

Selective Hg²⁺ sensing behaviors of rhodamine derivatives with extended conjugation based on two successive ring-opening processes

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Supporting Information

X-Ray Diffraction Measurement

Single crystals of *cis*-**1** and *trans*-**1**, *cis*-**2** and *trans*-**2** suitable for X-ray crystallographic studies were obtained by the slow diffusion of diethyl ether vapor into a concentrated dichloromethane solution of the corresponding compounds. The X-ray diffraction data were collected on a Bruker Smart CCD 1000 using graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å). Raw frame data were integrated using the SAINT program.^{S1} Semiempirical absorption corrections with SADABS^{S2} were applied. The structures were solved by direct methods employing the SHELXS-97 program^{S3} and refined by full-matrix least-squares on F^2 using the SHELXL-97 program.^{S3} All non-H atoms were refined anisotropically. The positions of H atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms and participated in the calculation of final *R*-indices. CCDC-831119 (*cis*-**1**), CCDC-925954 (*trans*-**1**), CCDC-831120 (*cis*-**2**), and CCDC-831122 (*trans*-**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1 Crystal and structure determination data of *cis-1* and *trans-1*, *cis-2* and *trans-2*

Complex	<i>cis-1</i> •CH ₂ Cl ₂	<i>trans-1</i>	<i>cis-2</i> •Et ₂ O	<i>trans-2</i>
empirical formula	C ₄₂ H ₃₆ N ₂ O ₆ •CH ₂ Cl ₂	C ₄₂ H ₃₆ N ₂ O ₆	C ₄₂ H ₄₀ N ₆ O ₄ •C ₄ H ₁₀ O	C ₄₂ H ₄₀ N ₆ O ₄
formula weight	749.65	664.73	766.92	692.80
temperature, K	298(1)	305(1)	298(1)	297(1)
wavelength, Å	0.71073	0.71073	0.71073	0.71073
crystal system	Monoclinic	Orthorhombic	Triclinic	Monoclinic
space group	P2 ₁ /c (#14)	Pbcn (#60)	P $\bar{1}$ (#2)	P2 ₁ /n (#14)
<i>a</i> , Å	16.048 (3)	14.8537 (10)	8.9410 (8)	20.534 (4)
<i>b</i> , Å	16.026 (3)	19.5680 (13)	14.7110 (13)	11.363 (2)
<i>c</i> , Å	17.851 (3)	12.1682 (8)	17.4371 (16)	21.140 (5)
α , deg	90	90	73.616 (1)	90
β , deg	123.639 (3)	90	89.426 (1)	97.541 (4)
γ , deg	90	90	78.606 (1)	90
volume	3822.4 (12)	3536.8 (4)	2154.5 (3)	4889.6 (18)
<i>Z</i> , Å ³	4	4	2	4
density (calculated), gcm ⁻³	1.303	1.248	1.182	0.941
crystal size, mm×mm×mm	0.28×0.09×0.07	0.27×0.21×0.10	0.27×0.09×0.02	0.48×0.19×0.07
index ranges	$-19 \leq h \leq 19$ $-15 \leq k \leq 19$ $-21 \leq l \leq 21$	$-19 \leq h \leq 9$ $-26 \leq k \leq 25$ $-16 \leq l \leq 15$	$-10 \leq h \leq 10$ $-17 \leq k \leq 17$ $-20 \leq l \leq 19$	$-24 \leq h \leq 24$ $0 \leq k \leq 13$ $0 \leq l \leq 25$
reflections collected/unique	27900/6740	18534/4381	15972/7496	35247/8584
goodness-of-fit on F^2	1.05	1.02	1.03	0.84
final <i>R</i> indices ^a	<i>R</i> = 0.095	<i>R</i> ₁ = 0.060	<i>R</i> ₁ = 0.071	<i>R</i> ₁ = 0.085
[<i>I</i> > 2σ(<i>I</i>)]	w <i>R</i> = 0.334	w <i>R</i> = 0.176	w <i>R</i> = 0.247	w <i>R</i> = 0.247
largest diff peak and hole, e Å ⁻³	0.60 and -0.75	0.42 and -0.30	0.42 and -0.25	0.25 and -0.28

Table S2 Selected singlet excited states of *cis*-1-p, *cis*-1-f, **4** and Rhodamine 6G_oxadiazole computed by TD-DFT at B3LYP/6-31G(d) at the optimized ground state geometries

Compound	Electron transition	Main transition configuration (CI coeff)	Excitation energy	Calculated wavelength (nm)	Oscillator strength <i>f</i>
<i>cis</i> -1-p (partial ring- opened form)	S ₀ -S ₁	HOMO→LUMO (1.00)	1.79	693.26	0.0133
	S ₀ -S ₂	HOMO-1→LUMO (0.97)	2.63	471.03	1.0346
	S ₀ -S ₃	HOMO-2→LUMO (0.90)	2.93	423.72	0.0045
	S ₀ -S ₄	HOMO-3→LUMO (0.85)	3.33	372.01	0.1028
	S ₀ -S ₅	HOMO→LUMO+2 (0.53) HOMO→LUMO+1 (0.46)	3.38	366.90	0.0022
<i>cis</i> -1-f (full ring- Opened form)	S ₀ -S ₁	HOMO→LUMO (0.98)	2.32	534.63	1.3279
	S ₀ -S ₂	HOMO→LUMO+1 (0.64) HOMO-1→LUMO (0.32)	2.74	452.01	0.0205
	S ₀ -S ₃	HOMO-2→LUMO (0.94)	2.82	440.23	0.0192
	S ₀ -S ₄	HOMO-1→LUMO (0.55) HOMO→LUMO+1 (0.32)	2.94	421.84	0.2522
	S ₀ -S ₅	HOMO-3→LUMO (0.90)	3.05	405.85	0.0122
4	S ₀ -S ₁	HOMO→LUMO (0.98)	1.52	814.42	0.0010
	S ₀ -S ₂	HOMO-1→LUMO (0.99)	1.73	717.50	0.0002
	S ₀ -S ₃	HOMO→LUMO+1 (0.98)	2.11	586.42	0.0010
	S ₀ -S ₄	HOMO-2→LUMO (0.66) HOMO-1→LUMO+1 (0.32)	2.30	538.07	0.8495
	S ₀ -S ₅	HOMO-2→LUMO (0.31) HOMO-1→LUMO+1 (0.67)	2.31	536.99	0.4180
Rhodamine 6G_oxadiazole	S ₀ -S ₁	HOMO→LUMO (0.94)	2.63	470.69	0.7001
	S ₀ -S ₂	HOMO→LUMO+1 (0.97)	2.99	415.13	0.0667
	S ₀ -S ₃	HOMO-1→LUMO (0.98)	3.12	396.91	0.0068
	S ₀ -S ₄	HOMO-3→LUMO (0.96)	3.23	383.86	0.0010
	S ₀ -S ₅	HOMO-2→LUMO (0.91)	3.39	365.27	0.1671

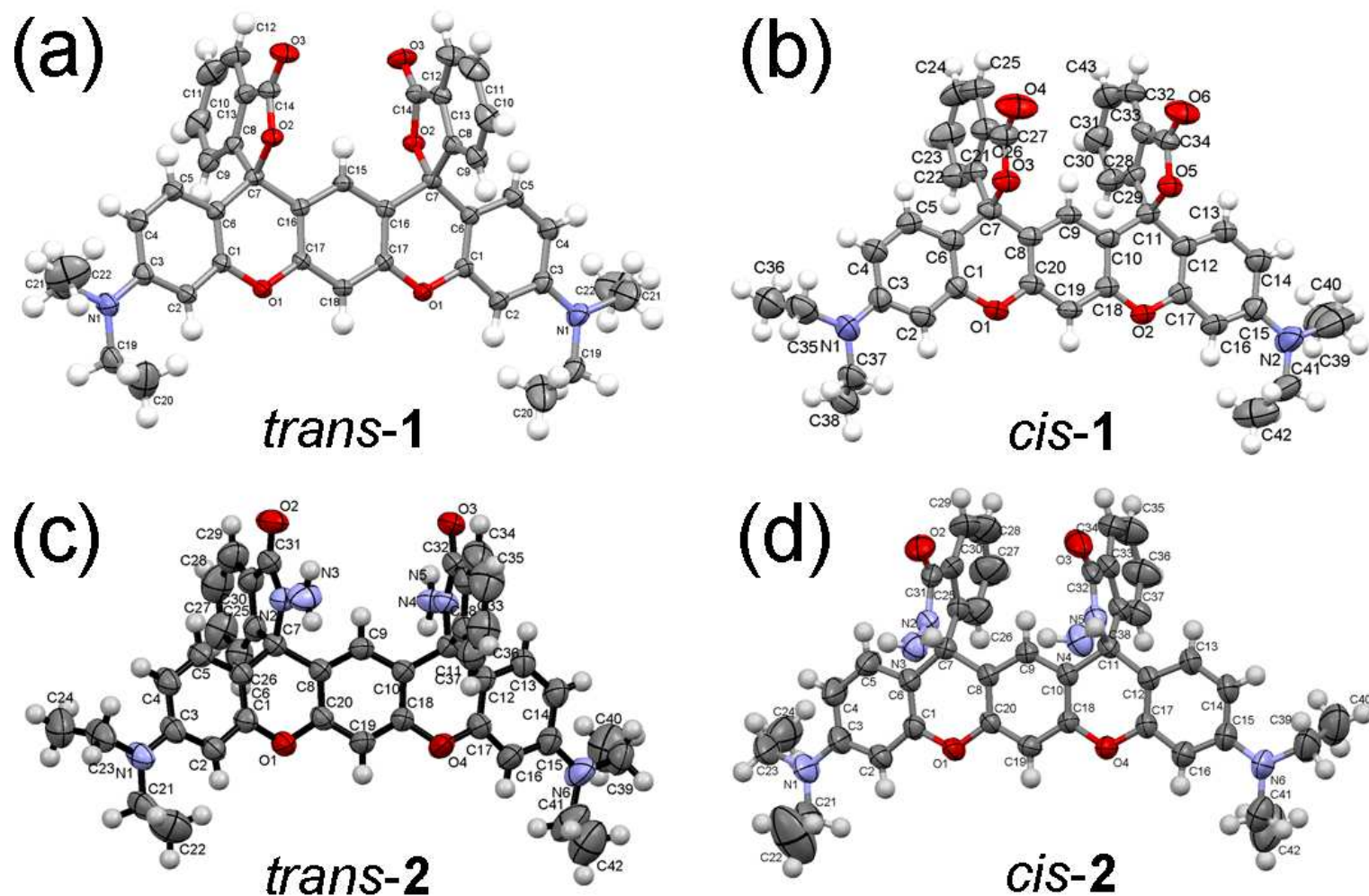


Figure S1 Perspective views of (a) *trans-1*, (b) *cis-1*, (c) *trans-2* and (d) *cis-2* were shown at 50% (30% for *trans-1*) probability thermal ellipsoids with the atom numbering scheme. Solvent molecules were omitted for the clarity.

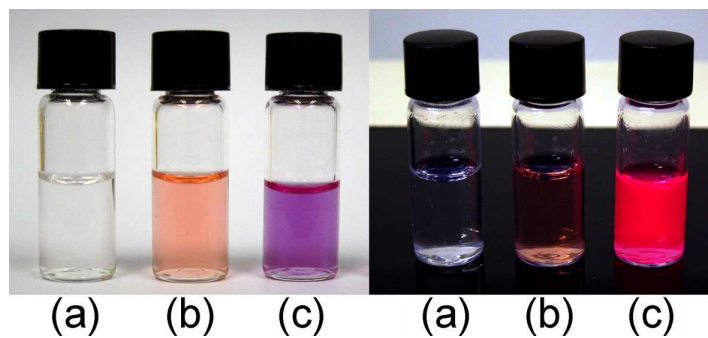


Figure S2 Photographs of *trans*-**1** in MeOH showing the color changes (left) and emission enhancement (right) in the absence of Hg(II) ion (a), and in the presence of small amount of Hg(II) ion (b) and excess amount of Hg(II) ion (c).

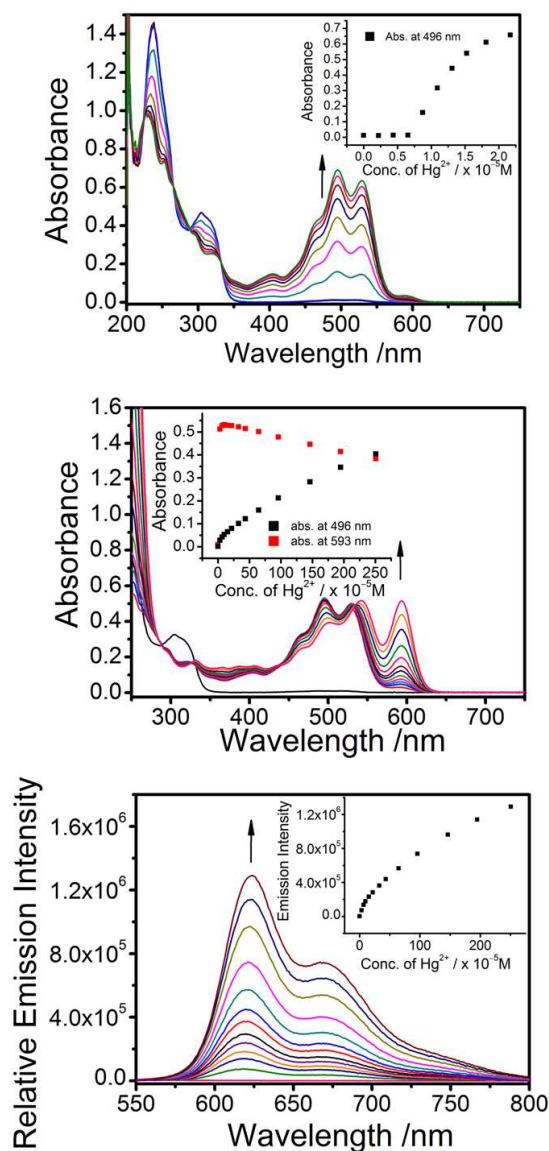


Figure S3 Electronic absorption spectral changes of *trans*-**1** (conc. = 1.79×10^{-5} M) in MeOH in the presence of low concentrations of Hg(II) ion (top); electronic absorption (middle) and emission (bottom) spectral changes of *trans*-**1** (conc. = 1.25×10^{-5} M) in the presence of high concentrations of Hg(II) ion. Insets show the plot of absorbance or emission intensity as a function of the concentration of Hg(II) ion.

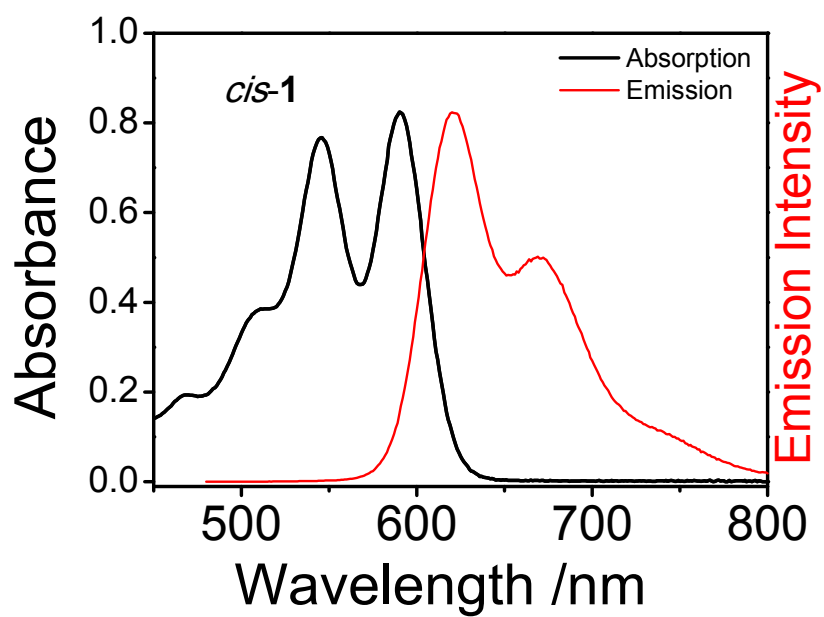


Figure S4 Electronic absorption and emission spectra of *cis-1* upon addition of excess Hg(II) ion in MeOH.

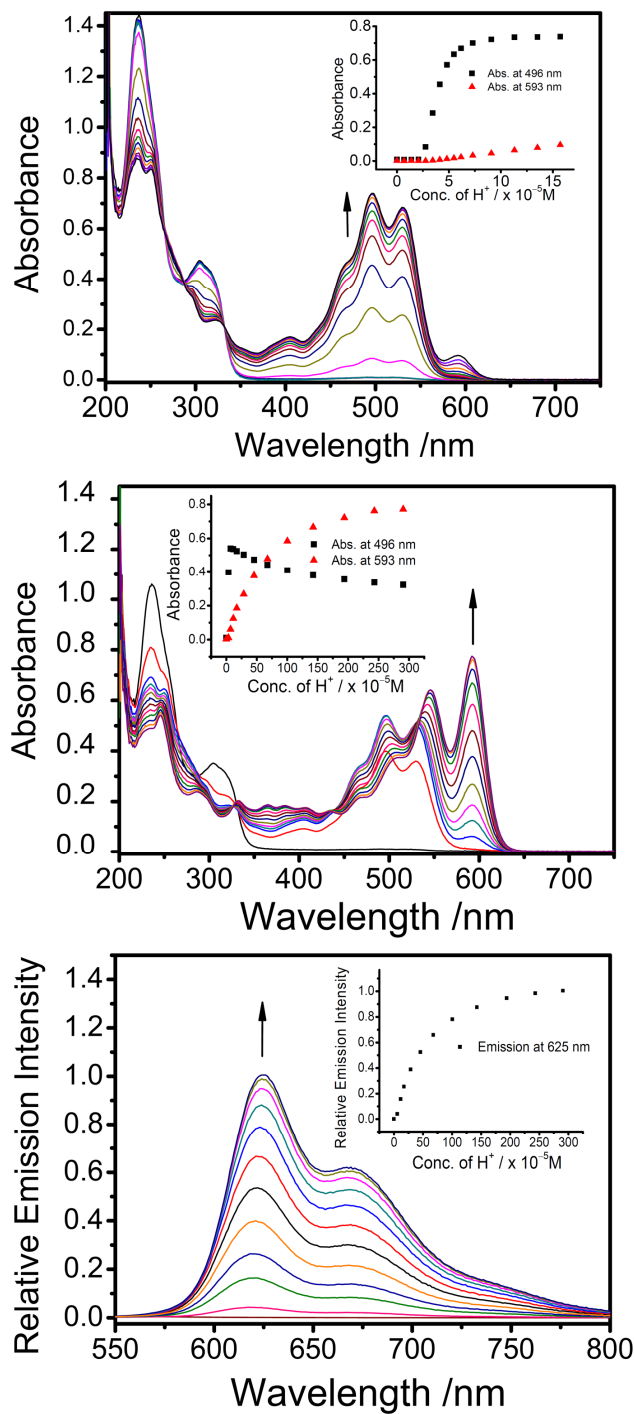


Figure S5 Electronic absorption spectral changes of *cis*-1 (conc. = 1.7×10^{-5} M) in MeOH in the presence of low concentrations of acid (top, left); electronic absorption (middle, left) and emission (bottom, left) spectral changes of *cis*-1 (conc. = 1.19×10^{-5} M) in the presence of high concentrations of acid. The right column shows the plot of absorbance or emission intensity as a function of the concentration of acid.

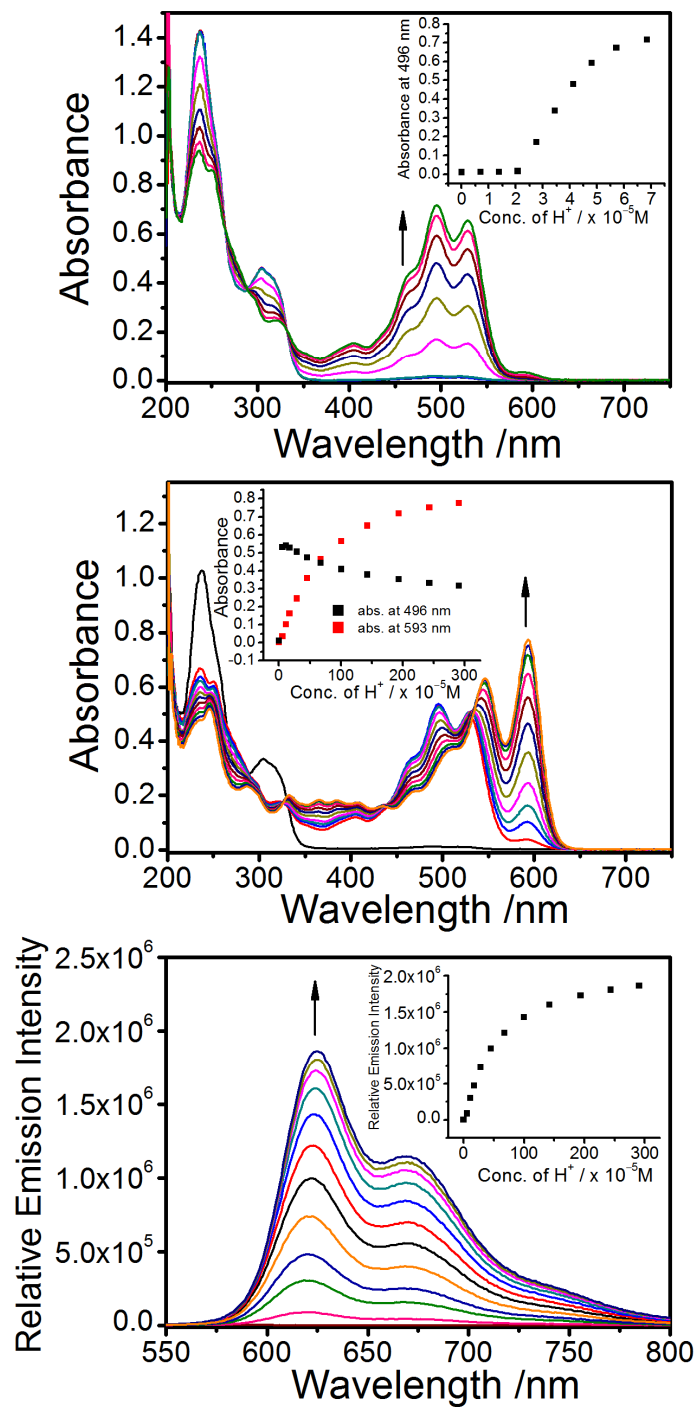


Figure S6 Electronic absorption spectral changes of *trans*-**1** (conc. = 1.79×10^{-5} M) in MeOH in the presence of low concentrations of acid (top); electronic absorption (middle) and emission (bottom) spectral changes of *trans*-**1** (conc. = 1.25×10^{-5} M) in the presence of high concentrations of acid. Insets show the plot of absorbance or emission intensity as a function of the concentration of acid.



Figure S7 Photographs showing the color changes of **3** in acetonitrile-buffer (1:1, v/v) solution upon addition of various ions. From left to right: Hg^{2+} , Cu^{2+} , Pb^{2+} , Ag^+ , Cd^{2+} , Mg^{2+} , Li^+ , F^- , I^- , blank. (buffer = HEPES buffer solution (pH = 7.0, 10 mmol) in water)

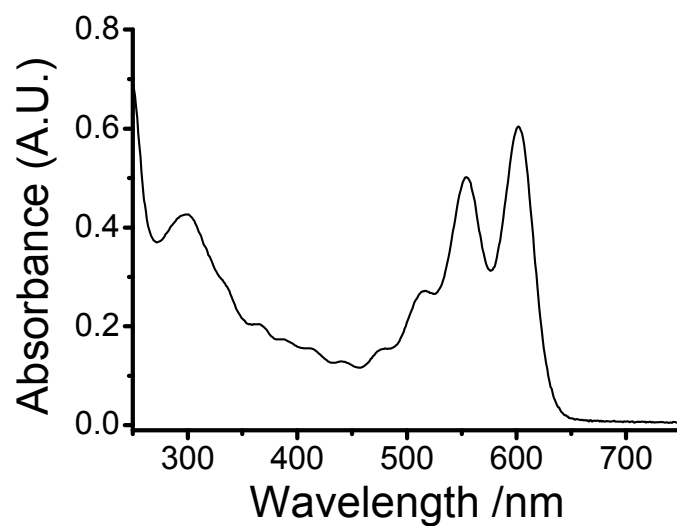


Figure S8 Electronic absorption spectrum of compound **4** in acetonitrile-buffer (1:1, v/v) solution.
(buffer = HEPES buffer solution (pH = 7.0, 10 mmol) in water)

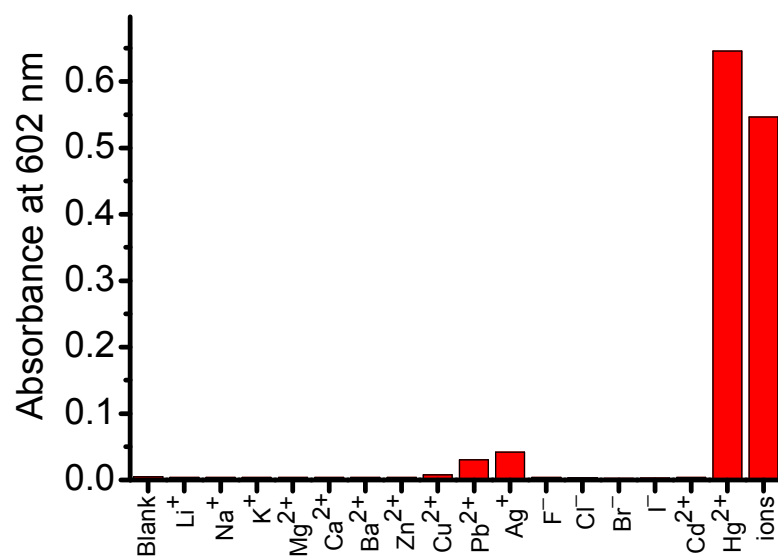


Figure S9 Measurement of selectivity of **3** (conc. = 12×10^{-6} M, 2 equivalents of Hg^{2+} or 10 equivalents of other ions) and interference of **3** (column ions, conc. = 12×10^{-6} M, 2 equivalent of Hg^{2+} and all 10 equivalents of other ions in acetonitrile-buffer (1:1, v/v) solution. (buffer = HEPES buffer solution (pH = 7.0, 10 mmol) in water)

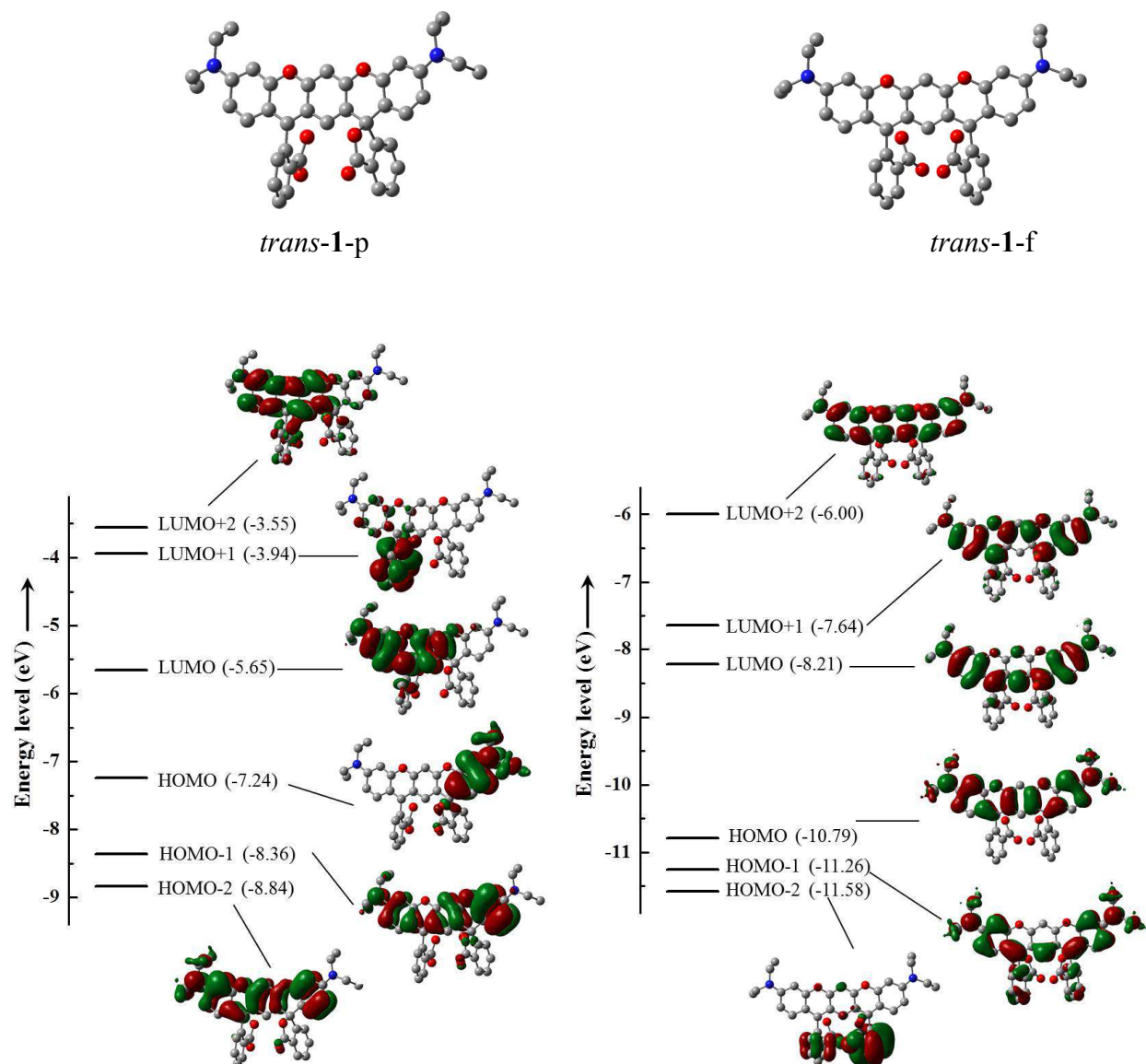


Figure S10 The optimized ground state geometries, frontier molecular orbital energies and electron density distributions of *trans*-1-p (left) and *trans*-1-f (right).

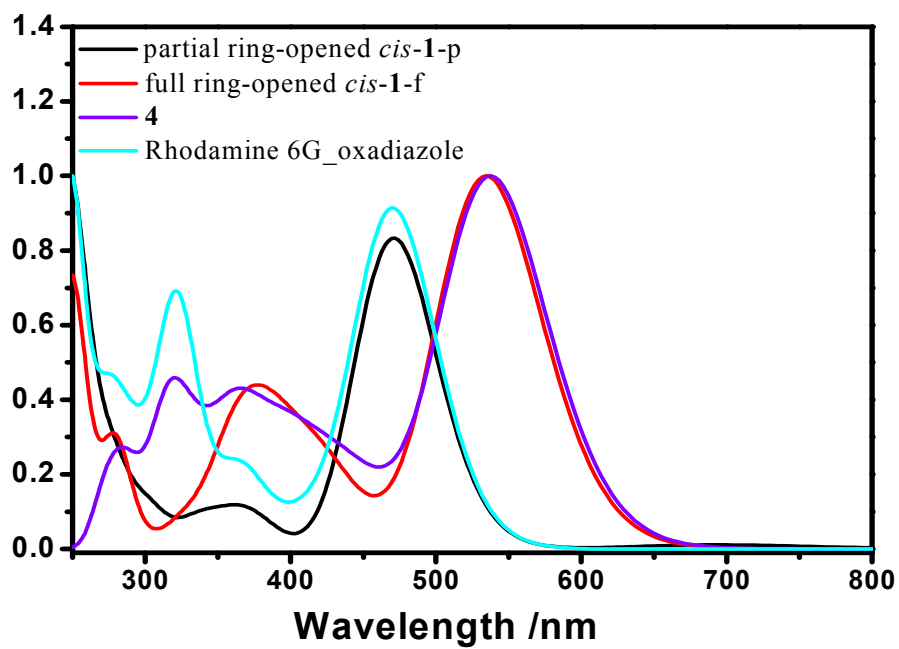


Figure S11 The simulated absorption spectra of the partial (left) or full (right) ring-opened *cis*-1 (The carboxylic acid form was adopted in order to simplify the calculation) in methanol, **4** and rhodamine 6G_oxadiazole in acetonitrile.

Reference

- S1 Bruker AXS Inc. (2006). *SAINT*, version 7.34A, Madison, Wisconsin, USA.
- S2 Sheldrick, G. M. (2004). *SADABS*, Göttingen University, Göttingen, Germany.
- S3 Sheldrick, G. M. (2008). *SHELX* programs: *SHELXL97*, *SHELXS97*. *Acta Cryst.* **E68**, 112-122.