table S3. Bond lengths (Å) for **CR1b** obtained by its optimized structure calculated at the CAM-RB3LYP/6-31G(d,p) levels for closed-shell singlet and CAM-UB3LYP/6-31G(d,p) levels for triplet state.



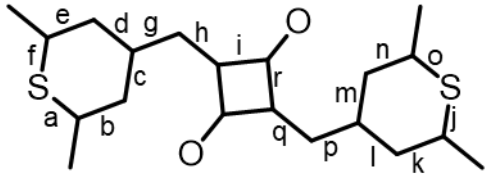
bond		Closed-shell singlet/ Å	Open-shell singlet / Å	Triplet /Å
a	j	1.74551	1.74942	1.75108
b	k	1.35114	1.35276	1.35373
c	l	1.43540	1.43243	1.43078
d	m	1.43939	1.43553	1.43328
e	n	1.35000	1.35160	1.35265
f	o	1.74200	1.74654	1.74851
g	p	1.39607	1.40735	1.41335
h	q	1.39288	1.38321	1.37807
i	r	1.46675	1.47982	1.48553

Table S4. Bond lengths (Å) for **SQ1a** obtained by its optimized structure calculated at the CAM-RB3LYP/6-31G(d,p) levels for closed-shell singlet and CAM-UB3LYP/6-31G(d,p) levels for triplet state.



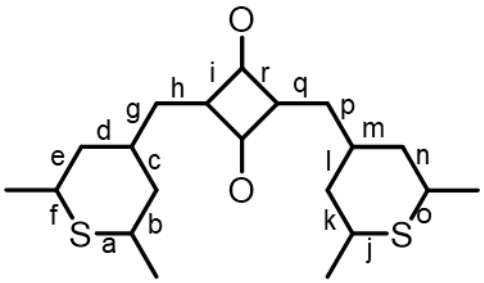
bond		Closed-shell singlet/ Å	Open-shell singlet / Å	Triplet /Å
a	j	1.36631	1.36721	1.37090
b	k	1.34491	1.34536	1.34813
c	l	1.44068	1.43968	1.43415
d	m	1.48982	1.43843	1.43083
e	n	1.34612	1.34656	1.34951
f	o	1.35720	1.35882	1.36618
g	p	1.38301	1.38764	1.41129
h	q	1.39527	1.39034	1.36653
i	r	1.46519	1.46948	1.48801

Table S5. Bond lengths (Å) for **SQ1b** (*trans*) obtained by its optimized structure calculated at the CAM-RB3LYP/6-31G(d,p) levels for closed-shell singlet and CAM-UB3LYP/6-31G(d,p) levels for triplet state.



bond		Closed-shell singlet/ Å	Open-shell singlet / Å	Triplet /Å
a	j	1.75031	1.75229	1.75551
b	k	1.34778	1.34937	1.35306
c	l	1.44098	1.43786	1.43100
d	m	1.44123	1.43707	1.42779
e	n	1.34796	1.34982	1.35434
f	o	1.74539	1.74787	1.75247
g	p	1.38698	1.39735	1.42029
h	q	1.39393	1.38387	1.36263
i	r	1.46648	1.47415	1.48882

Table S6. Bond lengths (Å) for **SQ1b** (*cis*) obtained by its optimized structure calculated at the CAM-RB3LYP/6-31G(d,p) levels for closed-shell singlet and CAM-UB3LYP/6-31G(d,p) levels for triplet state.



bond		Closed-shell singlet/ Å	Open-shell singlet / Å	Triplet /Å
a	j	1.75001	1.75197	1.75500
b	k	1.34778	1.34938	1.35307
c	l	1.44078	1.43764	1.43077
d	m	1.44158	1.43735	1.42817
e	n	1.34780	1.34978	1.35422
f	o	1.74587	1.74834	1.75278
g	p	1.38686	1.39746	1.42052
h	q	1.39428	1.38408	1.36292
i	r	1.47251	1.47881	1.49121

9. NICS(1) values

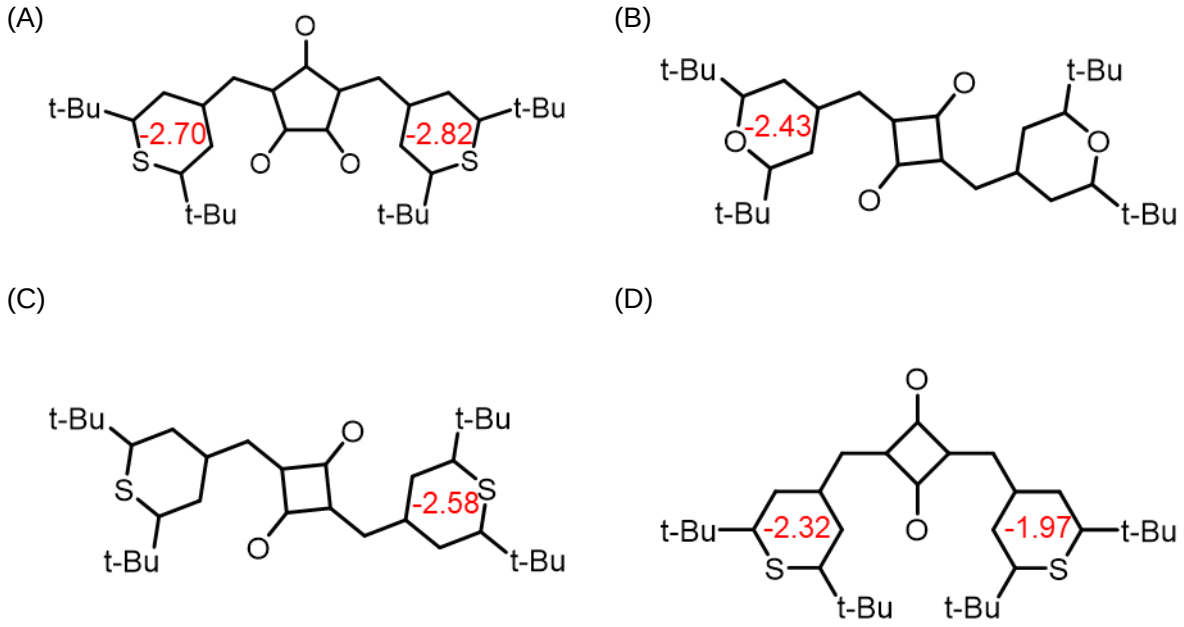


Fig. S14. NICS(1) values of pyrylium and thiopyrylium components calculated at GAIO UB3LYP/6-31G* are shown in red. (**CR1b** (A), **SQ1a** (B), *transoid* (C) and *cisoid* **SQ1b** (D))

10. Spin density of open-shell singlet

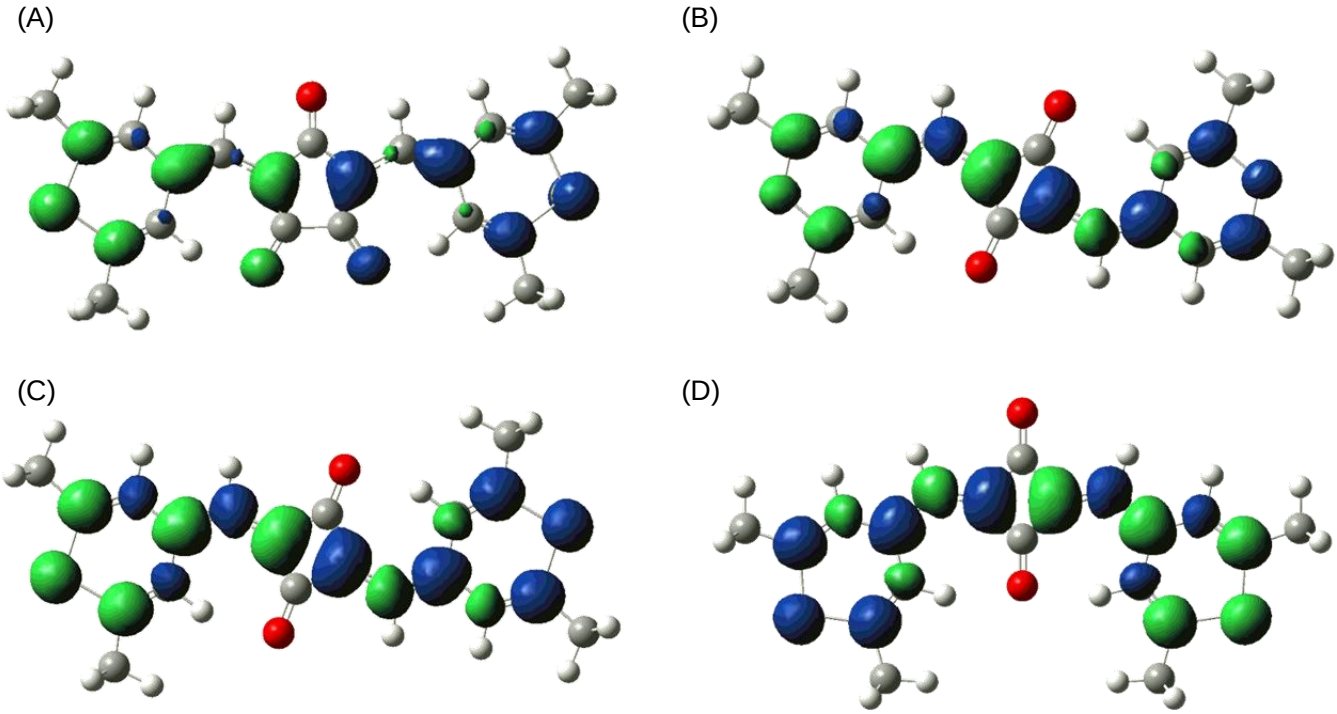


Fig. S15. Mulliken spin density maps of open-shell singlet states for **CR1b** (A), **SQ1a** (B), *transoid* **SQ1b** (C), and *cisoid* **SQ1b** (D) calculated at the CAM-UBLYP/6-31G(d,p) level of theory with an isovalue of 0.002.

11. Electrochemical properties

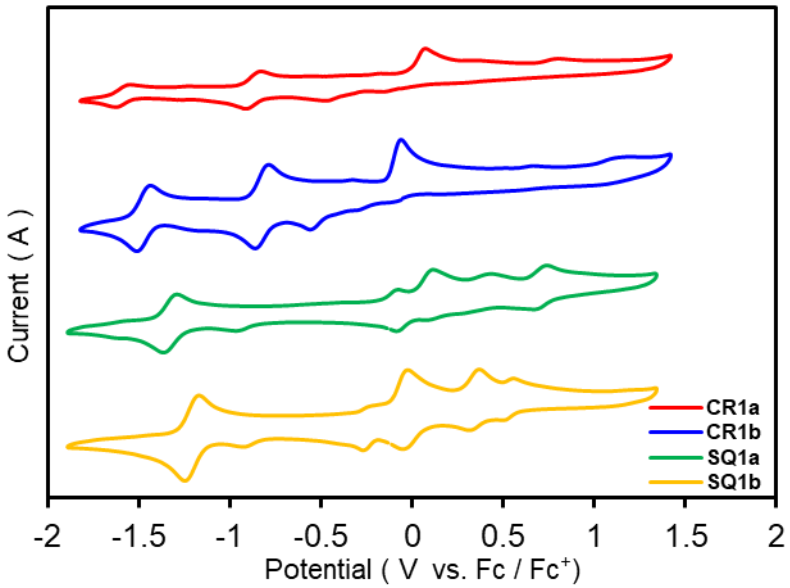


Fig. S16. Cyclic voltammetry of **CR1a** (green), **CR1b** (red), **SQ1a** (purple), and **SQ1b** (blue) in CH_2Cl_2 ; 0.1 M tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte. A glassy carbon working electrode, a Pt counter electrode, and a nonaqueous $Ag/AgNO_3$ reference electrode were used; scan rate: 100 mV/s.

Table S7. Electrochemical properties of **CR1a-b** and **SQ1a-b** and their HOMO and LUMO energies.

	$E_{ox\ onset}$[a] /V	HOMO[b] / eV	$E_{1/2,red}$[a] /V	LUMO[b] / eV	E_{gap}[c] /eV	λ_{onset}[d] /nm	E_{opt}[e] /eV
CR1a	−0.087	−4.71	−0.81	−3.99	0.72	1400	0.89
CR1b	−0.14	−4.66	−0.89	−3.91	0.75	1600	0.78
SQ1a	−0.17	−4.63	−1.35	−3.45	1.18	900	1.4
SQ1b	−0.11	−4.69	−1.28	−3.52	1.17	950	1.3

[a]The oxidation and reduction potentials were measured on 0.1 M tetrabutylammonium hexafluorophosphate in CH_2Cl_2 (working electrode: glassy carbon; reference electrode: nonaqueous $Ag/AgNO_3$ calibrated with ferrocene/ferrocenium (Fc/Fc^+) as an internal reference; counter electrode: Pt). [b]Estimated from the E_{ox} and E_{red} values assuming a value of −4.80 eV for Fc/Fc^+. [c]E_{gap} = [HOMO]–[LUMO] . [d]Onset values of absorption spectra. [e]$E_{opt} = 1240/\lambda_{onset}$

12. Absorption spectra

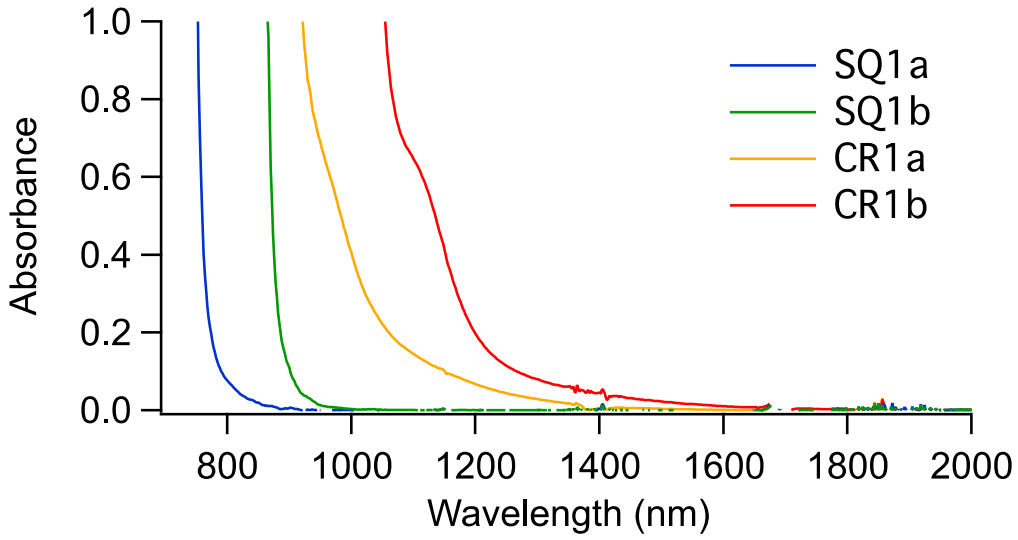


Fig. S17. Spectral tails of one-photon absorption of the high concentration solutions of **SQ1a** (blue, 2.8 mM), **SQ1b** (green, 2.8 mM), **CR1a** (orange, 3.2 mM) and **CR1b** (red, 2.9 mM) used for the two-photon absorption measurements.

13. Two-photo absortion measurement

Two-photon absorption (TPA) spectra of the sample solutions were measured by the open-aperture Z-scan methods,[7] in which nonlinear absorption (NLA) was detected as decrease of transmittance of the focused laser beam through sample near and at the focal point by scanning the sample along the beam. A femtosecond optical parametric amplifier (*Spectra-Physics Topas Prime*, pumped by a Ti:S regenerative amplifier operating at 1 kHz) was used as light source by changing the optical configuration depending on the wavelength. The details of setup were described elsewhere.[8] The measurement gives open-aperture Z-scan trace, i.e., a transmittance curve as a function of sample position with a dip at focal point when NLA exists. The transmittance is normalized to that at the sample position far enough from the focal point. The obtained open-aperture Z-scan traces were analyzed with the theoretical formular assuming the spatial and temporal Gaussian pulsed beam attenuated only by TPA process.[8] The Rayleigh range was 7-14 mm depending on the wavelength, which was much longer than optical pathlength L of the sample and the thin sample condition necessary for the analysis was hold. On-axis two-photon absorbance at the focal point q_0 was obtained from the curve fit. TPA coefficient of the sample $\alpha^{(2)}$was obtained from the convention $q_0 = \alpha^{(2)} I_0 L_{\text{eff}}$, where I_0 is the peak on-axis intensity of incident laser pulse, L_{eff} is the effective pathlength of the sample defined as $L_{\text{eff}} = (1 - 10^{-A})L/(A \ln 10)$ with A is absorbance (one-photon absorption) of the sample at the incident wavelength. TPA coefficient $\sigma^{(2)}$ was calculated with $\sigma^{(2)} = h\nu N^{-1}\alpha^{(2)}$, where N is number density calculated from sample concentration and $h\nu$ is the photon energy. $\sigma^{(2)}$ was expressed in the Göppert-Mayer (GM) unit defined as 1 GM = 10^{-50} cm^4 s molecule^{-1} photon^{-1}.

TPA spectral measurement by the Z-scan method were performed in two different procedures; one is that measurement was repeated by changing wavelength at a fixed incident power (referred as *wavelength scan*). The other is that measurement was repeated for different incident power for each wavelength (referred as *power scan*). We employed *wavelength scan* to obtain outline of the spectral shape and then did power scan to confirmed that the obtained NLA signal was originated from TPA process by checking proportionality of q_0 and incident power (thus, I_0). Typical open-aperture Z-scan

traces and the proportionality plots of the samples are shown in Figs. S18–S21. The concentrations were 2.8–3.2 mM for **CR1a**, 2.4–2.9 mM for **CR1b**, 1.0–3.4 mM for **SQ1a**, and 0.9–3.1 mM for **SQ1b**. The solvent was spectroscopic grade chloroform for all. The obtained values of $\sigma^{(2)}$ were corrected by using the standard compounds measured at the same time (MPPBT in DMSO for 800–960 nm,[9] rhodamine B in methanol for 960–1000 nm,[10] and PAB101 (Compound **4** in ref. 11) in dichloromethane for 1200–1600 nm).

The short-wavelength side of the TPA spectral measurement was limited by saturable absorption (SA) of one-photon transition for all compounds. That is, tail of one-photon absorption exists at such wavelength and transmission increase (over unity in normalized transmittance) by SA. It gives the open-aperture Z-scan trace that has bump (instead of dip) or M-letter like shape when it occurs with strong TPA at the same time. The observed absorption tail of one-photon absorption was shown in Fig. S17. Examples of the open-aperture Z-scan traces that show SA are shown in Fig. S22. At the wavelengths where SA occurs, the reliable estimation of was difficult.

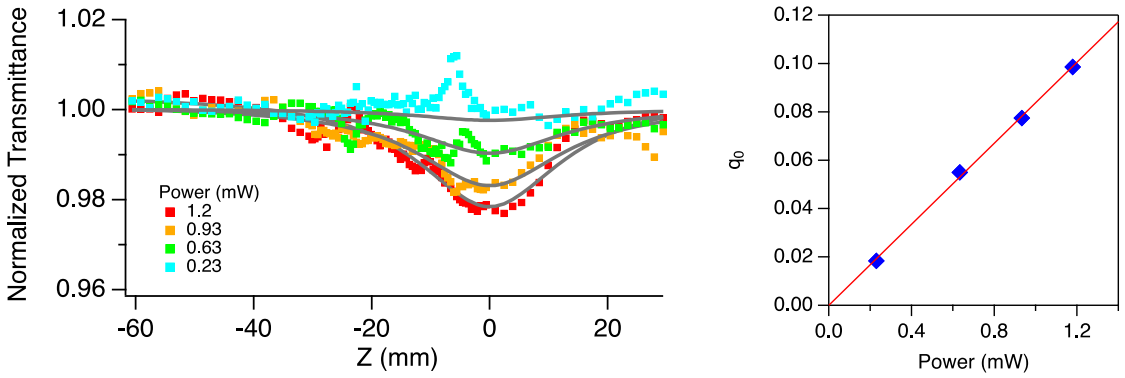


Fig. S18. (left) Open-aperture Z-scan traces of **CR1a** in chloroform (3.2 mM) at 1507 nm with different incident powers (squares) with theoretical fits (grey curves). (right) Plot of two-photon absorbance q_0 obtained by the curve fitting against the incident power.

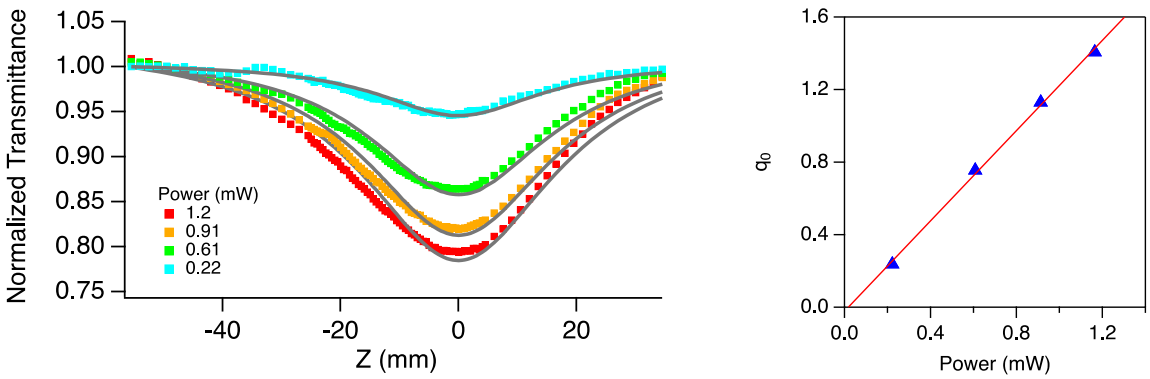


Fig. S19. (left) Open-aperture Z-scan traces of **CR1b** in dichloromethane (2.9 mM) at 1308 nm with different incident powers (squares) with theoretical fits (grey curves). (right) Plot of two-photon absorbance q_0 obtained by the curve fitting against the incident power.

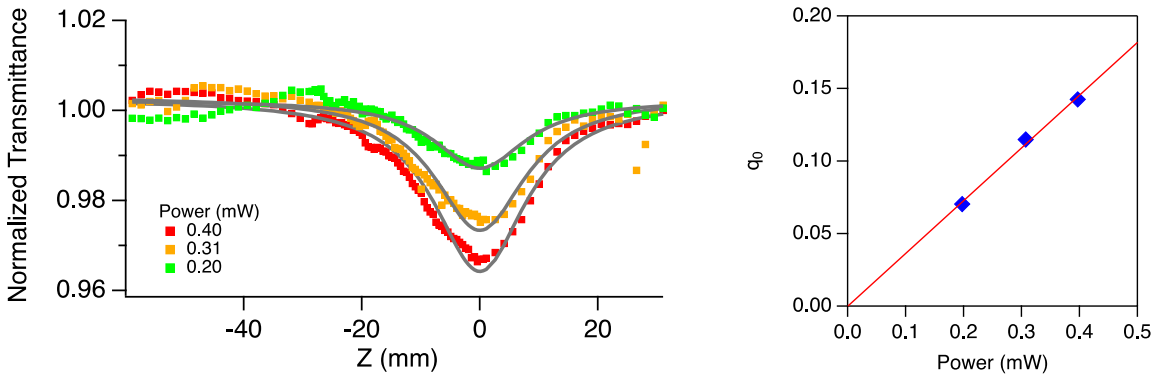


Fig. S20. (left) Open-aperture Z-scan traces of **SQ1a** in chloroform (3.4 mM) at 965 nm with different incident powers (squares) with theoretical fits (grey curves). (right) Plot of two-photon absorbance q_0 obtained by the curve fitting against the incident power.

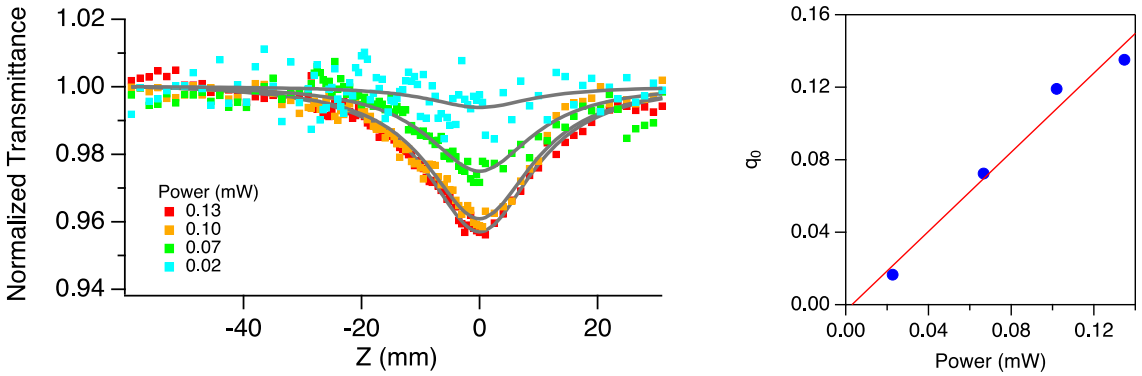


Fig. S21. (left) Open-aperture Z-scan traces of **SQ1b** in chloroform (2.7 mM) at 1096 nm with different incident powers (squares) with theoretical fits (grey curves). (right) Plot of two-photon absorbance q_0 obtained by the curve fitting against the incident power.

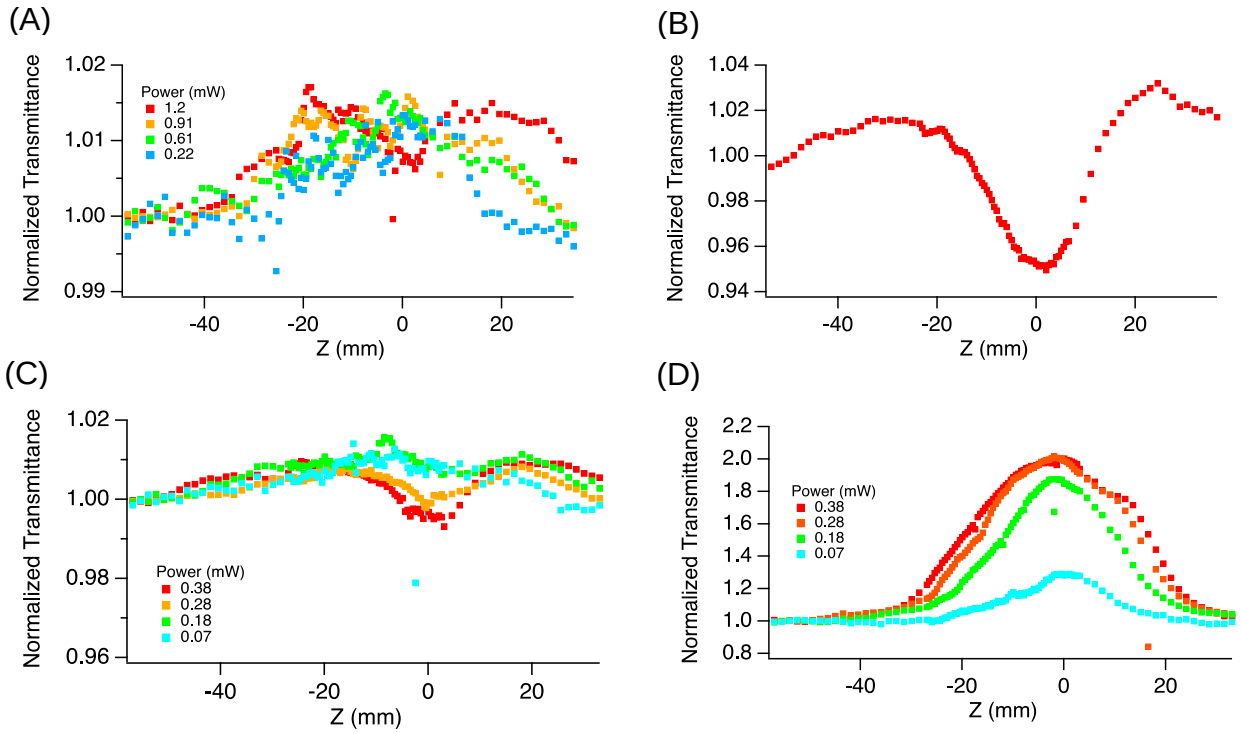


Fig. S22. Examples of open-aperture Z-scan traces showing saturable absorption of (A) **CR1a** at 1308 nm, (B) **CR1b** at 1364 nm (Power=1.2 mW), (C) **SQ1a** at 866 nm, and (D) **SQ1b** at 866 nm all in chloroform.

14. Spectral simulation by quantum chemical calculation

Quantum chemical calculations of the compounds were performed for spectral simulation of one- and two-photon absorptions by using Gaussian09 programming package.[4] Geometry optimization, time-dependent, and the Tamm–Dancoff approximation (TDA)[12] calculations were performed at the CAM-B3LYP/6-31+G(d) level of theory. Coordinates of the optimized geometries are shown in the section 18. TDA calculation gives the transition energy and transition dipole moment from the ground state to the destination excited state, the transition dipole moments between the excited states, and the permanent dipole moments of all states, which are needed for the spectral simulation by the reported method.[13] Up to 30th excited states were taken into account. The effect of solvent was considered by using polarizable continuum model (PCM). Dichloromethane was used as solvent for calculation instead of chloroform used for the experiments, but no significant difference is expected. Note that these calculations do not include the contribution of double excitation. The obtained TPA spectra together with the OPA spectra are shown in Fig. S23. The empirical relaxation constants for one- and two-photon resonance was chosen to be 0.24 eV. The electronic configuration of the excited states are shown in Table S8.

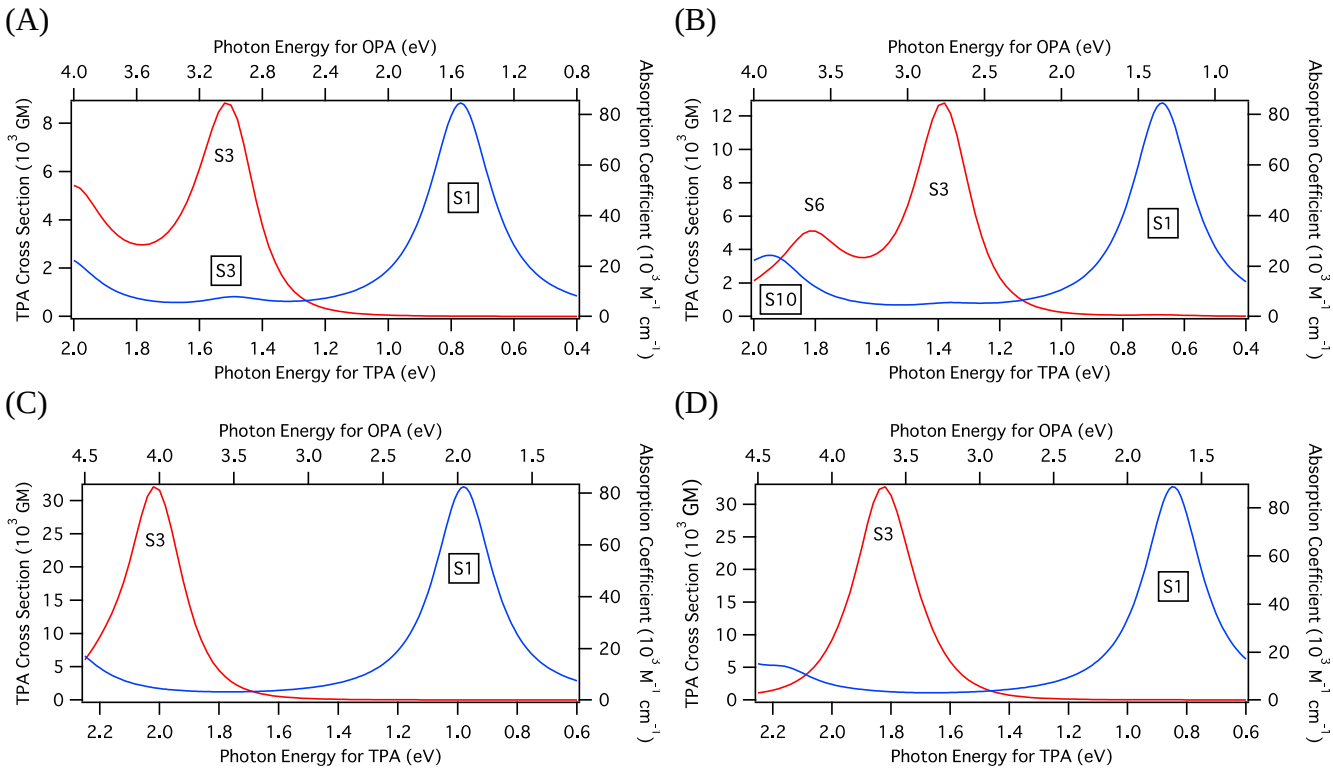


Fig. S23. Simulated two-photon absorption spectra (red; bottom and left axes) and one-photon absorption spectra (blue; right and top axes) of (A) **CR1a** (B) **CR1b**, (C) **SQ1a**, and (D) **SQ1b**. The calculations were made at CAM-B3LYP/6-31+G(d) level. The solvent effect was involved by using PCM.

Table S8. Transition energy, electronic configuration of the compounds of the first four excited states calculated at TDA-PCM(dichloromethane)-CAM-B3LYP/6-31+G(d).

State	**CR1a**	**CR1b**	**SQ1a**	**SQ1b**
S_1	1.89 eV, H→L	1.68 eV, H→L	2.22 eV, H→L	1.97 eV, H→L
S_2	2.78 eV, H-1→L	2.76 eV, H-1→L	3.18 eV, H-1→L	3.06 eV, H-1→L
S_3	3.08 eV, H→L+1	2.83 eV, H→L+1	4.11 eV, H→L+1	3.74 eV, H→L+1
S_4	3.15 eV, H-2→L	3.14 eV, H-3→L	4.29 eV, H-4→L	3.91 eV, H→L+2

15. Correlation between the experimentally deduced and calculated diradical characters

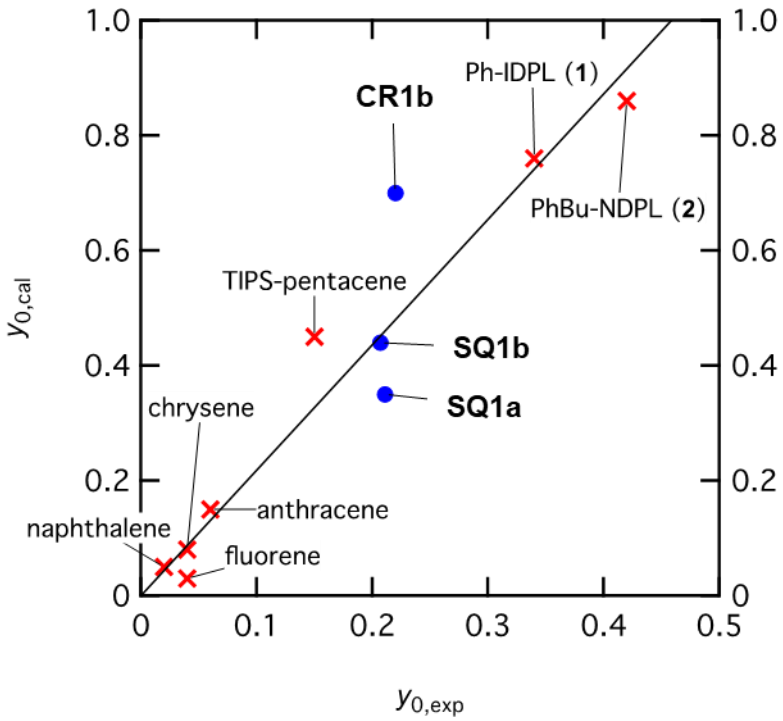


Fig. S24. Correlation between the experimental values and calculated values of diradical character ($y_{0,exp}$) and $y_{0,cal}$, respectively. $y_{0,exp}$ for **CR1b**, **SQ1a** and **SQ1b** were calculated by using eq. (1) and $y_{0,calc}$ are taken from Ref. 14. Other values are taken from Ref. 15.

16. Reported results of diradical character y_0 obtained by the quantum chemical calculation

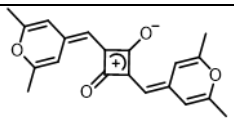
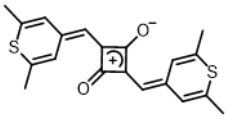
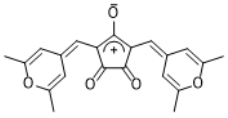
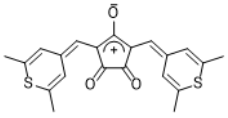
The singlet diradical character y_0 for the present croconaine and squaraine dyes was reported by Srinivas et al. (*J. Phys. Chem. A* **2007**, *111*, 3378.) and López-Carballeira et al. (*ChemPhysChem*, **2018**, *19*, 2224.).[15,16] These values were estimated using the following equation:

$$y_0 = 1 - 2T_i / (1+T_i^2)$$

where T_i is defined as the orbital overlap between the corresponding occupied and unoccupied orbital pairs (HOMO−*i* and LUMO−*i*) and T_i is calculated using the occupation number (*n*) of unrestricted formalism natural orbitals:

$$T_i = (n_{HOMO-i} - n_{LUMO-i}) / 2$$

Table S9. Reported diradical character y_0 and transition energy for the present dyes.

Structure	Srinivas *et al*.			López-Carballeira *et al*.	
	HLG[a] / eV	ΔE_{ST}[b] / kcal mol^{-1}	y_0[c]	S_1[d] / eV	y_0[e]
	1.93	20	0.347	2.13	0.35
	1.70	16.9	0.439	1.93	0.44
	1.51	10.1	0.602	1.79	0.62
	1.33	7.8	0.665	1.64	0.68

[a] HOMO-LUMO energy gap esmimated at B3LYP/6-311+G(d,p) level. [b] Singlet−Triplet energy gap. [c] Using the HOMO and LUMO of the UHF natural orbitals. [d] Calculated with TDDFT at the B3PW91/6-31+G(d,p) level of theory [e] Caluculated by the spin-projected unrestricted Hartree-Fock (PUHF) theory using the 6-311++G(d,p) basis set.

17. NMR and MS spectra

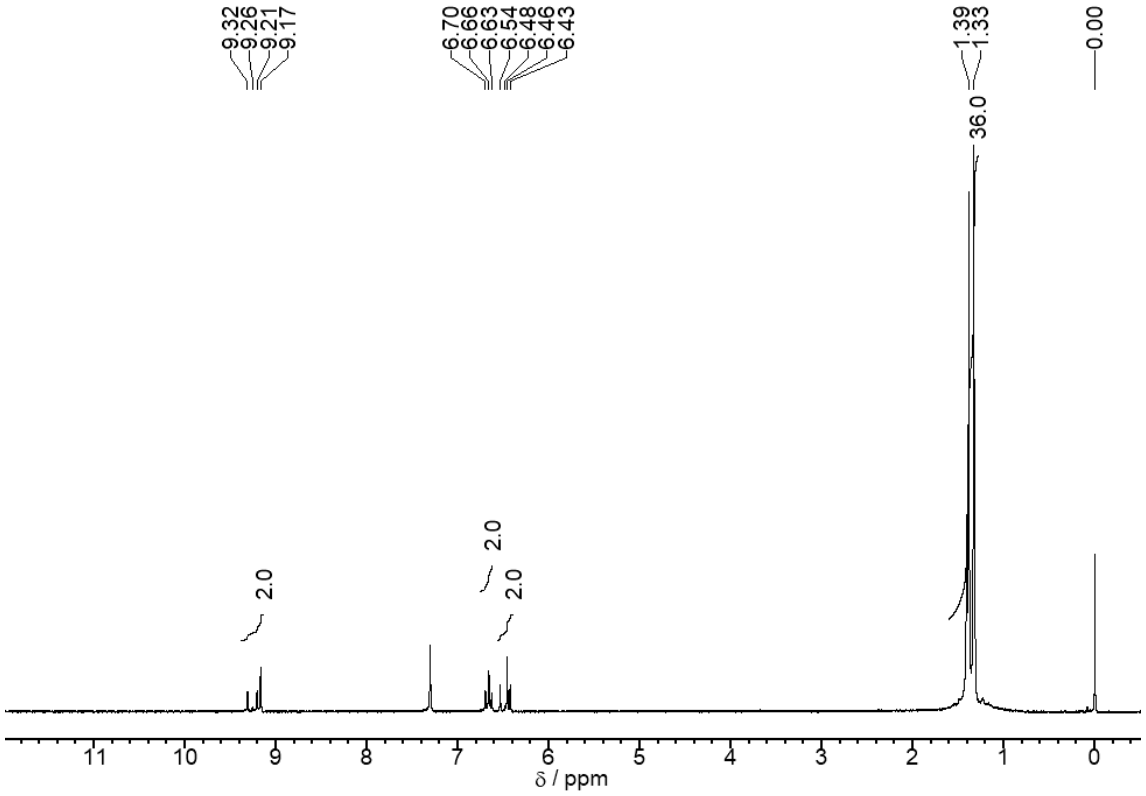


Fig. S25. ^{1}H-NMR spectrum ($CDCl_3$, 213K) of **CR1a**.

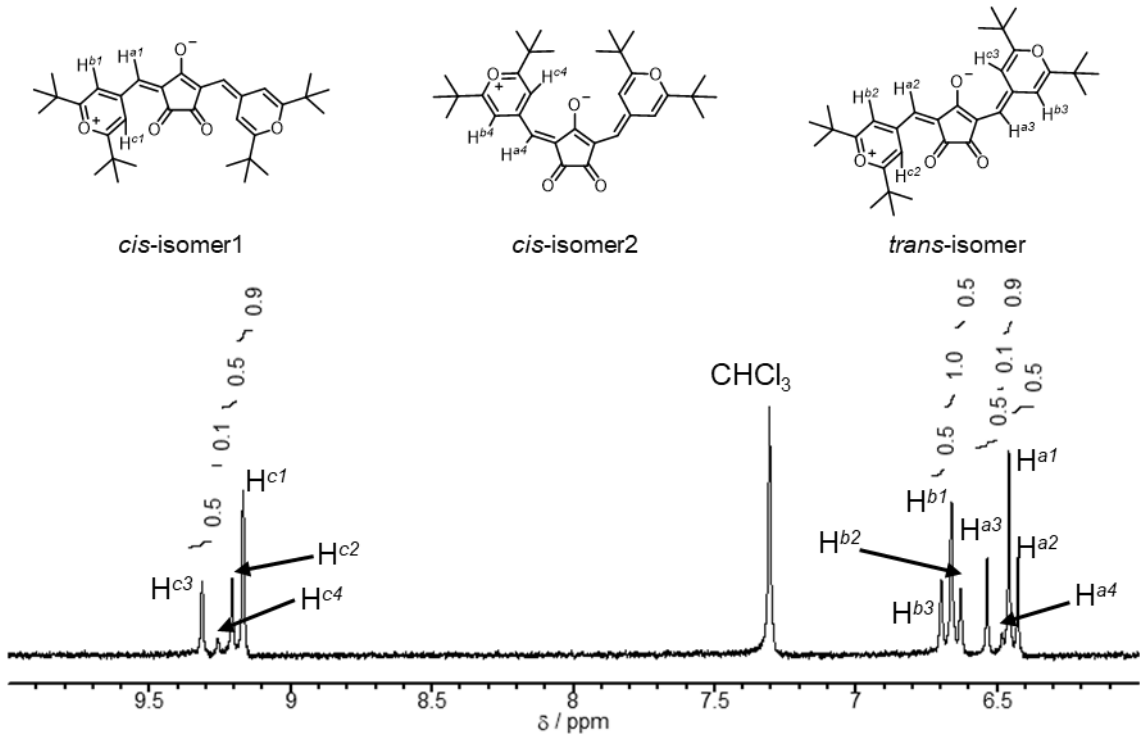


Fig. S26. ^{1}H-NMR spectrum ($CDCl_3$, 213K) of **CR1a** in the range from 10.0 to 6.0 ppm.

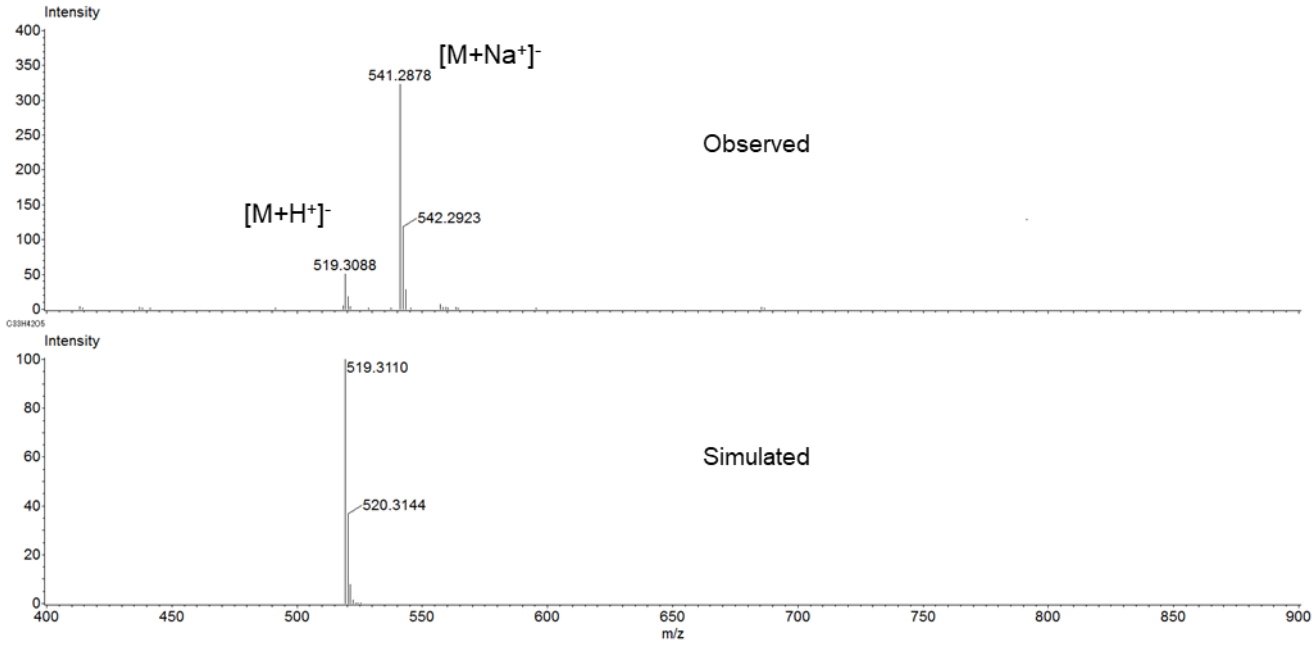


Fig. S27. ESI-MS spectrum of **CR1a**.

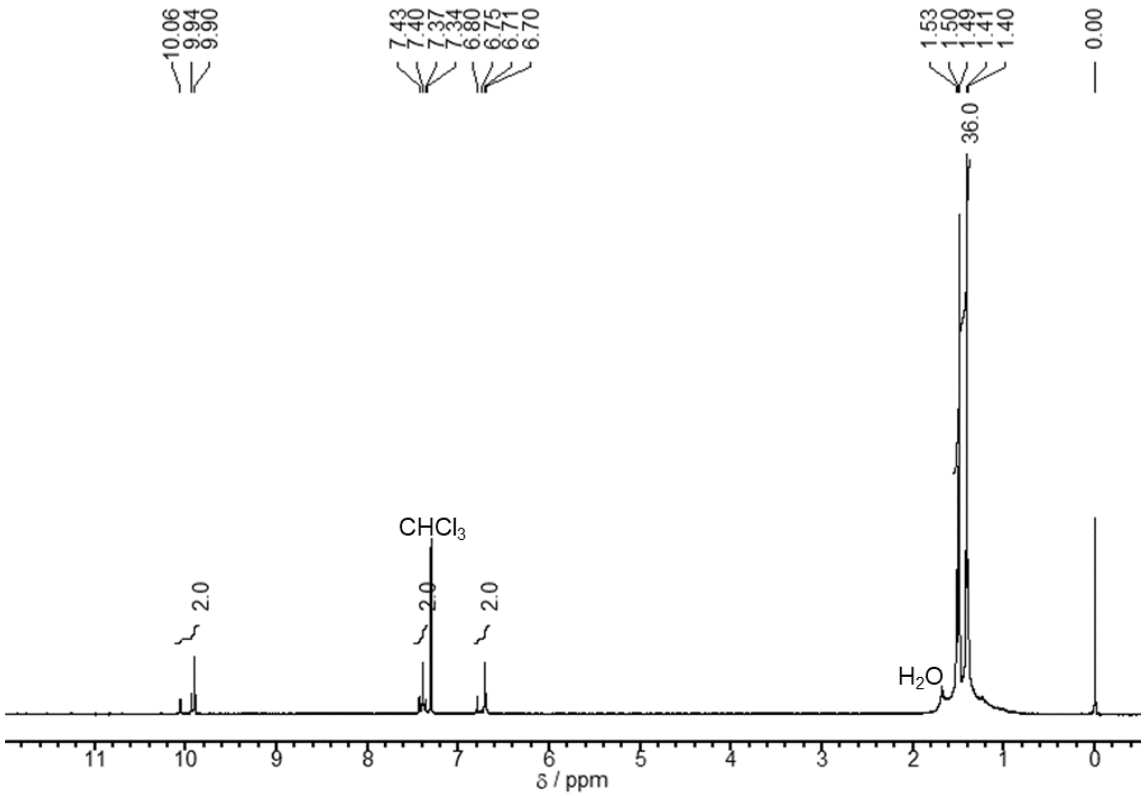


Fig. S28. ^{1}H-NMR spectrum ($CDCl_3$, 213K) of **CR1b**.

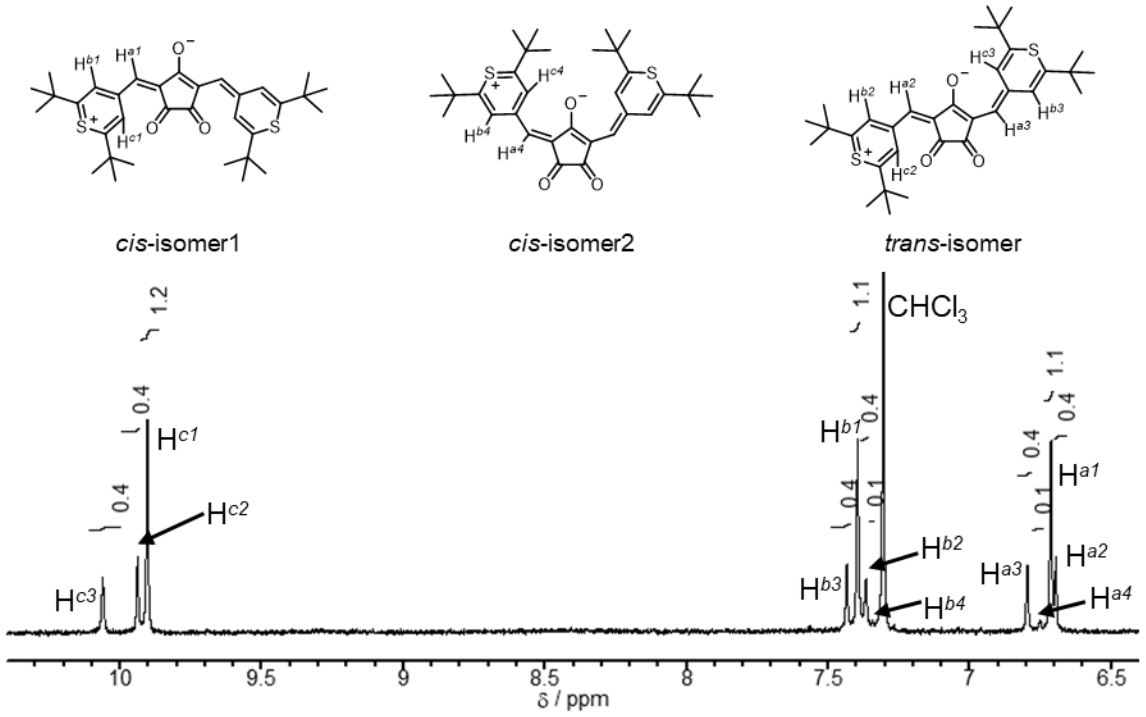


Fig. S29. ^{1}H-NMR spectrum ($CDCl_3$, 213K) of **CR1b** in the range from 10.4 to 6.4 ppm.

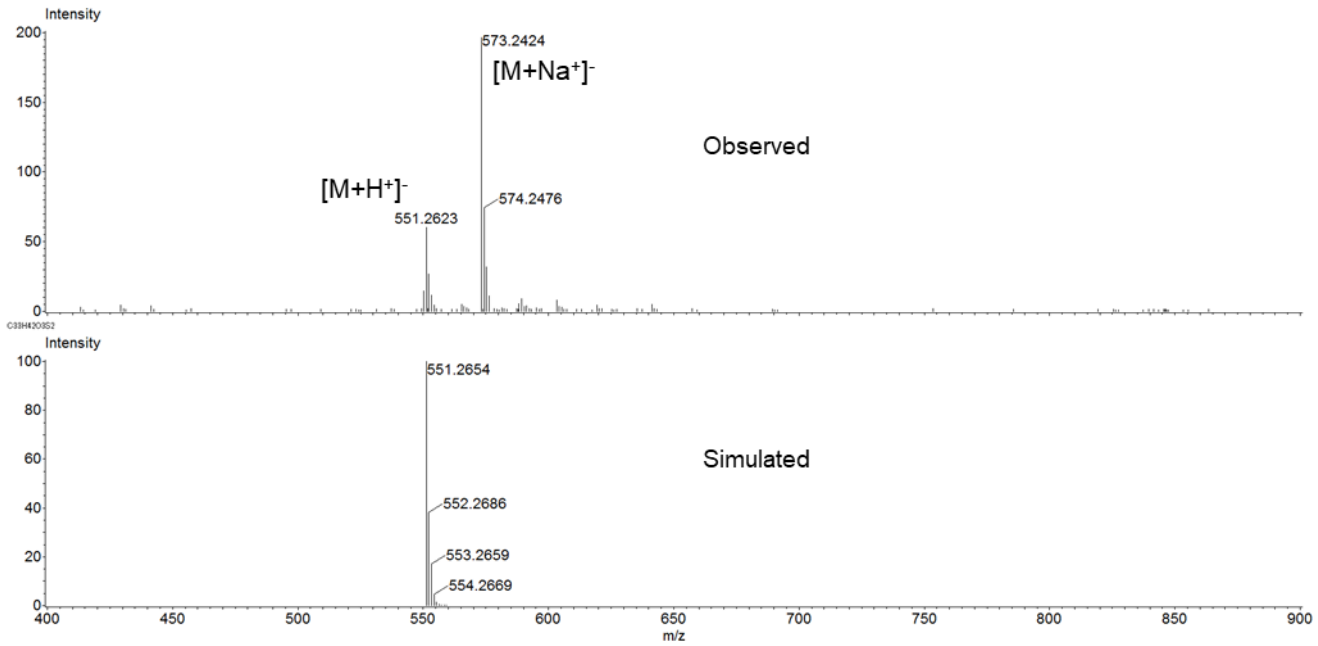


Fig. S30. ESI-MS spectrum of **CR1b**.

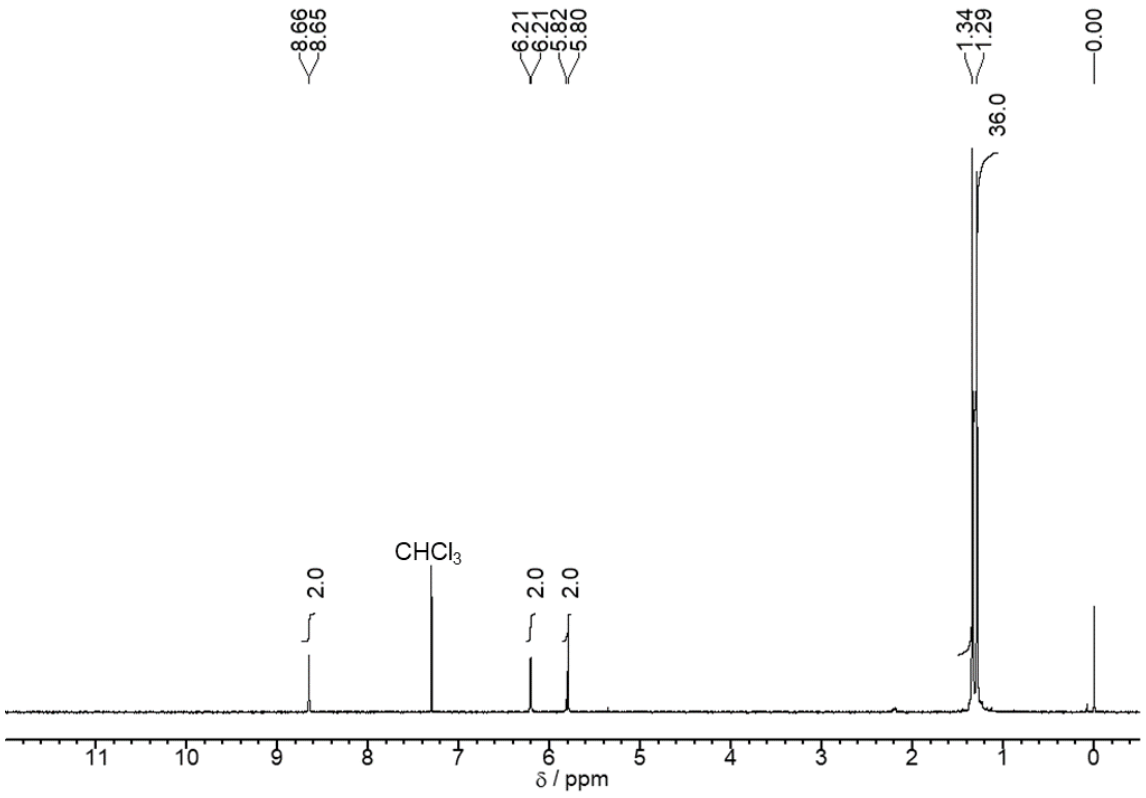


Fig. S31. ^{1}H-NMR spectrum ($CDCl_3$, 213K) of **SQ1a**.

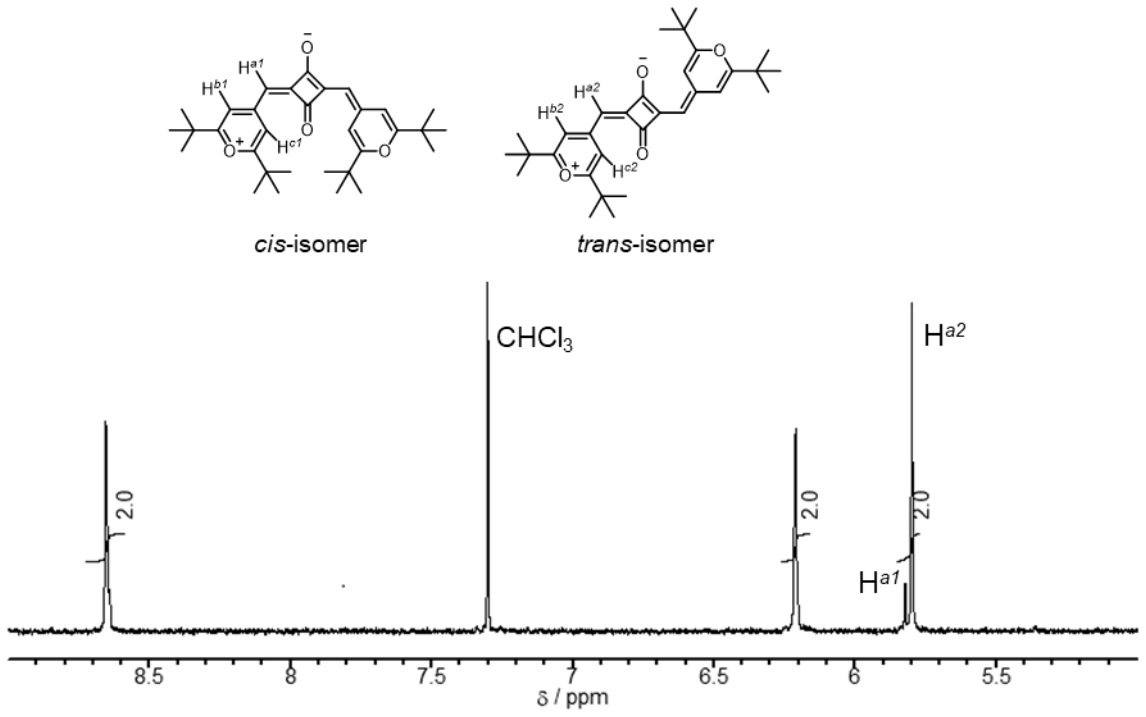


Fig. S32. ^{1}H-NMR spectrum ($CDCl_3$, 213K) of **SQ1a** in the range from 9.0 to 5.0 ppm.

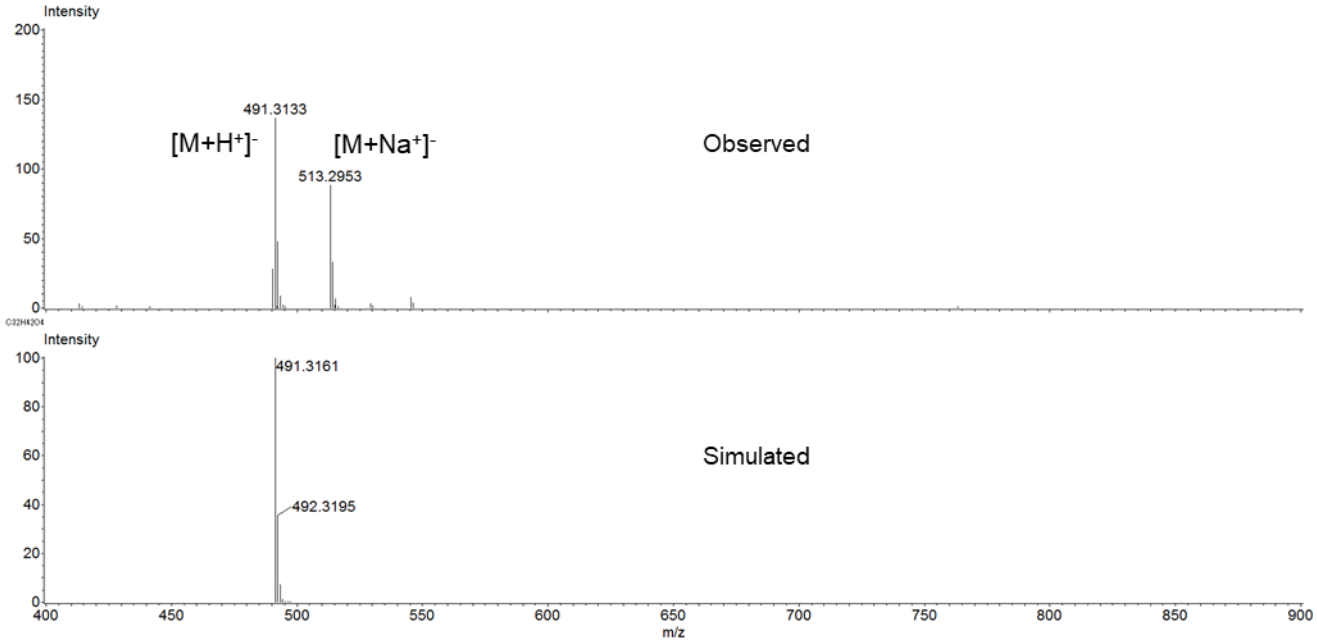


Fig. S33. ESI-MS spectrum of **SQ1a**.

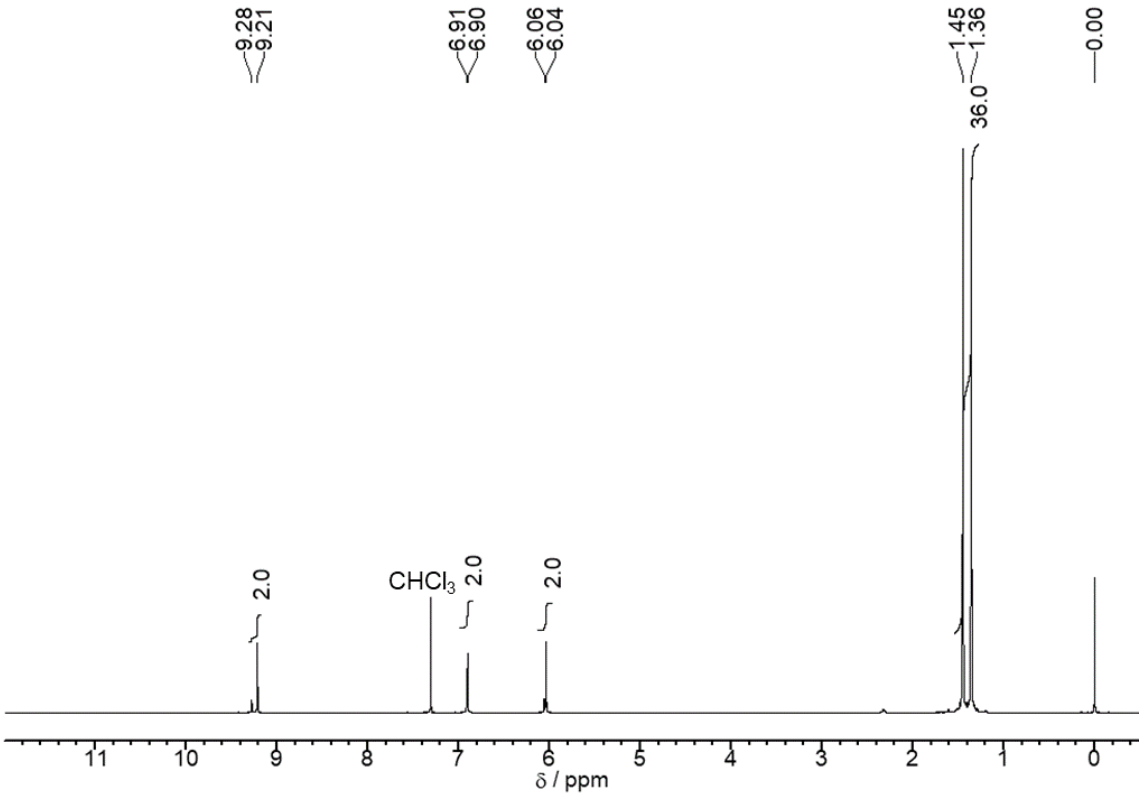


Fig. S34. ^{1}H-NMR spectrum ($CDCl_3$, 213K) of **SQ1b**.

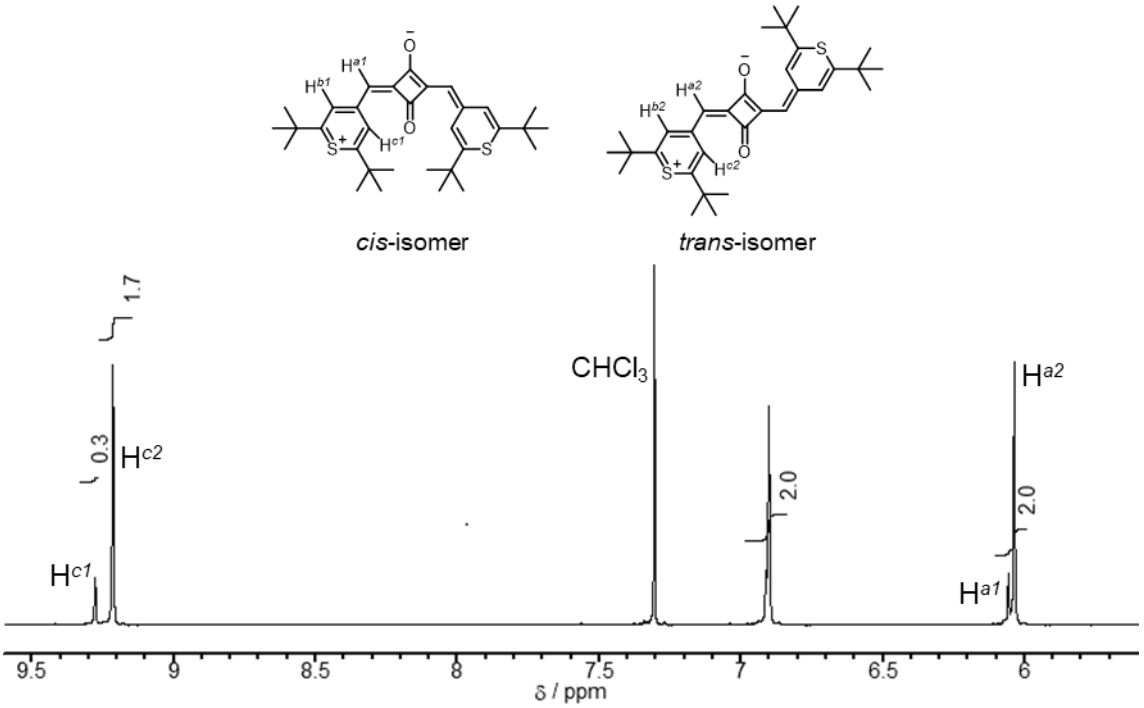


Fig. S35. ^{1}H-NMR spectrum ($CDCl_3$, 213K) of **SQ1b** in the range from 9.6 to 5.6 ppm.

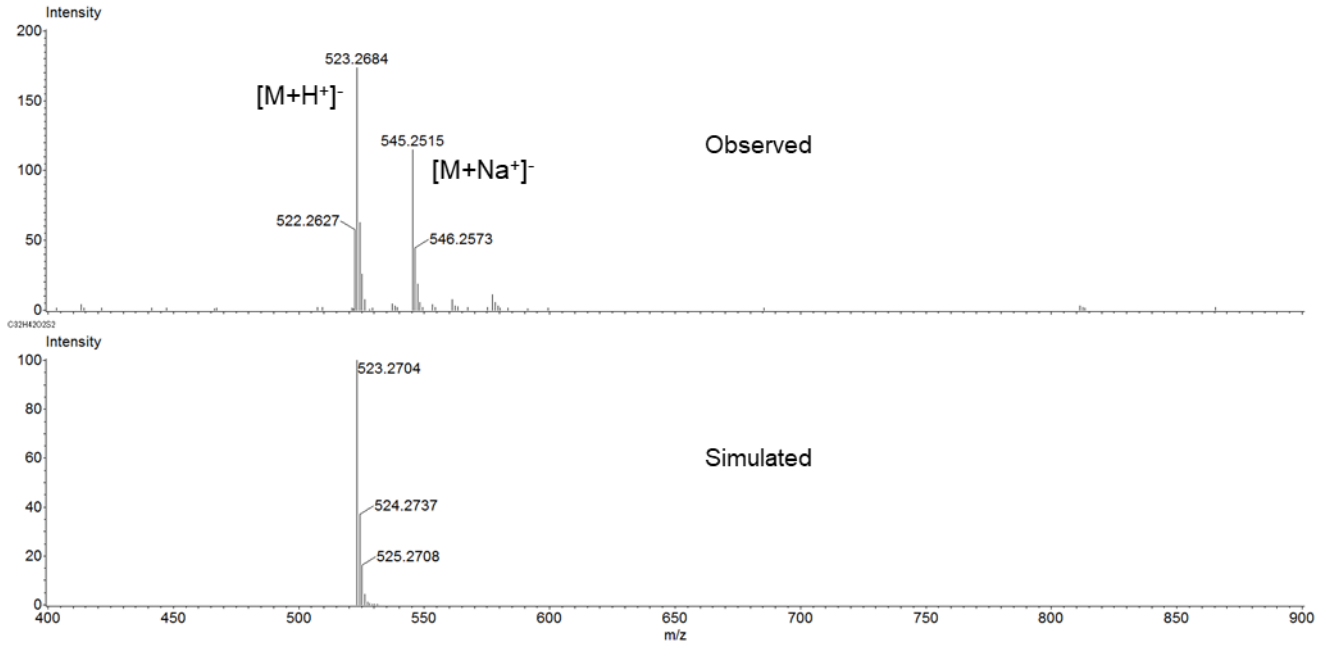


Fig. S36. ESI-MS spectrum of **SQ1b**.

18. Cartesian Coordinates of quantum chemical calculations

Table S10. Optimized cartesian coordinate of **CR1a** CAM-B3LYP/6-31G+(d) (PCM=CH_2Cl_2).

O	-1.407230	1.871007	-0.085321	H	-4.283975	3.422001	-0.911050
C	-0.753253	0.826764	-0.038029	H	-4.269364	3.423467	0.862612
C	0.753201	0.826819	0.020922	H	-5.362501	4.500210	-0.016225
C	1.198200	-0.556670	0.009653	H	-6.317963	2.504496	-2.176865
C	0.000016	-1.399566	-0.008150	H	-7.333029	3.637555	-1.267358
O	0.000041	-2.639057	-0.008659	H	-7.729957	1.911335	-1.279388
C	-1.198242	-0.556728	-0.024606	H	-6.285071	2.510814	2.162968
C	-2.444494	-1.175501	-0.027691	H	-7.711209	1.916960	1.288731
C	-3.757583	-0.675897	-0.024382	H	-7.312286	3.642575	1.265689
C	-4.142091	0.701246	-0.025119	H	-8.474134	-0.689796	1.325558
C	-5.450269	1.053970	-0.011201	H	-7.597469	-1.963485	2.196810
C	-6.026860	2.452297	-0.008940	H	-9.088062	-2.351383	1.319378
C	-4.912518	3.502876	-0.019065	H	-8.518406	-0.687824	-1.239998
C	-6.905949	2.629679	-1.261637	H	-9.132777	-2.348968	-1.213998
C	-6.886647	2.634121	1.256341	H	-7.673722	-1.961068	-2.142916
O	-6.423015	0.110077	0.003102	H	-6.433560	-3.841732	0.894158
C	-6.129312	-1.211299	0.002160	H	-6.462254	-3.839805	-0.883202
C	-7.375828	-2.067549	0.022280	H	-7.944104	-4.144091	0.029457
C	-8.179120	-1.741984	1.295945	H	-4.617027	-2.676691	-0.012552
C	-8.223131	-1.740177	-1.221893	H	2.369245	-2.260641	0.007452
C	-7.020669	-3.557695	0.015045	H	3.372093	1.460334	0.031707
C	-4.838246	-1.617658	-0.012674	H	7.725979	1.909774	1.289912
C	2.444450	-1.175515	0.015423	H	6.311241	2.501632	2.183878
C	3.757525	-0.675983	0.017221	H	7.328938	3.635970	1.278941
C	4.141985	0.701173	0.021150	H	7.714944	1.918670	-1.278256
C	5.450188	1.053949	0.013467	H	7.316057	3.644294	-1.254085
C	6.026700	2.452309	0.015054	H	6.291476	2.513803	-2.156000
C	6.901965	2.628069	1.270585	H	4.280717	3.420345	0.912933
C	6.890334	2.635850	-1.247412	H	4.272061	3.424896	-0.860735
C	4.912264	3.502820	0.023215	H	5.362177	4.500190	0.023589
O	6.423018	0.110101	0.002526	H	8.482355	-0.686867	-1.307318
C	6.129352	-1.211286	0.000586	H	7.611311	-1.958781	-2.186757
C	7.376021	-2.067438	-0.013887	H	9.096385	-2.348411	-1.300772
C	8.187251	-1.739135	-1.281780	H	8.510869	-0.690388	1.258223
C	8.215560	-1.742660	1.236231	H	9.125138	-2.351590	1.232831
C	7.020897	-3.557612	-0.012038	H	7.660363	-1.965247	2.153365
C	4.838256	-1.617714	0.008856	H	6.438995	-3.839719	-0.895232
O	1.407163	1.871186	0.066281	H	6.457206	-3.841750	0.882264
H	-2.369341	-2.260639	-0.020569	H	7.944426	-4.143946	-0.022275
H	-3.372331	1.460493	-0.038560	H	4.617052	-2.676750	0.006447

Table S11. Optimized cartesian coordinate of **CR1b** CAM-B3LYP/6-31G+(d) (PCM=CH_2Cl_2).

O	-1.385239	-1.776617	-0.054170	H	-3.292030	-2.918944	0.797707
C	-0.752520	-0.707610	-0.047291	H	-3.410630	-2.975881	-0.978035
C	0.743718	-0.655382	-0.097453	H	-3.920162	-4.374115	-0.011826
C	1.146640	0.731551	-0.016528	H	-5.351003	-2.824864	2.284466
C	-0.036781	1.548448	0.022129	H	-5.917425	-4.309785	1.520893
O	-0.047126	2.780795	0.025794	H	-6.963171	-2.895854	1.566805
C	-1.254479	0.668973	-0.004622	H	-5.810903	-3.055871	-2.061063
C	-2.503896	1.267830	0.011825	H	-7.238783	-3.093457	-1.019796
C	-3.814248	0.709464	0.004404	H	-6.137299	-4.469364	-1.045629
C	-4.035907	-0.682303	0.006322	H	-8.602034	1.255474	-1.496255
C	-5.253310	-1.277025	0.014427	H	-7.392996	2.312735	-2.240123
C	-5.323889	-2.782560	0.074165	H	-8.829268	3.007162	-1.467041
C	-3.898931	-3.285113	-0.046924	H	-8.869644	1.244561	1.121504
C	-5.926891	-3.221563	1.443257	H	-9.059008	2.989858	1.103217
C	-6.181981	-3.374720	-1.082098	H	-7.798442	2.256453	2.098612
S	-6.726312	-0.391042	0.015569	H	-5.982562	3.878161	-0.813850
C	-6.220207	1.263356	-0.000675	H	-6.138683	3.887761	0.955370
C	-7.321193	2.329651	-0.049959	H	-7.466863	4.475638	-0.029000
C	-8.082093	2.208127	-1.397424	H	-4.647850	2.680199	-0.003205
C	-8.316335	2.189931	1.134684	H	2.410121	2.410425	0.157598
C	-6.679282	3.718605	0.024082	H	3.026291	-1.264234	0.035619
C	-4.898331	1.616334	0.012618	H	7.208379	-2.446915	-1.271985
C	2.424861	1.323420	0.061938	H	5.727822	-2.768594	-2.213558
C	3.701877	0.757051	0.036696	H	6.530408	-4.090562	-1.344978
C	3.936489	-0.661781	-0.008414	H	7.222257	-2.582209	1.250838
C	5.161327	-1.262514	-0.033486	H	6.491160	-4.189593	1.180153
C	5.444967	-2.754259	-0.042605	H	5.709808	-2.905144	2.123898
C	6.276268	-3.030610	-1.300159	H	3.513476	-3.525998	-0.923398
C	6.264553	-3.117236	1.204061	H	3.551032	-3.413905	0.843000
C	4.157272	-3.635980	-0.049222	H	4.439409	-4.689609	-0.029255
S	6.670912	-0.354870	-0.001217	H	8.721356	1.261799	1.259970
C	6.142102	1.328438	0.073360	H	7.677708	2.334310	2.206690
C	7.253939	2.369031	0.042871	H	8.982028	2.999261	1.206873
C	8.209898	2.224963	1.253081	H	8.522664	1.183274	-1.290539
C	8.053589	2.173895	-1.267760	H	8.846559	2.926661	-1.339977
C	6.644032	3.775963	0.079717	H	7.412795	2.272134	-2.151038
C	4.818387	1.671638	0.073075	H	6.086879	3.937025	1.009142
O	1.431590	-1.680733	-0.148573	H	5.970389	3.962181	-0.766102
H	-2.465897	2.356578	0.034933	H	7.443053	4.521450	0.028797
H	-3.145907	-1.316293	0.027141	H	4.561679	2.737040	0.100855

Table S12. Optimized cartesian coordinate of **SQ1a** CAM-B3LYP/6-31G+(d) (PCM=CH_2Cl_2)

C	-7.919965	-1.542378	1.258316	H	-7.759261	-3.952767	-0.000733
C	-7.107624	-1.900378	-0.000529	H	-6.251442	-3.709319	0.887784
C	-6.812985	-3.403615	-0.000746	H	-6.251617	-3.709086	-0.889465
C	-7.919972	-1.542018	-1.259237	H	-8.854367	-2.112319	-1.265865
C	-5.827094	-1.094410	-0.000362	H	-7.364479	-1.788110	-2.170256
O	-6.071719	0.239648	-0.000326	H	-8.170239	-0.478218	-1.284691
C	-5.057668	1.145780	0.000032	H	-7.294486	2.089830	-1.285090
C	-5.582784	2.564838	0.000084	H	-5.854563	2.632530	-2.169461
C	-6.444941	2.777518	-1.258607	H	-6.835094	3.800421	-1.265907
C	-6.445350	2.777264	1.258553	H	-7.294875	2.089529	1.284630
C	-4.431344	3.574467	0.000364	H	-6.835555	3.800148	1.265937
C	-3.767694	0.742957	0.000283	H	-5.855242	2.632117	2.169555
C	-3.437098	-0.654867	0.000111	H	-3.798017	3.470381	-0.885752
C	-2.138295	-1.158646	0.000231	H	-3.798217	3.470161	0.886592
C	-0.942826	-0.442707	0.000666	H	-4.844764	4.587651	0.000460
C	-0.434752	0.934659	0.000795	H	-2.970564	1.477808	0.000565
O	-0.929027	2.069535	0.000978	H	-2.030171	-2.241698	0.000022
C	0.942765	0.442536	0.000748	H	2.030041	2.241541	0.000370
C	2.138226	1.158490	0.000422	H	4.377572	2.621477	0.000047
C	3.437039	0.654778	0.000250	H	7.363770	1.788395	-2.170407
C	4.556617	1.554383	0.000033	H	8.169779	0.478427	-1.285173
C	5.827017	1.094465	-0.000170	H	8.853919	2.112515	-1.266416
C	7.107515	1.900480	-0.000589	H	6.251081	3.709250	-0.889046
C	7.919519	1.542223	-1.259566	H	7.759084	3.952919	-0.000951
C	6.812834	3.403723	-0.000590	H	6.251668	3.709335	0.888209
C	7.920217	1.542394	1.257982	H	8.170646	0.478635	1.283502
O	6.071711	-0.239574	-0.000227	H	7.364919	1.788520	2.169108
C	5.057729	-1.145774	0.000024	H	8.854520	2.112845	1.264287
C	5.582953	-2.564797	0.000116	H	7.294530	-2.089831	-1.285242
C	6.445010	-2.777547	-1.258637	H	5.854539	-2.632640	-2.169442
C	6.445648	-2.777046	1.258526	H	6.835207	-3.800434	-1.265911
C	4.431584	-3.574502	0.000623	H	7.295150	-2.089278	1.284447
C	3.767731	-0.743044	0.000266	H	6.835877	-3.799920	1.265968
C	0.434700	-0.934840	0.000645	H	5.855624	-2.631829	2.169569
O	0.928967	-2.069743	0.000726	H	3.798058	-3.470467	-0.885353
C	-4.556713	-1.554401	-0.000200	H	3.798640	-3.470223	0.886988
H	-8.854232	-2.112890	1.264923	H	4.845062	-4.587664	0.000632
H	-8.170460	-0.478641	1.283928	H	2.970628	-1.477933	0.000463
H	-7.364354	-1.788488	2.169255	H	-4.377766	-2.621511	-0.000281

Table S13. Optimized cartesian coordinate of **SQ1b** CAM-B3LYP/6-31G+(d) (PCM=CH_2Cl_2).

C	-7.870294	2.094496	1.195692	H	-8.372586	1.025581	-1.309835
C	-7.001003	2.221535	-0.071073	H	-7.278575	2.068316	-2.235247
C	-7.876294	2.000299	-1.320486	H	-7.269239	4.355857	-0.153053
C	-6.436527	3.646694	-0.125850	H	-5.830749	3.813256	-1.021968
C	-5.878251	1.178240	-0.034619	H	-5.830635	3.881986	0.754654
S	-6.437573	-0.475615	0.023071	H	-7.132349	-2.855613	1.195463
C	-4.973576	-1.434648	0.051338	H	-5.690622	-2.985837	2.218582
C	-5.232926	-2.946238	0.079859	H	-6.272986	-4.393486	1.311827
C	-6.139300	-3.307657	1.273076	H	-6.894137	-2.895792	-1.364045
C	-5.918262	-3.372950	-1.233805	H	-6.074158	-4.456776	-1.230161
C	-3.923465	-3.731360	0.220115	H	-5.296448	-3.120620	-2.098810
C	-3.740618	-0.875048	0.033376	H	-3.393053	-3.478374	1.142901
C	-3.467652	0.538462	-0.010152	H	-3.243252	-3.556996	-0.617430
C	-2.175265	1.058493	-0.022126	H	-4.155815	-4.800566	0.247397
C	-0.950769	0.387288	-0.012653	H	-2.877927	-1.533548	0.050235
C	-0.380079	-0.962624	-0.014462	H	-2.088469	2.143658	-0.042057
O	-0.819053	-2.118156	-0.021289	H	2.118210	-2.156414	-0.032127
C	0.977708	-0.406072	-0.009837	H	4.325307	-2.512013	-0.066245
C	2.195685	-1.070580	-0.015254	H	5.828951	-3.680359	1.090803
C	3.492276	-0.537800	-0.003006	H	6.886297	-2.649080	2.069724
C	4.588137	-1.459065	-0.031718	H	7.574708	-3.959369	1.093136
C	5.907346	-1.143162	-0.023838	H	5.879118	-3.483692	-1.482580
C	6.996908	-2.225819	-0.072041	H	7.623846	-3.779962	-1.449300
C	6.802422	-3.183599	1.118033	H	6.985177	-2.335394	-2.255702
C	6.856249	-3.000783	-1.395902	H	8.594042	-1.101797	0.933365
C	8.418924	-1.650242	0.002292	H	8.642530	-0.987643	-0.839926
S	6.448132	0.502450	0.030269	H	9.135938	-2.475769	-0.032324
C	4.979840	1.447310	0.055019	H	7.132209	2.891264	1.184398
C	5.225426	2.961453	0.078950	H	5.694529	3.010515	2.215239
C	6.135050	3.333587	1.266386	H	6.258831	4.420585	1.301342
C	5.900063	3.389226	-1.240049	H	6.880178	2.921401	-1.373261
C	3.909145	3.734032	0.223933	H	6.045506	4.474405	-1.241036
C	3.750121	0.875639	0.038200	H	5.276482	3.127925	-2.101039
C	0.398830	0.946718	-0.013858	H	3.385396	3.477423	1.149478
O	0.841417	2.101296	-0.019992	H	3.226760	3.552413	-0.610197
C	-4.559827	1.477263	-0.041258	H	4.131890	4.805240	0.248804
H	-8.645803	2.867144	1.185691	H	2.881397	1.526724	0.053620
H	-7.267459	2.227101	2.099956	H	-4.277359	2.522907	-0.074760
H	-8.369249	1.123136	1.258489				
H	-8.654426	2.769247	-1.362888				

Table S14. Optimized cartesian coordinate of **CR1a** CAM-RB3LYP/6-31G (d,p) Singlet

C	-0.7578881	0.9818184	-0.0003713	C	5.4055987	1.2106889	0.0002071
O	-1.4109838	2.0177172	-0.0000580	C	6.1127904	-1.0302216	0.0001527
C	0.0000002	-1.2656050	-0.0003770	C	-7.3365268	-1.8779295	0.0003310
O	0.0000008	-2.4958708	-0.0002503	H	-7.0707337	-2.9348312	0.0003369
C	-1.1895201	-0.4108693	-0.0003050	H	-7.9476168	-1.6656084	0.8823120
C	-2.4332709	-1.0397171	-0.0001765	H	-7.9478026	-1.6656644	-0.8815345
H	-2.3408233	-2.1240808	-0.0001539	C	-5.9313443	2.6028910	0.0000053
C	1.1895197	-0.4108683	-0.0002273	H	-6.5544603	2.7771205	0.8821986
C	-3.7311295	-0.5369377	-0.0000749	H	-5.1078134	3.3161251	-0.0001417
C	-4.8351545	-1.4585895	0.0000679	H	-6.5546903	2.7770198	-0.8820448
C	-4.1073351	0.8482622	-0.0000944	C	7.3365261	-1.8779307	0.0002123
H	-4.6432678	-2.5247978	0.0000928	H	7.9476423	-1.6656723	0.8821901
H	-3.3304153	1.6055787	-0.0002187	H	7.0707321	-2.9348321	0.0001505
C	2.4332709	-1.0397157	-0.0001626	H	7.9477763	-1.6656038	-0.8816564
H	2.3408232	-2.1240794	-0.0002352	C	5.9313466	2.6028907	0.0003176
C	3.7311298	-0.5369368	-0.0000274	H	6.5546283	2.7771203	-0.8817585
C	4.8351543	-1.4585891	0.0000198	H	5.1078163	3.3161256	0.0003101
C	4.1073362	0.8482630	0.0000764	H	6.5545271	2.7770185	0.8824850
H	4.6432671	-2.5247972	-0.0000517	C	0.7578860	0.9818189	-0.0001751
H	3.3304168	1.6055799	0.0000431	O	1.4109804	2.0177188	-0.0000733
C	-6.1127904	-1.0302215	0.0001753	O	-6.4129747	0.2926639	0.0001510
C	-5.4055976	1.2106887	0.0000164	O	6.4129755	0.2926633	0.0002475

Table S15. Optimized cartesian coordinate of **CR1a** CAM-UB3LYP/6-31G (d,p) Singlet

C	-0.7677412	0.9825998	0.0001056	C	5.4300683	1.2096697	-0.0000239
O	-1.4089254	2.0238221	0.0000717	C	6.1289024	-1.0384663	0.0000056
C	0.0000000	-1.2605923	0.0000979	C	-7.3496758	-1.8904815	-0.0001300
O	-0.0000001	-2.4856166	0.0000176	H	-7.0802677	-2.9466379	-0.0001419
C	-1.2040243	-0.4050490	0.0000670	H	-7.9622440	-1.6812773	0.8817060
C	-2.4425404	-1.0290684	0.0000204	H	-7.9622044	-1.6812467	-0.8819861
H	-2.3517508	-2.1145541	0.0000128	C	-5.9620473	2.5996329	-0.0000477
C	1.2040245	-0.4050493	0.0000610	H	-6.5861338	2.7717181	0.8819713
C	-3.7510232	-0.5329667	-0.0000136	H	-5.1421514	3.3172534	-0.0000491
C	-4.8486364	-1.4598309	-0.0000540	H	-6.5861376	2.7717157	-0.8820641
C	-4.1304467	0.8502504	-0.0000122	C	7.3496759	-1.8904813	0.0000018
H	-4.6530044	-2.5256662	-0.0000575	H	7.9622446	-1.6812363	0.8818277
H	-3.3591646	1.6120792	0.0000131	H	7.0802677	-2.9466377	0.0000380
C	2.4425404	-1.0290688	0.0000541	H	7.9622041	-1.6812872	-0.8818643
H	2.3517507	-2.1145545	0.0000740	C	5.9620469	2.5996330	-0.0000594
C	3.7510232	-0.5329672	0.0000284	H	6.5861001	2.7717080	-0.8821039
C	4.8486366	-1.4598311	0.0000292	H	5.1421510	3.3172535	-0.0000352
C	4.1304464	0.8502502	-0.0000006	H	6.5861704	2.7717259	0.8819316
H	4.6530049	-2.5256664	0.0000499	C	0.7677415	0.9825996	0.0000452
H	3.3591641	1.6120787	-0.0000046	O	1.4089260	2.0238218	0.0000722
C	-6.1289023	-1.0384666	-0.0000880	O	-6.4365176	0.2865685	-0.0000857
C	-5.4300688	1.2096696	-0.0000470	O	6.4365174	0.2865687	-0.0000204

Table S16. Optimized cartesian coordinate of **CR1a** CAM-UB3LYP/6-31G (d,p) Triplet

C	-0.7746012	-0.9802694	0.0000785	C	5.4461185	-1.2103872	-0.0000752
O	-1.4073471	-2.0249832	0.0000039	C	6.1418072	1.0417387	-0.0001163
C	-0.0000001	1.2574995	0.0001627	C	-7.3612679	1.8955972	-0.0000690
O	0.0000001	2.4809519	0.0001163	H	-7.0904245	2.9514581	-0.0000373
C	-1.2154637	0.4052057	0.0000986	H	-7.9746704	1.6879989	-0.8817975
C	-2.4506685	1.0241757	0.0000756	H	-7.9747468	1.6879653	0.8815976
H	-2.3621986	2.1105127	0.0000941	C	-5.9804977	-2.5994390	-0.0000397
C	1.2154668	0.4052058	0.0001144	H	-6.6049556	-2.7710109	-0.8819512
C	-3.7657618	0.5307840	0.0000347	H	-5.1622744	-3.3190577	0.0000616
C	-4.8599770	1.4597522	0.0000058	H	-6.6051410	-2.7709672	0.8817485
C	-4.1459103	-0.8512840	0.0000160	C	7.3612685	1.8955942	-0.0001728
H	-4.6629613	2.5255091	0.0000072	H	7.9746870	1.6879542	-0.8818797
H	-3.3771830	-1.6148902	0.0000477	H	7.0904210	2.9514538	-0.0001966
C	2.4506683	1.0241808	0.0000612	H	7.9747336	1.6880075	0.8815148
H	2.3621948	2.1105176	0.0000683	C	5.9804962	-2.5994390	-0.0000878
C	3.7657633	0.5307925	0.0000021	H	6.6050332	-2.7709988	0.8817699
C	4.8599801	1.4597552	-0.0000509	H	5.1622784	-3.3190645	-0.0001102
C	4.1459059	-0.8512789	-0.0000101	H	6.6050615	-2.7709703	-0.8819303
H	4.6629720	2.5255132	-0.0000403	C	0.7746046	-0.9802692	0.0001450
H	3.3771736	-1.6148808	0.0000300	O	1.4073502	-2.0249831	0.0000786
C	-6.1418050	1.0417462	-0.0000282	O	-6.4526839	-0.2849122	-0.0000328
C	-5.4461283	-1.2103823	-0.0000188	O	6.4526825	-0.2849137	-0.0001347

Table S17. Optimized cartesian coordinate of **CR1b** CAM-RB3LYP/6-31G (d,p) Singlet

C	0.7591523	-1.0232692	-0.0001550	C	6.1179555	1.2887406	0.0000970
O	1.4075501	-2.0610807	-0.0000419	C	5.3651544	-1.3336587	0.0001123
C	0.0000007	1.2235120	-0.0002815	C	-5.3651464	-1.3336582	0.0000065
O	0.0000040	2.4528384	-0.0002143	C	-6.1179575	1.2887387	0.0001227
C	1.1923824	0.3693605	-0.0001824	C	7.1483539	2.3801366	0.0001382
C	2.4298002	1.0088257	-0.0001297	H	6.6623531	3.3568640	0.0000689
H	2.3150689	2.0913538	-0.0001717	H	7.7923101	2.3161468	0.8824592
C	-1.1923851	0.3693665	-0.0002229	H	7.7924442	2.3160882	-0.8820805
C	3.7439412	0.5375980	-0.0000363	C	5.6706290	-2.8034125	0.0001599
C	4.7891794	1.5272054	0.0000057	H	6.2519791	-3.0876315	0.8827704
C	4.1026844	-0.8522505	0.0000205	H	4.7407974	-3.3732261	0.0001192
H	4.4758838	2.5674531	-0.0000401	H	6.2520775	-3.0876676	-0.8823742
H	3.2844656	-1.5683391	-0.0000233	C	-7.1483602	2.3801307	0.0002209
C	-2.4298010	1.0088348	-0.0001347	H	-7.7924503	2.3161254	-0.8820012
H	-2.3150692	2.0913628	-0.0001267	H	-7.7923161	2.3160926	0.8825386
C	-3.7439407	0.5376049	-0.0000578	H	-6.6623632	3.3568600	0.0002022
C	-4.7891823	1.5272086	0.0000366	C	-5.6706154	-2.8034131	-0.0000205
C	-4.1026783	-0.8522451	-0.0000671	H	-6.2520681	-3.0876246	-0.8825659
H	-4.4758906	2.5674575	0.0000400	H	-4.7407817	-3.3732233	-0.0000965
H	-3.2844564	-1.5683302	-0.0001552	H	-6.2519592	-3.0876801	0.8825788
S	6.7861745	-0.3200012	0.0001797	C	-0.7591633	-1.0232651	-0.0002612
S	-6.7861703	-0.3200058	0.0001309	O	-1.4075684	-2.0610719	-0.0000360

Table S18. Optimized cartesian coordinate of **CR1b** CAM-UB3LYP/6-31G (d,p) Singlet

C	0.7693192	-1.0267485	0.0000423	C	6.1325229	1.2989059	0.0000022
O	1.4055164	-2.0692292	0.0000545	C	5.3934061	-1.3341121	-0.0000398
C	-0.0000002	1.2171739	0.0000990	C	-5.3934077	-1.3341122	-0.0000350
O	-0.0000008	2.4409255	0.0000331	C	-6.1325224	1.2989063	-0.0000471
C	1.2077174	0.3620198	0.0000586	C	7.1573031	2.3950497	0.0000118
C	2.4378266	0.9945463	0.0000502	H	6.6668159	3.3697829	0.0000261
H	2.3257799	2.0784413	0.0000730	H	7.8022187	2.3352901	0.8821872
C	-1.2077168	0.3620185	0.0000660	H	7.8022121	2.3353127	-0.8821699
C	3.7664475	0.5304464	0.0000213	C	5.7085171	-2.8014964	-0.0000765
C	4.8002192	1.5264637	0.0000258	H	6.2919110	-3.0826996	0.8823445
C	4.1281125	-0.8555794	-0.0000116	H	4.7830391	-3.3787027	-0.0000685
H	4.4811015	2.5653830	0.0000511	H	6.2918726	-3.0826631	-0.8825347
H	3.3156024	-1.5766813	-0.0000165	C	-7.1573018	2.3950509	-0.0000665
C	-2.4378264	0.9945445	0.0000352	H	-7.8022002	2.3353009	-0.8822550
H	-2.3257799	2.0784395	0.0000388	H	-7.8022280	2.3353054	0.8821021
C	-3.7664476	0.5304451	0.0000045	H	-6.6668138	3.3697838	-0.0000612
C	-4.8002186	1.5264631	-0.0000172	C	-5.7085198	-2.8014962	-0.0000475
C	-4.1281137	-0.8555805	-0.0000058	H	-6.2918699	-3.0826784	-0.8825043
H	-4.4811001	2.5653821	-0.0000082	H	-4.7830423	-3.3787032	-0.0000231
H	-3.3156043	-1.5766831	0.0000085	H	-6.2919197	-3.0826831	0.8823749
S	6.8118233	-0.3101131	-0.0000396	C	-0.7693170	-1.0267494	0.0000855
S	-6.8118241	-0.3101121	-0.0000648	O	-1.4055128	-2.0692310	0.0000586

Table S19. Optimized cartesian coordinate of **CR1b** CAM-UB3LYP/6-31G (d,p) Triplet

C	-0.7750421	-1.0261669	0.0000913	C	-6.1418541	1.3022491	-0.0000652
O	-1.4042477	-2.0711152	0.0000402	C	-5.4065249	-1.3351184	-0.0000181
C	0.0000007	1.2141369	0.0000894	C	5.4065325	-1.3351189	-0.0000110
O	0.0000038	2.4365918	0.0000661	C	6.1418521	1.3022509	-0.0000241
C	-1.2167131	0.3616724	0.0000665	C	-7.1649005	2.3996011	-0.0001080
C	-2.4431339	0.9901440	0.0000307	H	-6.6731122	3.3738010	-0.0000787
H	-2.3336931	2.0747705	0.0000240	H	-7.8102420	2.3414379	-0.8822604
C	1.2167106	0.3616665	0.0000630	H	-7.8103285	2.3414283	0.8819801
C	-3.7788041	0.5280423	0.0000025	C	-5.7244513	-2.8016057	-0.0000067
C	-4.8078031	1.5257589	-0.0000336	H	-6.3084539	-3.0821940	-0.8823694
C	-4.1402905	-0.8563209	0.0000083	H	-4.8003187	-3.3811344	0.0000071
H	-4.4870366	2.5643936	-0.0000364	H	-6.3084684	-3.0821760	0.8823522
H	-3.3297074	-1.5790474	0.0000372	C	7.1648944	2.3996067	-0.0000465
C	2.4431333	0.9901353	0.0000450	H	7.8103088	2.3414324	0.8820515
H	2.3336929	2.0747618	0.0000503	H	7.8102499	2.3414500	-0.8821890
C	3.7788045	0.5280357	0.0000201	H	6.6731024	3.3738048	-0.0000204
C	4.8078003	1.5257558	0.0000015	C	5.7244643	-2.8016050	-0.0000115
C	4.1402963	-0.8563261	0.0000127	H	6.3084795	-3.0821811	0.8823469
H	4.4870301	2.5643894	0.0000078	H	4.8003337	-3.3811369	-0.0000057
H	3.3297163	-1.5790558	0.0000322	H	6.3084708	-3.0821833	-0.8823747
S	-6.8243920	-0.3075373	-0.0000650	C	0.7750319	-1.0261709	0.0000598
S	6.8243960	-0.3075328	-0.0000376	O	1.4042305	-2.0711235	0.0000300

Table S20. Optimized cartesian coordinate of **SQ1a** CAM-RB3LYP/6-31G (d,p) Singlet

O	6.0389331	-0.3957125	-0.0000365	C	-4.9712879	1.2483209	0.0000258
O	-0.9240833	2.0732303	0.0000146	C	-7.0996405	-1.7097825	0.0000569
C	5.8224500	0.9441082	-0.0000415	C	-5.4085651	2.6711030	0.0000174
C	4.5779513	1.4572112	-0.0000302	C	-2.1416394	-1.1446216	0.0000135
C	3.4159071	0.6070737	-0.0000169	C	-0.9378775	-0.4391100	0.0000136
C	3.7015433	-0.8050061	-0.0000171	C	0.4368245	-0.9460450	0.0000107
C	4.9712878	-1.2483209	-0.0000255	H	-4.4572721	-2.5339495	0.0000134
C	7.0996406	1.7097824	-0.0000899	H	-2.8825633	1.5219069	0.0000288
C	5.4085650	-2.6711030	-0.0000123	H	-2.0460220	-2.2279331	0.0000096
C	2.1416395	1.1446216	-0.0000057	H	6.9049386	2.7821371	0.0001206
C	0.9378775	0.4391100	0.0000057	H	7.6954592	1.4574380	-0.8819954
C	-0.4368244	0.9460450	0.0000190	H	7.6957073	1.4571257	0.8815557
H	4.4572721	2.5339495	-0.0000312	H	6.0196826	-2.8843232	-0.8820816
H	2.8825632	-1.5219069	-0.0000098	H	6.0195584	-2.8843457	0.8821386
H	2.0460221	2.2279332	-0.0000056	H	4.5412889	-3.3306582	-0.0000783
O	-6.0389332	0.3957125	0.0000239	H	-6.9049385	-2.7821372	-0.0001587
O	0.9240833	-2.0732302	0.0000042	H	-7.6957007	-1.4571205	-0.8815916
C	-5.8224500	-0.9441083	0.0000226	H	-7.6954657	-1.4574435	0.8819594
C	-4.5779513	-1.4572112	0.0000178	H	-6.0195473	2.8843521	-0.8821397
C	-3.4159071	-0.6070737	0.0000181	H	-6.0196939	2.8843167	0.8820805
C	-3.7015434	0.8050062	0.0000244	H	-4.5412890	3.3306582	0.0000990

Table S21. Optimized cartesian coordinate of **SQ1a** CAM-UB3LYP/6-31G (d,p) Singlet

O	6.0501337	-0.3938643	-0.0000338	C	-4.9836024	1.2493077	0.0000287
O	-0.9201858	2.0734351	0.0000134	C	-7.1054950	-1.7152214	0.0000691
C	5.8299691	0.9470033	-0.0000341	C	-5.4245353	2.6709113	0.0000208
C	4.5834050	1.4562169	-0.0000255	C	-2.1450359	-1.1383692	0.0000093
C	3.4252784	0.6030958	-0.0000187	C	-0.9434092	-0.4389789	0.0000037
C	3.7128241	-0.8075774	-0.0000222	C	0.4352625	-0.9475334	-0.0000059
C	4.9836024	-1.2493077	-0.0000288	H	-4.4602127	-2.5328020	0.0000245
C	7.1054950	1.7152214	-0.0000678	H	-2.8959924	1.5260150	0.0000174
C	5.4245353	-2.6709113	-0.0000219	H	-2.0512319	-2.2222684	0.0000062
C	2.1450359	1.1383692	-0.0000096	H	6.9086198	2.7872550	0.0000913
C	0.9434092	0.4389789	-0.0000043	H	7.7022042	1.4644888	-0.8819096
C	-0.4352625	0.9475334	0.0000057	H	7.7023872	1.4642530	0.8815810
H	4.4602127	2.5328020	-0.0000239	H	6.0362563	-2.8827952	-0.8820471
H	2.8959924	-1.5260150	-0.0000184	H	6.0361633	-2.8828164	0.8820634
H	2.0512319	2.2222684	-0.0000064	H	4.5592479	-3.3331569	-0.0000731
O	-6.0501337	0.3938643	0.0000343	H	-6.9086198	-2.7872550	-0.0000899
O	0.9201858	-2.0734351	-0.0000136	H	-7.7023875	-1.4642531	-0.8815795
C	-5.8299691	-0.9470033	0.0000348	H	-7.7022039	-1.4644888	0.8819111
C	-4.5834050	-1.4562169	0.0000259	H	-6.0361601	2.8828168	-0.8820666
C	-3.4252784	-0.6030958	0.0000187	H	-6.0362594	2.8827948	0.8820439
C	-3.7128241	0.8075774	0.0000218	H	-4.5592479	3.3331569	0.0000751

Table S22. Optimized cartesian coordinate of **SQ1a** CAM-UB3LYP/6-31G (d,p) Triplet

O	6.1002123	0.3867101	0.0000250	C	-5.0385991	-1.2540825	-0.0000256
O	-0.9006881	-2.0755037	-0.0000092	C	-7.1322280	1.7392762	-0.0000833
C	5.8648195	-0.9590407	0.0000273	C	-5.4930360	-2.6710669	-0.0000131
C	4.6081234	-1.4508528	0.0000220	C	-2.1591919	1.1120789	-0.0000041
C	3.4685889	-0.5855528	0.0000171	C	-0.9698479	0.4391344	0.0000014
C	3.7629201	0.8180666	0.0000213	C	0.4267223	0.9527269	0.0000103
C	5.0385992	1.2540825	0.0000243	H	-4.4736021	2.5266750	-0.0000239
C	7.1322280	-1.7392763	0.0000712	H	-2.9553845	-1.5437394	-0.0000150
C	5.4930360	2.6710669	0.0000127	H	-2.0719049	2.1983628	-0.0000002
C	2.1591919	-1.1120789	0.0000090	H	6.9242656	-2.8095160	-0.0001455
C	0.9698479	-0.4391344	0.0000055	H	7.7333617	-1.4968242	0.8817548
C	-0.4267223	-0.9527269	-0.0000026	H	7.7336077	-1.4965042	-0.8813536
H	4.4736021	-2.5266750	0.0000205	H	6.1072649	2.8784838	0.8817069
H	2.9553846	1.5437394	0.0000212	H	6.1071276	2.8785157	-0.8817707
H	2.0719049	-2.1983628	0.0000042	H	4.6351632	3.3432656	0.0000884
O	-6.1002123	-0.3867101	-0.0000310	H	-6.9242657	2.8095160	0.0001333
O	0.9006880	2.0755037	0.0000187	H	-7.7336110	1.4965049	0.8813394
C	-5.8648195	0.9590406	-0.0000338	H	-7.7333584	1.4968234	-0.8817689
C	-4.6081234	1.4508528	-0.0000245	H	-6.1071259	-2.8785157	0.8817714
C	-3.4685889	0.5855528	-0.0000151	H	-6.1072665	-2.8784837	-0.8817062
C	-3.7629200	-0.8180666	-0.0000187	H	-4.6351632	-3.3432656	-0.0000902

Table S23. Optimized cartesian coordinate of **SQ1b** (trans) CAM-RB3LYP/6-31G (d,p) Singlet

C	-0.4214096	0.9536364	-0.0002166	S	-6.4050804	0.4928547	0.0001213
O	-0.8894312	2.0874366	0.0000462	C	5.8581354	1.1646182	0.0001791
C	0.4214101	-0.9536348	-0.0003199	C	4.9065261	-1.3972504	-0.0000792
O	0.8894318	-2.0874350	-0.0004129	C	-4.9065272	1.3972501	0.0000004
C	0.9462459	0.4243992	-0.0001666	C	-5.8581348	-1.1646191	0.0001641
C	2.1530534	1.1220050	-0.0000390	C	6.9706570	2.1723264	0.0003525
H	2.0508688	2.2050805	0.0000387	H	6.5631752	3.1844387	0.0002394
C	-0.9462455	-0.4243977	-0.0002016	H	7.6075483	2.0574338	0.8826335
C	3.4364430	0.5960614	-0.0000066	H	7.6078940	2.0573737	-0.8816695
C	4.5541186	1.5059768	0.0001310	C	5.1004016	-2.8857883	-0.0001881
C	3.6872330	-0.8229298	-0.0001016	H	5.6589176	-3.2128852	0.8823800
H	4.3203454	2.5671655	0.0002013	H	4.1295849	-3.3829657	-0.0002442
H	2.8223988	-1.4863426	-0.0001956	H	5.6589482	-3.2127490	-0.8827876
C	-2.1530528	-1.1220037	-0.0001286	C	-6.9706557	-2.1723280	0.0003997
H	-2.0508679	-2.2050791	-0.0001403	H	-7.6082655	-2.0570439	-0.8813075
C	-3.4364427	-0.5960607	-0.0000424	H	-6.5631735	-3.1844400	-0.0002636
C	-4.5541177	-1.5059769	0.0000725	H	-7.6071740	-2.0577680	0.8829951
C	-3.6872337	0.8229303	-0.0000629	C	-5.1004037	2.8857878	-0.0000427
H	-4.3203439	-2.5671654	0.0000909	H	-5.6587908	3.2128570	0.8826177
H	-2.8224000	1.4863438	-0.0001699	H	-4.1295873	3.3829659	-0.0002238
S	6.4050799	-0.4928560	0.0000704	H	-5.6590796	3.2127756	-0.8825499

Table S24. Optimized cartesian coordinate of **SQ1b** (trans) CAM-UB3LYP/6-31G (d,p) Singlet

C	-0.4183446	0.9564982	0.0000194	S	-6.4248301	0.4873665	0.0000207
O	-0.8815950	2.0883540	0.0001777	C	5.8699284	1.1700789	0.0000148
C	0.4183444	-0.9564986	-0.0000711	C	4.9289164	-1.3999144	-0.0000605
O	0.8815948	-2.0883545	-0.0002106	C	-4.9289160	1.3999145	0.0000376
C	0.9561476	0.4236930	-0.0000010	C	-5.8699286	-1.1700786	0.0000111
C	2.1576629	1.1103141	0.0000294	C	6.9777274	2.1824114	0.0000642
H	2.0584689	2.1944353	0.0000737	H	6.5658292	3.1928887	-0.0000251
C	-0.9561477	-0.4236934	-0.0000296	H	7.6157399	2.0712664	0.8822282
C	3.4537082	0.5879644	0.0000075	H	7.6159095	2.0711785	-0.8819649
C	4.5618111	1.5029994	0.0000324	C	5.1302197	-2.8871315	-0.0001040
C	3.7070220	-0.8274085	-0.0000353	H	5.6904835	-3.2119361	0.8823457
H	4.3230361	2.5633493	0.0000673	H	4.1623570	-3.3902415	-0.0000846
H	2.8451067	-1.4932315	-0.0000380	H	5.6904237	-3.2118907	-0.8826087
C	-2.1576631	-1.1103145	-0.0000442	C	-6.9777279	-2.1824109	0.0000992
H	-2.0584692	-2.1944357	-0.0000825	H	-7.6161860	-2.0709259	-0.8816968
C	-3.4537083	-0.5879647	-0.0000129	H	-6.5658298	-3.1928882	-0.0004062
C	-4.5618113	-1.5029994	-0.0000123	H	-7.6154641	-2.0715179	0.8824961
C	-3.7070218	0.8274083	0.0000199	C	-5.1302190	2.8871316	0.0000656
H	-4.3230365	-2.5633493	-0.0000298	H	-5.6903855	3.2119036	0.8825895
H	-2.8451063	1.4932312	0.0000133	H	-4.1623563	3.3902414	-0.0000023
S	6.4248303	-0.4873661	-0.0000474	H	-5.6905204	3.2119237	-0.8823648

Table S25. Optimized cartesian coordinate of **SQ1b** (trans) CAM-UB3LYP/6-31G (d,p) Triplet

C	0.4121751	-0.9604800	-0.0000085	S	6.4629035	-0.4773769	-0.0000613
O	0.8672759	-2.0896661	-0.0000196	C	-5.8942205	-1.1802669	0.0000316
C	-0.4121711	0.9604916	-0.0000398	C	-4.9726128	1.4051890	-0.0000475
O	-0.8672708	2.0896783	-0.0000165	C	4.9726041	-1.4051918	0.0000196
C	-0.9765928	-0.4238997	-0.0000045	C	5.8942252	1.1802597	-0.0000301
C	-2.1656682	-1.0893738	0.0000118	C	-6.9929173	-2.2010220	0.0001137
H	-2.0726055	-2.1754381	0.0000338	H	-6.5724348	-3.2082698	-0.0000840
C	0.9765965	0.4239110	-0.0000158	H	-7.6330493	-2.0974976	0.8822211
C	-3.4887230	-0.5729036	0.0000049	H	-7.6333852	-2.0972909	-0.8817234
C	-4.5773710	-1.4967159	0.0000357	C	-5.1866979	2.8897685	-0.0001062
C	-3.7456364	0.8348496	-0.0000329	H	-5.7499347	3.2111380	0.8820924
H	-4.3292926	-2.5554852	0.0000673	H	-4.2239542	3.4030442	-0.0000766
H	-2.8892292	1.5055632	-0.0000621	H	-5.7498458	3.2110783	-0.8823837
C	2.1656723	1.0893838	-0.0000229	C	6.9929271	2.2010096	0.0001342
H	2.0726120	2.1754482	-0.0000450	H	7.6338567	2.0968675	-0.8813158
C	3.4887250	0.5729088	-0.0000092	H	6.5724496	3.2082592	-0.0007493
C	4.5773774	1.4967157	-0.0000225	H	7.6325958	2.0978905	0.8826279
C	3.7456309	-0.8348458	0.0000273	C	5.1866823	-2.8897722	0.0000782
H	4.3293044	2.5554863	-0.0000253	H	5.7497848	-3.2110891	0.8823823
H	2.8892197	-1.5055545	0.0000683	H	4.2239363	-3.4030436	-0.0000024
S	-6.4629073	0.4773670	-0.0000229	H	5.7499614	-3.2111398	-0.8820939

Table S26. Optimized cartesian coordinate of **SQ1b** (cis) CAM-RB3LYP/6-31G (d,p) Singlet

C	-0.0000001	0.5420685	0.0000249	S	5.6923501	-1.4401379	0.0002847
O	-0.0000001	-0.6935052	0.0000310	C	-5.8436636	0.2991661	-0.0003369
C	0.0000000	2.6278444	-0.0000305	C	-3.9587525	-1.6792698	-0.0001524
O	0.0000000	3.8454276	-0.0000649	C	3.9587526	-1.6792698	0.0002436
C	-1.0373078	1.5827264	-0.0000682	C	5.8436636	0.2991661	0.0002624
C	-2.4243797	1.7243401	-0.0001582	C	-7.2636446	0.7855786	-0.0004628
H	-2.7659576	2.7573422	-0.0002081	H	-7.2890082	1.8763141	-0.0004002
C	1.0373077	1.5827264	0.0000371	H	-7.8034605	0.4284720	-0.8827067
C	-3.3935252	0.7322990	-0.0001905	H	-7.8036607	0.4283652	0.8816145
C	-4.7800273	1.1269529	-0.0002922	C	-3.5504635	-3.1238695	-0.0000741
C	-3.0649337	-0.6705110	-0.0001264	H	-3.9349440	-3.6446879	-0.8825711
H	-4.9836698	2.1942924	-0.0003384	H	-2.4623392	-3.1987028	-0.0000200
H	-2.0086017	-0.9364797	-0.0000461	H	-3.9350254	-3.6446137	0.8824313
C	2.4243796	1.7243401	0.0000883	C	7.2636446	0.7855788	0.0003768
H	2.7659576	2.7573422	0.0000727	H	7.8037586	0.4280899	-0.8815278
C	3.3935252	0.7322990	0.0001557	H	7.2890082	1.8763142	-0.0000217
C	4.7800272	1.1269529	0.0001988	H	7.8033625	0.4287477	0.8827932
C	3.0649337	-0.6705111	0.0001870	C	3.5504636	-3.1238695	0.0002789
H	4.9836697	2.1942924	0.0001802	H	3.9349113	-3.6446061	0.8828386
H	2.0086018	-0.9364798	0.0001632	H	2.4623394	-3.1987029	0.0001929
S	-5.6923500	-1.4401380	-0.0002710	H	3.9350584	-3.6446955	-0.8821637

Table S27. Optimized cartesian coordinate of **SQ1b** (cis) CAM-UB3LYP/6-31G (d,p) Singlet

C	0.0000000	0.5311382	0.0000248	S	5.7224881	-1.4308031	0.0003018
O	0.0000000	-0.6991653	0.0000561	C	-5.8606823	0.3120716	-0.0003471
C	0.0000000	2.6196065	-0.0000457	C	-3.9889290	-1.6841346	-0.0001493
O	0.0000000	3.8350201	-0.0000901	C	3.9889290	-1.6841346	0.0002603
C	-1.0462092	1.5744617	-0.0000771	C	5.8606823	0.3120717	0.0002681
C	-2.4232951	1.7133822	-0.0001670	C	-7.2765098	0.8093021	-0.0004751
H	-2.7644895	2.7472926	-0.0002244	H	-7.2935579	1.9003392	-0.0004422
C	1.0462092	1.5744617	0.0000315	H	-7.8199136	0.4569697	-0.8826466
C	-3.4088859	0.7226705	-0.0001960	H	-7.8200986	0.4569129	0.8815591
C	-4.7872293	1.1302758	-0.0003028	C	-3.5924812	-3.1316865	-0.0000671
C	-3.0887733	-0.6788770	-0.0001252	H	-3.9809885	-3.6499197	-0.8824658
H	-4.9825425	2.1994476	-0.0003539	H	-2.5049814	-3.2165244	-0.0000042
H	-2.0352199	-0.9522742	-0.0000440	H	-3.9810840	-3.6498442	0.8823340
C	2.4232951	1.7133822	0.0000844	C	7.2765098	0.8093022	0.0003595
H	2.7644895	2.7472926	0.0000622	H	7.8201636	0.4566834	-0.8815421
C	3.4088859	0.7226705	0.0001589	H	7.2935579	1.9003392	0.0000447
C	4.7872293	1.1302759	0.0002007	H	7.8198486	0.4571993	0.8826635
C	3.0887733	-0.6788770	0.0001969	C	3.5924812	-3.1316865	0.0003016
H	4.9825425	2.1994476	0.0001758	H	3.9809735	-3.6498377	0.8827552
H	2.0352199	-0.9522742	0.0001713	H	2.5049814	-3.2165244	0.0002290
S	-5.7224881	-1.4308031	-0.0002744	H	3.9810990	-3.6499262	-0.8820445

Table S28. Optimized cartesian coordinate of **SQ1b** (cis) CAM-UB3LYP/6-31G (d,p) Triplet

C	-0.0000003	-0.5148421	0.0000068	S	-5.7768285	1.4150449	0.0002863
O	-0.0000004	0.7073371	0.0000419	C	5.8933310	-0.3338601	-0.0003224
C	-0.0000005	-2.6053660	-0.0000581	C	4.0440498	1.6934523	-0.0001518
O	-0.0000013	-3.8176588	-0.0000987	C	-4.0440490	1.6934522	0.0002412
C	1.0651995	-1.5617864	-0.0000872	C	-5.8933310	-0.3338595	0.0002783
C	2.4215492	-1.6954757	-0.0001681	C	7.3014669	-0.8497067	-0.0004382
H	2.7629400	-2.7307759	-0.0002188	H	7.3036724	-1.9411449	-0.0003375
C	-1.0651997	-1.5617860	0.0000187	H	7.8515291	-0.5062905	-0.8825234
C	3.4395709	-0.7047594	-0.0001948	H	7.8517396	-0.5061270	0.8814513
C	4.8014230	-1.1348969	-0.0002864	C	3.6673875	3.1454244	-0.0000819
C	3.1332385	0.6928362	-0.0001342	H	4.0624366	3.6597181	-0.8822533
H	4.9820844	-2.2072001	-0.0003321	H	2.5810907	3.2467953	-0.0000489
H	2.0844661	0.9792065	-0.0000692	H	4.0624824	3.6596437	0.8821125
C	-2.4215495	-1.6954758	0.0000746	C	-7.3014670	-0.8497058	0.0004093
H	-2.7629396	-2.7307762	0.0000578	H	-7.8518898	-0.5057638	-0.8812442
C	-3.4395711	-0.7047597	0.0001520	H	-7.3036729	-1.9411438	-0.0001388
C	-4.8014234	-1.1348969	0.0002094	H	-7.8513787	-0.5066516	0.8827302
C	-3.1332382	0.6928359	0.0001811	C	-3.6673866	3.1454243	0.0002758
H	-4.9820851	-2.2072000	0.0001980	H	-4.0623646	3.6596335	0.8825285
H	-2.0844656	0.9792056	0.0001524	H	-2.5810898	3.2467952	0.0001657
S	5.7768291	1.4150446	-0.0002539	H	-4.0625525	3.6597281	-0.8818374

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