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Four-way-output molecular response system based on the dihydrodibenzo[*c*,*g*]phenanthrene skeleton: modulation of CD and FDCD activity by acid and electron-transfer

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Abstract

Presence or absence of electron-accepting dye chromophores is the key function for ON/OFF switching of fluorescence from the dihydrodibenzo[*c*,*g*]phenanthrene skeleton in $\mathbf{2}^{2+}/\mathbf{3}$. The helical fluorophore in $\mathbf{2}^{2+}$ could be generated stereoselectively upon electrolysis of binaphthylic donor **1** through intramolecular chirality transmission. Huge chiroptical signals are easily detected by circular dichroism (CD) and fluorescence-detected CD (FDCD) techniques to realize novel four-way-output response.

Keywords: Molecular response system; Dynamic redox system; Chirality; Electrochiroptics; Fluorescence; CD; FDCD; Dication; Helicity

Molecules that exhibit fluorescence ON/OFF switching in response to external stimuli such as light, electric potential, pH, and metal ions have got greatly increased interest from the viewpoint of application to develop molecular devices such as sensors, data storage devices, and logic gates.[1] The chiral fluorescence switches have advantages in terms of more sensitive detection by using fluorescence-detected CD (FDCD) technique[2] to read out. However, only a small number of chiral fluorophores have been studied to date to develop such an advanced material.[3] The dihydrodibenzo[*c*,*g*]phenanthrene (dihydro[5]helicene) with a stable configuration of helicity emits strong fluorescence.[4] We have now succeeded in facile formation of this helical structure enantioselectively in the form of dications $\mathbf{2}^{2+}$ via the dynamic redox reactions of electron-donating binaphthyls **1** with an axial chirality.[5] Fluorescence ON/OFF switching occurs upon acid/base-induced interconversion between dications $\mathbf{2}^{2+}$ and bridged ethers **3** (Scheme 1), which can be also monitored by FDCD technique. Because interconversions of $\mathbf{1}/\mathbf{2}^{2+}$ and $\mathbf{2}^{2+}/\mathbf{3}$ are accompanied by huge changes in chiroptical properties, the present molecular system can be regarded as the prototype exhibiting novel multi-output response over the three states ($\mathbf{1}/\mathbf{2}^{2+}/\mathbf{3}$), whose details will be reported herein.

The reaction of *rac*-2,2′-dimethyl-1,1′-binaphthyl with *n*-BuLi in the presence of TMEDA gave 2,2′-bis(lithiomethyl) derivative, which was then reacted with thioxanthen-9-one. Dehydration of the resulting diol proceeded smoothly upon treatment with a catalytic amount of TsOH in refluxing benzene (Dean–Stark) to give *rac*-**1a**[6] in a two-step yield of 56%. By starting with optically pure (*R*)-dimethylbinaphthyl, (*R*)-**1a**[6] was obtained by the similar procedures (Scheme 2). No signs of racemization were observed during the transformation. According to the X-ray analysis of *rac*-**1a**,[7] the binaphthyl skeleton is twisted almost perpendicularly (dihedral angle 87.5°) (Fig. 1a). The

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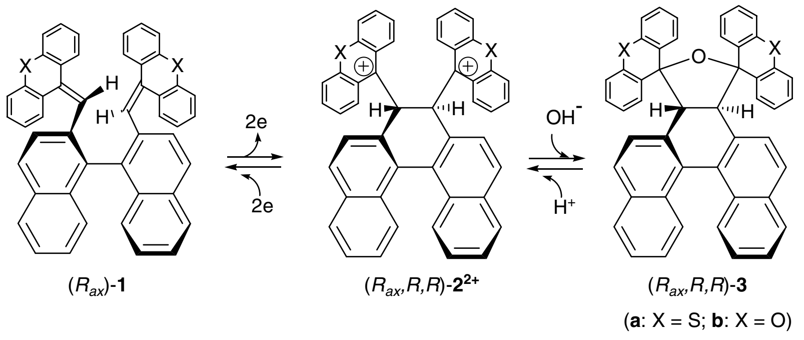
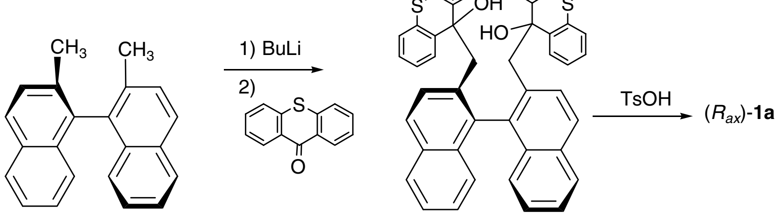


Scheme 1.



Scheme 2.

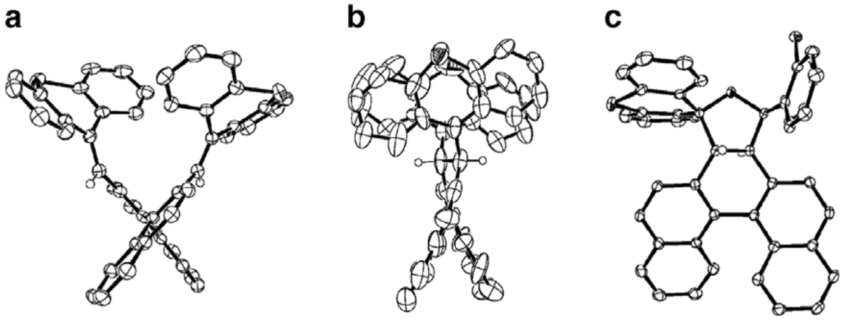


Fig. 1. X-ray structures of (a) binaphthylic electron donor **1a**, (b) dication **2a**$^{2+}$ in $(SbCl_6^-)_2$ salt, and (c) bridged ether **3a**. All of analyses were carried out for the racemates, and the molecules with the $(R)_{ax}$-binaphthyl unit are shown.

large thioxanthenylidene moieties are directing outward to prevent steric repulsion. Thus, the non-bonded contact between two vinylic protons is only 4.31 Å, and separation of two benzylidene carbons is also small (3.72 Å), between which the new C–C bond is formed upon oxidation (vide infra).

According to the voltammetric measurement, electron donor **1a** undergoes irreversible 2e-oxidation at +1.18 V versus SCE in MeCN, and a new peak was observed in the far cathodic region (+0.30 V) in the return cycle of the voltammogram. Such a large shift of redox peaks is indicative of the chemical process such as C–C bond formation that follows electron-transfer. In fact, upon treatment of yellow solid of *rac*-**1a** with 2 equiv of $(4\text{-}BrC_6H_4)_3N^{+\cdot}SbCl_6^-$ in CH_2Cl_2, purple $SbCl_6^-$ salt[6] of dihydrodibenzo[*c*,*g*]phenanthrene-type dication *rac*-**2a**$^{2+}$ was obtained in 82% isolated yield without contamination of diastereomers. Its structure was deduced on the basis of the ^1H NMR spectrum with a sharp singlet at δ 7.23 for the acidic methine protons and further confirmed by X-ray analysis (vide infra). Upon treatment of the salt of **2a**$^{2+}$ with Zn powder in MeCN, the starting diolefin **1a** was regenerated in quantitative yield. Such a high-yield interconversion indicates that **1a**/**2a**$^{2+}$ can be considered as a sort of reversible redox pair ('dynamic redox pair'[8]), for which the C–C bond formation/cleavage is accompanied by 2e-transfer.

The X-ray structure[7] determined on *rac*-**2a**$^{2+}$ shows that the central six-membered ring adopts the half-chair conformation, and the two methine protons are located in the trans fashion at the pseudo-axial positions (Fig. 1b). In the crystal of centrosymmerty, there are two kinds of stereoisomers: one with the $(R)_{ax}$-binaphthyl unit and newly formed point chiralities of (R,R)-configuration [(R_{ax},R,R)-**2a**$^{2+}$] and the other is the enantiomer [(S_{ax},S,S)-**2a**$^{2+}$]. There must be no chance for the configuration of binaphthyl moiety in **2a**$^{2+}$ to be inverted upon oxidation of **1a**. Thus, the axial chirality of (*R*)-**1a** should have been transmitted[9] into point chiralities of (*R*,*R*) in the dication **2a**$^{2+}$ to give the single stereoisomer. This is in accord with the assumption that the sterically demanded geometries of **1a** and **2a**$^{2+}$ in solution are identical to those found in crystal.

Upon electrochemical oxidation of (*R*)-**1a** to (*R*,*R*)-**2a**$^{2+}$, both UV–vis and exciton-type CD[10] spectra changed drastically (electrochiroptical response[5,11]) (Fig. 2). As the oxidation proceeds, the signal at 350 nm assignable to thioxanthenylidenethenyl groups decreases, whereas signals at 277 nm and around 510 nm increase that are characteristic absorptions of thioxanthenylium chromophore. Observation of several isosbestic points in both UV–vis and CD spectra indicates the clean interconversion as well as negligible steady-state concentration of the intermediary cation radical of high reactivity.

Although dihydrodibenzo[*c*,*g*]phenanthrene is well-known as a strong fluorophore,[4] the dication **2a**$^{2+}$ does not emit fluorescence at all. This observation can be accounted for by electron-transfer quenching through the intramolecular charge shift from the electron-donating naphthalene rings to the electron-accepting thioxanthenylium moieties. Treatment of non-fluorescent dication **2a**$^{2+}$ with aqueous $NaHCO_3$ in MeCN induced strong fluorescence emission by chemical transformation, whose product does not possess the electron-accepting dye moieties to quench the emission. Abstraction of the C–H protons adjacent to the cationic part in **2a**$^{2+}$ is unlikely by considering the highly hindered structure for the resulting conjugated diene. The bridged ether (tetrahydrofuran derivative) **3a**[6] (y. 100%) formed by nucleophilic attack of hydroxide toward the cationic center is most likely, and we have finally confirmed the structure by spectroscopic and crystallographic methods.[7]

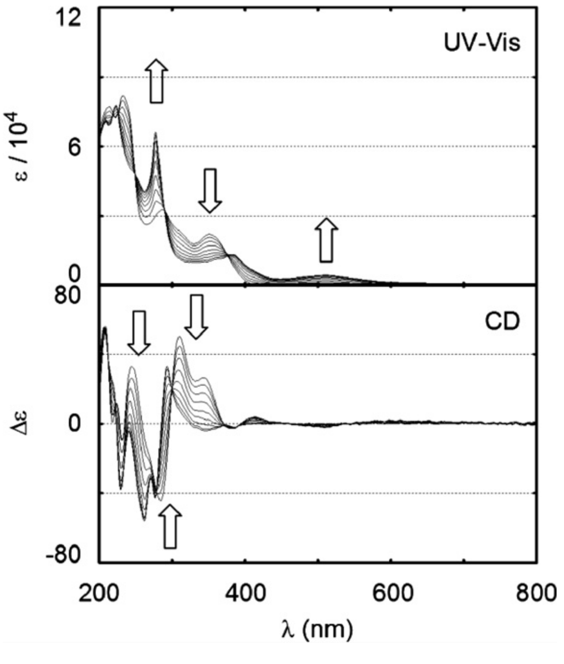


Fig. 2. UV–vis and CD spectral changes of (*R*)-**1a** (1.65×10^{-5} M) upon constant-current electrochemical oxidation in MeCN (28 micro A, every 5 min) to generate (*R*,*R*)-**2a**$^{2+}$.

As shown in Figure 1c, the dihydrodibenzo[*c*,*g*]phenanthrene skeleton in **3a** adopts similar conformation to that of **2a**$^{2+}$, thus (*R*,*R*)-**2a**$^{2+}$ should have been transferred into (*R*,*R*)-**3a** without scrambling of the stereochemistry. The fluorescence quantum yield of **3a** was determined to be 0.87,[12] which endows very efficient fluorescence output (vide infra). Upon treatment with HBF_4, ether **3a** regenerated dication **2a**$^{2+}$, which was isolated as BF_4^- salt (y. 100%). It is noteworthy that the transformation could also be carried out in the diluted solution. Thus, addition of $HBF_4{\cdot}OEt_2$ to a solution of (*R*,*R*)-**3a** in MeCN (10^{-5} M) resulted in vivid change in UV–vis, CD, and fluorescence spectra by reformation of (*R*,*R*)-**2a**$^{2+}$ (Fig. 3).[13] We confirmed that the related pair of oxygen analogues [(*R*,*R*)-**2b**$^{2+}$/(*R*,*R*)-**3b**] also exhibits the similar multi-output response (Fig. 4). Furthermore, the reaction could be also followed by FDCD spectroscopy (Fig. 5). Since only the

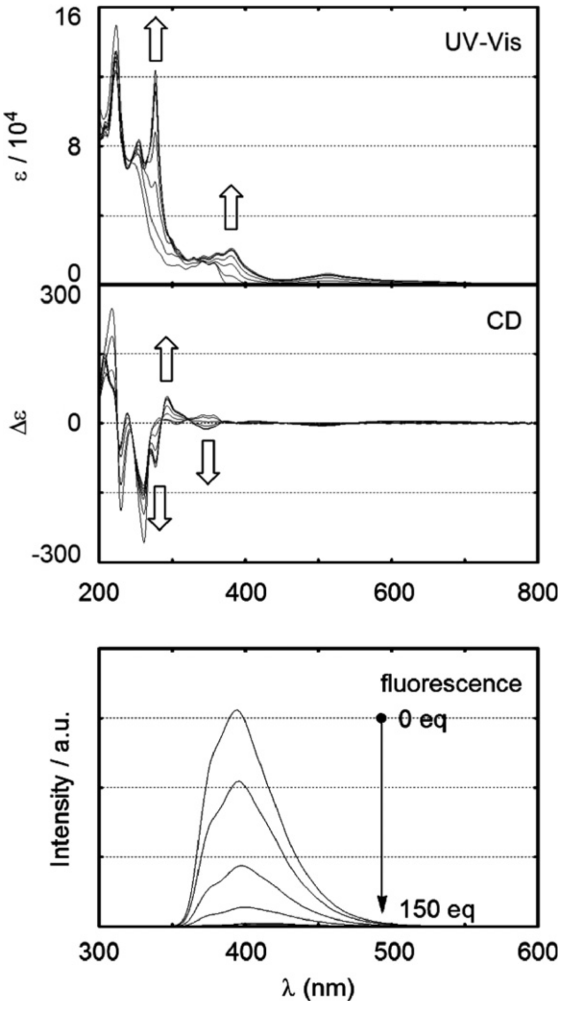


Fig. 3. UV–vis, CD, and fluorescence spectral changes of (*R*,*R*)-**3a** (1.51×10^{-5} M) upon addition of $HBF_4{\cdot}OEt_2$ in MeCN to generate (*R*,*R*)-**2a**$^{2+}$. The excitation wavelength is 340 nm for fluorescence measurement.

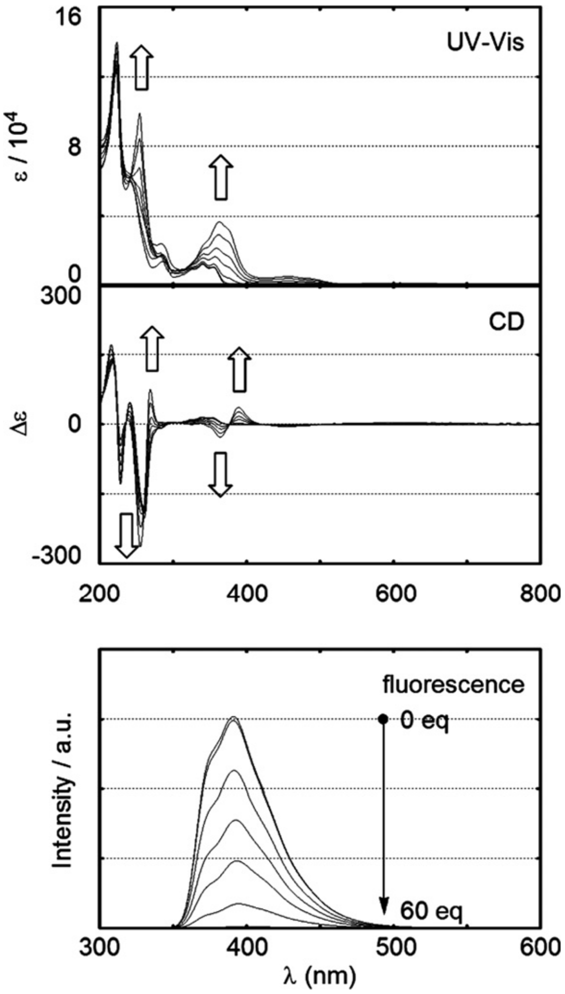


Fig. 4. UV–vis, CD, and fluorescence spectral changes of (*R*,*R*)-**3b** (1.57×10^{-5} M) upon addition of $HBF_4 \cdot OEt_2$ in MeCN to generate (*R*,*R*)-$\mathbf{2b}^{2+}$. The excitation wavelength is 340 nm for fluorescence measurement.

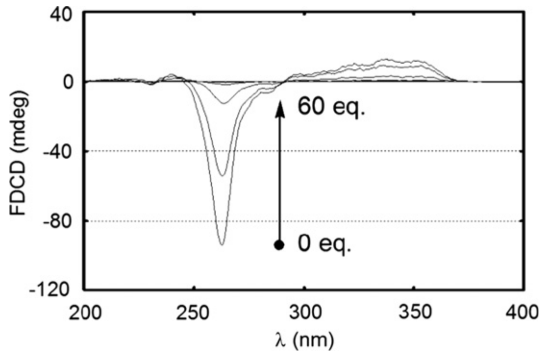


Fig. 5. FDCD spectral changes of (*R*,*R*)-**3b** [1.63×10^{-5} M] upon addition of $HBF_4 \cdot OEt_2$ in MeCN to generate (*R*,*R*)-$\mathbf{2b}^{2+}$.

bridged ether **3** is fluorescent and gives FDCD signals, the spectral changes obtained by CD and FDCD exhibit quite different pattern. So that, they can be considered as the independent spectral outputs. This is the successful demonstration of four-way-output response system.

In summary, we have constructed the novel fluorescence ON/OFF switching systems based on the dihydrodibenzo[*c*,*g*]phenanthrene-type dications (*R*,*R*)-$\mathbf{2}^{2+}$, which also exhibit electrochiroptical response upon reduction. Drastic structural changes upon electron-transfer for the pairs of $\mathbf{1}/\mathbf{2}^{2+}$ induce huge electrochiroptical response (UV–vis and CD), and presence or absence of intramolecular CT is the key feature for fluorescence switching in the pairs of $\mathbf{2}^{2+}/\mathbf{3}$. Thanks to the above two characteristics, the present molecular response systems over three states ($\mathbf{1}/\mathbf{2}^{2+}/\mathbf{3}$) could serve as new motifs for developing multi-input (electric potential and pH) and multi-output (UV–vis, CD, fluorescence, FDCD) response systems.

Acknowledgments

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Supplementary data

Experimental details for new compounds (**1a**, $\mathbf{2a}^{2+}(SbCl_6^-)_2$, **3a**) in pdf format. Crystallographic data (excluding structure factors) for the structures in this Letter has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 663450–663452. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 (0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk]. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.11.188.

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6. Experimental details are given in Supplementary data. The selected spectral data are as follows. Data for *rac*-**1a**: mp >300 °C; ^{1}H NMR

(300 MHz, C_6D_6) δ/ppm 7.80 (2H, ddd, $J = 8.1$, 8.1, 1.2 Hz), 7.62 (2H, dd, $J = 8.1$, 1.2 Hz), 7.53 (2H, d, $J = 8.7$ Hz), 7.44 (2H, d, $J = 8.7$ Hz), 7.39 (2H, dd, $J = 8.1$, 1.2 Hz), 7.20–7.15 (4H, m), 7.12 (2H, dd, $J = 8.1$, 1.2 Hz), 6.98 (2H, ddd, $J = 8.1$, 8.1, 1.2 Hz), 6.97 (2H, dd, $J = 8.1$, 1.2 Hz), 6.82 (2H, s), 6.69 (2H, dd, $J = 8.1$, 1.2 Hz), 6.68 (2H, ddd, $J = 8.1$, 8.1, 1.2 Hz), 6.67 (2H, ddd, $J = 8.1$, 8.1, 1.2 Hz), 6.54 (2H, ddd, $J = 8.1$, 8.1, 1.2 Hz); IR (KBr) ν_{max} 3052, 1613, 1582, 1501, 1460, 1437, 1270, 1158, 1123, 1064, 1032, 819, 760, 736 cm^{-1}; FD-MS m/z 670 ($M^+ - 1$, BP); UV–vis (MeCN) λ_{max} 350 (log ε 4.35), 287 (4.51), 233 (4.91), 215 (4.88) nm. Data for (*R*,*R*)-**1a**: mp >300 °C; $[\alpha]_D^{16}$ +393 (c 0.100, $CHCl_3$); CD (MeCN) λ 379 ($\Delta\varepsilon$ −2.38), 343 (+26.3), 334 (+24.5), 310 (+49.4), 284 (−43.9), 246 (+32.4), 231 (−9.36), 224 (+11.9), 218 (+0.506), 208 (+53.7) nm [g-factor × 10^4: 310 (+21.1), 274 (−13.6), 246 nm (+5.47), 208 (+7.35) nm]. Data for *rac*-$\mathbf{2a}^{2+}(SbCl_6^-)_2$: mp 181 °C; ^1H NMR (300 MHz, CD_3CN) δ/ppm 8.80 (2H, dd, $J = 8.7$, 1.2 Hz), 8.49 (2H, dd, $J = 8.7$, 1.2 Hz), 8.40 (2H, dd, $J = 8.7$, 1.2 Hz), 8.23 (2H, dd, $J = 8.7$, 1.2 Hz), 8.18 (2H, ddd, $J = 8.7$, 8.7, 1.2 Hz), 8.13 (2H, dd, $J = 8.7$, 1.2 Hz), 8.00 (2H, d, $J = 8.4$ Hz), 7.84 (2H, dd, $J = 8.7$, 1.2 Hz), 7.83 (2H, ddd, $J = 8.7$, 8.7, 1.2 Hz), 7.82 (2H, ddd, $J = 8.7$, 8.7, 1.2 Hz), 7.73 (2H, ddd, $J = 8.7$, 8.7, 1.2 Hz), 7.58 (2H, ddd, $J = 8.7$, 8.7, 1.2 Hz), 7.42 (2H, ddd, $J = 8.7$, 8.7, 1.2 Hz), 7.26 (2H, s), 7.25 (2H, d, $J = 8.4$ Hz); IR (KBr) cm^{-1} ν_{max}1653, 1591, 1544, 1453, 1428, 1374, 1335, 1291, 813, 751, 729 cm^{-1}; FD-MS m/z 667 ($M^+{-}3$, BP); UV–vis (MeCN) λ_{max} 513 (log ε 3.53), 381 (4.19), 362 (5.42), 342 (4.09), 277 (5.06), 252 (4.72), 223 (4.99) nm. Data for (*R*,*R*)-$\mathbf{2a}^{2+}(SbCl_6^-)_2$: mp 173 °C; CD (MeCN) λ 630 ($\Delta\varepsilon$ +5.85), 515 (−3.65), 408 (+4.73), 391 (+0.409), 373 (+4.59), 344 (−11.2), 293 (+43.1), 277 (−70.3), 271 (−39.3), 261 (−127), 239 (+13.6), 228 (−59.7), 207 (+126) nm [g-factor × 10^4: 344 (−9.09), 261 (−24.0), 207 (+18.8) nm]. Data for *rac*-**3a**: mp >300 °C; ^1H NMR (300 MHz, C_6D_6) δ/ppm 7.94 (2H, d, $J = 8.4$ Hz), 7.62 (2H, dd, $J = 8.7$, 1.2 Hz), 7.54 (2H, dd, $J = 8.7$, 1.2 Hz), 7.53 (2H, d, $J = 8.4$ Hz), 7.30 (2H, dd, $J = 8.7$, 1.2 Hz), 7.27 (2H, dd, $J = 7.8$, 1.2 Hz), 7.20–7.15 (4H, m), 7.12 (2H, ddd, $J = 8.7$, 8.7, 1.2 Hz), 6.93 (2H, ddd, $J = 8.7$, 8.7, 1.2 Hz), 6.89 (2H, ddd, $J = 8.7$, 8.7, 1.2), 6.88 (2H, ddd, $J = 8.7$, 8.7, 1.2 Hz), 6.68 (2H, ddd, $J = 7.8$, 7.8, 1.2 Hz), 6.41 (2H, ddd, $J = 7.8$, 7.8, 1.2 Hz), 5.38 (2H, s); IR (KBr) ν_{max} 3056, 2923, 2851, 1727, 1589, 1460, 1438, 1280, 1231, 1162, 1059, 991, 817, 801, 749 cm^{-1}; FD-MS m/z 474 (BP), 686 ($M^+{-}1$, 47%); UV–vis (MeCN) λ_{max} 356 (log ε 4.05), 342 (4.10), 329 (3.98), 309 (4.01), 247 sh (4.79), 224 (5.13) nm. Data for (*R*,*R*)-**3a**: mp 298 °C; $[\alpha]_D^{16}$ −287 (c 0.111, $CHCl_3$); CD (MeCN) λ 356 ($\Delta\varepsilon$ +15.8), 342 (+16.5), 329 (+10.3), 304 (−2.09), 282 (+10.6), 262 (−244), 243 (−13.3), 229 (−185), 218 (+229) nm [g-factor × 10^4: 262 (+59.0), 229 (−19.2), 218 (+19.7) nm].

7. Crystal data of **1a**: $C_{48}H_{30}S_2$, M 670.88, monoclinic $P2_1/n$ (No. 14), $a = 16.501(3)$, $b = 16.501(3)$, $c = 19.530(3)$ Å, $\beta = 103.2656(7)°$, $V = 3420.0(8)$ Å^3, D_c $(Z = 4) = 1.303$ g cm^{-3}, $T = 153$ K, $\mu = 1.91$ cm^{-1}. The final R value is 0.041 for 7730 independent reflections 451 parameters. CCDC 663450. Crystal data of $\mathbf{2a}^{2+}(SbCl_6^-)_2$: $C_{48}H_{30}S_2Sb_2Cl_{12}$, M 1339.82, monoclinic $P2_1/n$ (No. 14), $a = 16.414(8)$, $b = 10.190(5)$, $c = 34.07(2)$ Å, $\beta = 96.454(3)°$, $V = 5662.6(4)$ Å^3, D_c $(Z = 4) = 1.571$ g cm^{-3}, $T = 153$ K, $\mu = 16.23$ cm^{-1}. The final R value is 0.120 for 11632 independent reflections 577 parameters. CCDC 663451. Crystal data of **3a**: $C_{48}H_{30}OS_2$, M 696.88, triclinic $P\bar{1}$ (No. 2), $a = 11.417(3)$, $b = 12.139(3)$, $c = 14.960(3)$ Å, $\alpha = 93.280(3)$, $\beta = 91.700(3)$, $\gamma = 91.700(3)°$, $V = 1918.6(8)$ Å^3, D_c $(Z = 2) = 1.189$ g cm^{-3}, $T = 153$ K, $\mu = 1.74$ cm^{-1}. The final R value is 0.037 for 8410 independent reflections 514 parameters. CCDC 663452.
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12. This value was determined by using 9,10-diphenylanthracene as a standard ($\Phi_F = 0.95$ in MeCN), and that for the oxygen analogue **3b** was determined to be 0.97 under the similar conditions.
13. The amounts of acid required to complete quench of emission are different: 150 equiv for **3a**, and 60 equiv for **3b**, respectively. Such difference is accounted for by considering the thermodynamic stability of the cationic part, as suggested by the pK_{R+} values of 0.1 for 9-phenylthioxanthenylium and 1.1 for 9-phenylxanthenylium, respectively (Ref. 14).
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