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Spiropyran as a reusable chemosensor for selective colorimetric detection of aromatic thiols†

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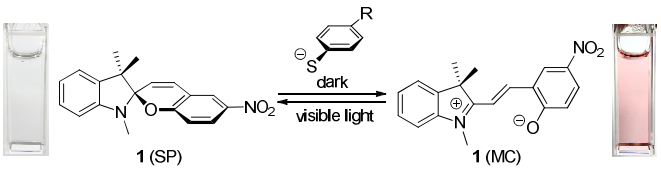
Design of optical molecular probes for selective detection of aromatic thiols has attracted much attention. Although several types of probes have been proposed, all of them exhibit colorimetric or fluorometric response via irreversible reaction with aromatic thiols and cannot be reused. Here we report that a spiropyran dye is a first example of reusable chemosensor for aromatic thiols. A colorless spiropyran dye (**1**) dissolved in aqueous media containing aromatic thiols is selectively isomerized to the colored merocyanine form in the dark condition. In contrast, visible light irradiation of the merocyanine form promotes successful reversion to the colorless spirocyclic form. Kinetic absorption analysis and *ab initio* calculations of the transition states revealed that this colorimetric response in the dark condition is ascribed to the decrease in activation energy for isomerization via the nucleophilic interaction between aromatic thiol and olefinic carbon of the dye.

Introduction

Thiols are a very important class of molecules in biological systems. Aliphatic thiols are a part of several biological molecules such as cysteine, homocysteine, and glutathione, which are associated with a variety of biologically important functions.[1–3] In contrast, aromatic thiols, while they are versatile intermediates for organic synthesis, are very toxic to the human body. Exposure to them induces serious damages to the central nervous system and other related pathologies including increased respiration, muscular weakness, paralysis, and coma.[4–7] The design of optical molecular probes, which facilitate selective detection of aromatic thiols by simple spectroanalysis in the environmental and biological samples, is therefore currently the focus of attention.

A number of optical molecular probes for thiols have been proposed so far; however, there are only a few reports of probes that can discriminate aromatic thiols over aliphatic ones.[8–13] All of the probes are based on nucleophilic reaction of sulfonamide, sulfonate, or ether group with a thiolate anion of aromatic thiols, resulting in colorimetric or fluorometric response. All of these reactions, however, occur irreversibly; these probes cannot be reused. Creation of molecular probes that facilitate selective detection of aromatic thiols based on a reversible interaction is therefore necessary.

Spiropyran dyes belong to a class of organic photochromes, which undergo ring opening/closing isomerization between the colorless spirocyclic (SP) form and the colored merocyanine (MC) form upon UV/visible light irradiation.[14–16] In the dark condition, SP→MC isomerization does not occur in common organic solvents because the ground state energy of the MC form is higher than that of the SP form. In contrast, hydrogen-bonding solvents such as water and alcohols promote spontaneous SP→MC isomerization because stabilization of the MC form by a hydrogen-bonding interaction lowers the ground state energy of the MC form,[17–19] although the isomerization is very slow.



Scheme 1 SP→MC isomerization of a spiropyran dye (**1**) promoted by aromatic thiols in aqueous media in the dark condition.

Here we report that a spiropyran dye is a first example of reusable chemosensor for aromatic thiols. As shown in Scheme 1, aromatic thiols, when added to an aqueous solution with a neutral pH containing a simple spiropyran dye (**1**), selectively enhance SP→MC isomerization, thus facilitating selective colorimetric detection of aromatic thiols. Kinetic absorption analysis and *ab initio* calculation revealed that the SP→MC isomerization enhanced by aromatic thiols is due to the decrease in activation energy for isomerization, via the

nucleophilic interaction between aromatic thiol and olefinic carbon of the spiropyran molecule.

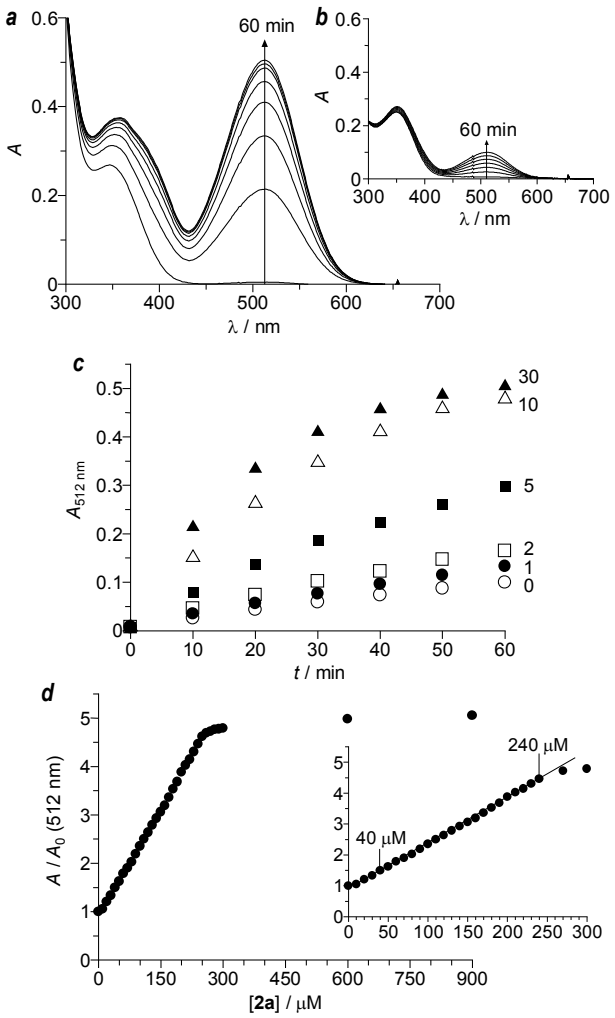


Fig. 1 Time-dependent change in the absorption spectra of **1** (30 μM) measured in the (a) presence and (b) absence of 30 equiv of benzenethiol (**2a**) in a buffered water/MeCN mixture (7/3 v/v; HEPES 0.1 M, pH 7.0) in the dark at 25 °C. (c) Change in absorbance at 512 nm monitored after addition of different amount of **2a** relative to that of **1** (equiv). (d) Change in the ratio of absorbance (A/A_0) at 512 nm with the concentration of **2a**, where A_0 is the absorbance in the absence of **2a**. All of the data were obtained after stirring each respective solution for 60 min in the presence of required amount of **2a**.

Results and Discussion

Fig. 1b shows the time-dependent change in absorption spectra of **1**[20] (30 μM), when stirred in a water/MeCN (7/3 v/v) mixture (HEPES 0.1 M, pH 7.0) at 25℃ in the dark condition. At time zero, almost no absorption appears at λ >450 nm, indicating that **1** exists as a SP form. As time advances, a distinctive band assigned to the MC form appears at 512 nm, although its increase is very slow. In contrast, as shown in Fig. 1a, 30 equiv of benzenethiol (**2a**), when added to the solution containing **1**, significantly enhances the SP → MC isomerization. As shown in Fig. 2, substituted benzenethiols (**2b**–**d**) also accelerate the isomerization, whereas other nucleophiles such as aliphatic thiols (**3a**–**d**), aniline, phenol, I^-, CN^-, AcO^-, NO_3^-, and $H_2PO_4^-$ do not. In addition, as shown in Fig. S1 (ESI†), the SP → MC isomerization of **1** enhanced by aromatic thiol is unaffected by other nucleophiles. These data clearly suggest that **1** allows selective colorimetric detection of aromatic thiols in aqueous media.

After stirring the solution containing **1** and **2a**, the solution was acidified (pH 3) and extracted with $CHCl_3$. GC analysis of the extract revealed that all of **2a** added remained unchanged. In addition, as shown in Fig. S2 (ESI†), the solution after stirring with **1** and **2a**, when irradiated with monochromatic light at 550 nm, leads to successful reversion to the SP form. Furthermore, repeated stirring under the dark and 550 nm light irradiation conditions shows reversible formation of the MC and SP forms. These data suggest that **1** reversibly interacts with aromatic thiol and undergoes rapid SP→MC isomerization. Fig. 1c shows the effect of the amount of **2a** added on the rate of isomerization of **1**. The isomerization rate increases with an increase in the amount of **2a**. These data suggest that aromatic thiols *catalytically* accelerate the SP→MC isomerization of **1**. Fig. 1d shows the change in the ratio of absorbance (A/A_0) of **1** at 512 nm with the concentration of **2a**, where A_0 is the absorbance in the absence of **2a** and the data were obtained after stirring each respective solution for 60 min. A strictly linear relationship is observed at <240 μM **2a**. The **2a** concentration at A/A_0 > 1.5 is 40 μM. This indicates that the present colorimetric system allows quantitative detection of **2a** in the range of 40–240 μM, although the system requires relatively long time for sensing (1 h).

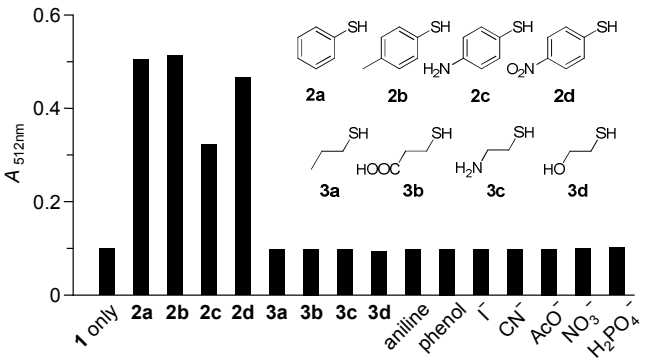


Fig. 2 Absorbance at 512 nm of a buffered water/MeCN mixture (7/3 v/v; HEPES 0.1 M, pH 7.0) containing **1** (30 μM), measured after stirring with respective nucleophiles (30 equiv) for 60 min at 25 °C in the dark.

Aromatic thiols do not affect the equilibrium of the SP and MC forms. This is confirmed by the standard enthalpy ($\Delta_r H$) and entropy ($\Delta_r S$) for SP→MC isomerization of **1**, determined by the equilibrium absorption analysis with different amount of **2a** at different temperatures (Fig. S3, ESI†).[17] Table 1 summarizes the data obtained at 25 °C. The equilibrium constants (K_{eq}) for the SP and MC forms are ca. 3 regardless of the absence and presence of **2a**. In addition, van′t Hoff plots of the equilibrium data (Fig. S4, ESI†) revealed that the $\Delta_r H$

Table 1. Equilibrium and kinetic parameters for SP → MC isomerization of **1** in a water/MeCN mixture (7/3 v/v; HEPES 0.1 M, pH 7.0), determined in the dark at 25 °C with different amount of **2a**[a]

2a / equiv[b]	K_{eq}	$\Delta_r H$ / kJ mol^{-1}	$\Delta_r S$ / J K^{-1} mol^{-1}	$k_{SP\rightarrow MC}$ / 10^{-4} s^{-1}	$\Delta H^{\neq}$ / kJ mol^{-1}	$\Delta S^{\neq}$ / J K^{-1} mol^{-1}
0	2.95	−6.61 ± 0.34	−13.2 ± 1.0	0.52	107.7 ± 2.9	32.5 ± 9.1
1	3.12	−6.61 ± 0.79	−12.8 ± 2.6	0.62	87.0 ± 3.6	−33.6 ± 12.1
2	3.09	−6.74 ± 0.54	−13.2 ± 1.8	0.72	74.8 ± 1.3	−73.3 ± 4.6
10	3.07	−6.73 ± 0.30	−13.2 ± 1.0	3.92	45.6 ± 3.5	−157.0 ± 11.9
30	3.05	−6.68 ± 0.40	−13.1 ± 1.3	7.38	44.0 ± 4.7	−157.6 ± 15.7

[a] The detailed procedures for equilibrium and kinetic absorption analysis are described in Supporting Information. The data obtained at different temperatures are summarized in Table S1 (ESI†). [b] The amount of **2a** added relative to that of **1**.

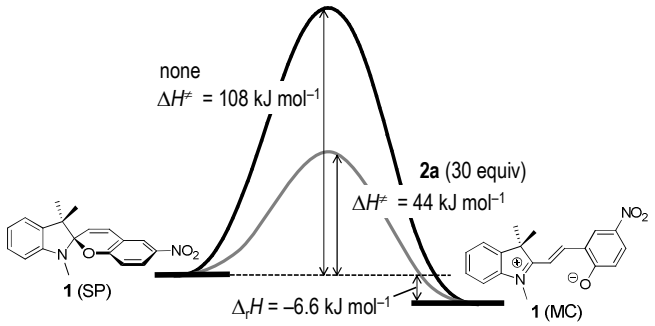


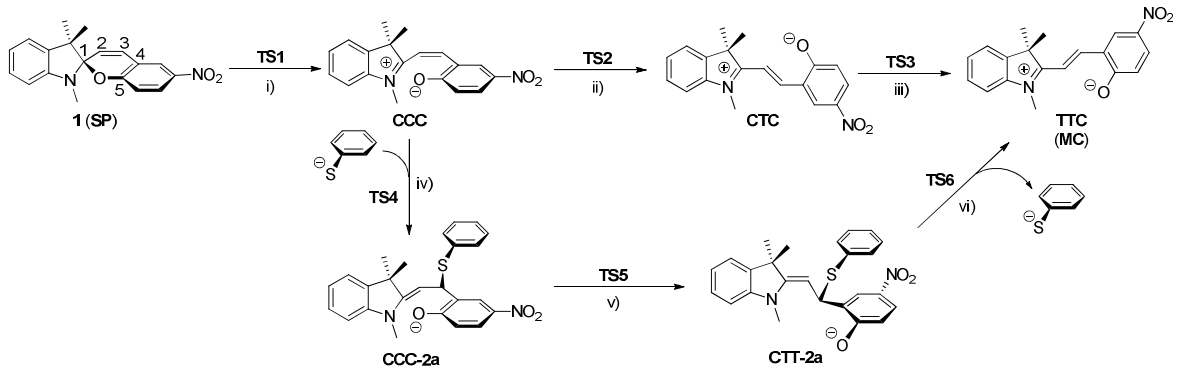
Fig. 3 Standard enthalpy ($\Delta_r H$) and activation enthalpy ($\Delta H^{\neq}$) for SP→MC isomerization of **1** in the absence and presence of 30 equiv of **2a**.

values for all of the systems are similar (ca. −6.6 kJ mol^{-1}). These data suggest that, as shown in Fig. 3, the ground state energy of the MC form scarcely changes even in the presence of **2a**. Furthermore, the $\Delta_r S$ values for all of the systems show similar negative values (ca. −13 J K^{-1} mol^{-1}) due to the rearrangement of the solvent molecules associated with the SP→MC isomerization.[21] These findings clearly suggest that aromatic thiols do not affect the equilibrium of the SP and MC forms.

The SP→MC isomerization of **1** accelerated by aromatic thiols is due to the decrease in activation energy. This is confirmed by the kinetic absorption analysis[18] for SP→MC isomerization of **1**, performed with different amount of **2a** at different temperatures (Fig. S5, ESI†). As shown in Table 1, the rate of SP→MC isomerization ($k_{SP\rightarrow MC}$) increases with an increase in the amount of **2a** added. The activation enthalpy ($\Delta H^{\neq}$) determined by the Arrhenius plot decreases with an increase in the amount of **2a** (Fig. S6, ESI†). This indicates that, as shown in Fig. 3, the interaction between **1** and **2a** indeed decreases the activation energy for isomerization of **1**, resulting in rapid SP→MC isomerization (Fig. 1).

As shown in Scheme 2, thermal SP→MC isomerization of a spiropyran dye involves three step reactions via the **CCC** and **CTC** intermediates,[22,23] where **C** and **T** denote *cis* and *trans* forms, respectively, for the dihedral angles of N–C_1–C_2–C_3, C_1–C_2–C_3–C_4, and C_2–C_3–C_4–C_5 moieties (Table S2, ESI†). The isomerization of **1** proceeds as follows: (i) the spiro C_1–O bond cleavage of the SP form produces **CCC** intermediate via the **TS1** transition state; (ii) *cis*→*trans* isomerization around the C_2=C_3 bond of the intermediate produces **CTC** intermediate via the **TS2** transition state; and, (iii) *cis*→*trans* isomerization around the C_1–C_2 bond of **CTC** results in a formation of MC form with a **TTC** structure via the **TS3** transition state. During the isomerization process, the reaction (ii) is the rate-determining step.[22,23] This is confirmed by *ab initio* calculation based on the density functional theory (DFT) within the Gaussian 09 program. Geometry optimizations of the SP form of **1**, intermediates, and the MC form of **1** were performed using the B3LYP function with 6-31G* basis set, where the polarizable continuum model (PCM) was employed with water as a solvent.[24] The transition states were optimized with QST2 and QST3 methods, where the nature of stationary points was checked by means of frequency calculations, and the transition states were verified by the intrinsic reaction coordinate (IRC) calculations.[25] Fig. 4 (black) summarizes the optimized structures of intermediates and transition states on the ground state potential surface, along with the relative energies with respect to the SP form of **1**. Comparison of the transition energies for **TS1**, **TS2**, and **TS3** clearly revealed that **TS2** (step ii) exhibits the highest transition energy (99.8 kJ mol^{-1}) and is indeed the rate-determining step for SP→MC isomerization of **1**. This suggests that, as reported,[22,23] a high rotational barrier around the C_2=C_3 bond results in very high transition energy. As a result of this, the compound **1** undergoes very slow SP→MC isomerization (Fig. 1).

Aromatic thiols exist as thiolate anions at a neutral pH.[26] They have a strong nucleophilic character[27] and, hence, undergo nucleophilic addition to the electron-deficient carbon atom for several types of molecules such as α,β-unsaturated ketones,[13,28] fullerenes,[29] and imines.[30] In the present case, as shown in Scheme 2, the thiolate anion undergoes nucleophilic addition to the electron-deficient C_3 atom of the ring-opened **CCC** intermediate of **1**. This transfers the double bond and increases the rotational mobility, resulting in a decrease in activation energy for isomerization. The isomerization process of **1** enhanced by aromatic thiolate (**2a**) involves following reactions (Scheme 2): Firstly, (iv) nucleophilic addition of **2a** to the C_3 atom of the **CCC** intermediate produces **CCC-2a** intermediate via the **TS4** transition state. According to this reaction, the C_1–C_2=C_3 bond becomes C_1=C_2–C_3. Secondly, (v) *cis*→*trans* isomerization around the single C_2–C_3 and C_3–C_4 bonds produces **CTT-2a** intermediate via the **TS5** transition



Scheme 2 Proposed mechanism for SP→MC isomerization of **1** in the absence and presence of **2a**.

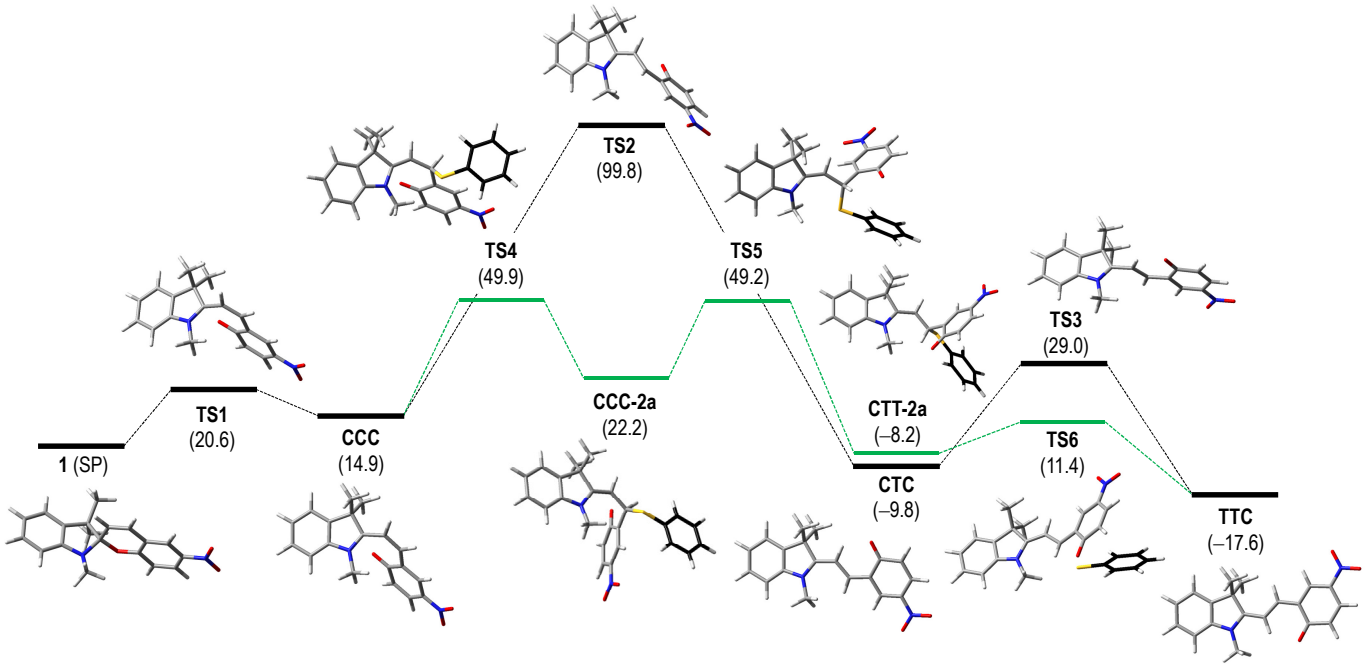


Fig. 4 Potential energy surfaces for thermal SP → MC isomerization of **1** determined by DFT calculation in the (black) absence and (green) presence of **2a**. The numbers in parenthesis are the relative energies (kJ mol^{-1}) with respect to that of the SP form of **1**. Optimizations of the transition states were carried out with QST3 (**TS1**, **2**, **4**, **5**, **6**) and QST2 (**TS3**) methods, respectively. The gray, blue, red, and yellow parts denote C, N, O, and S atoms, respectively. The benzene ring of the **2a** molecule is represented in black color for clarity. Cartesian coordinates for respective states are summarized in the end of ESI†.

state. Finally, (vi) elimination of the **2a** moiety followed by *cis*→*trans* rotation of the resulting single C_1–C_2 and C_3–C_4 bond produces the MC form with a **TTC** structure via the **TS6** transition state.

The above mechanism is confirmed by DFT calculations. Fig. 4 (green) shows the potential energy surface for the SP→MC isomerization of **1** calculated in the presence of **2a**. The transition energies for **TS4**, **TS5**, and **TS6** were determined to be 49.9, 49.2, and 11.4 kJ mol^{-1}, respectively, all of which are less than half that of **TS2** obtained without aromatic thiol (99.8 kJ mol^{-1}). These results are fully consistent with the $\Delta H^{\neq}$ values determined by the kinetic analysis in the absence and presence of **2a** (Fig. 3). These data suggest that nucleophilic addition of aromatic thiolate increases the rotational freedom around the C_1–C_2–C_3–C_4 bonds of spiropyran and significantly decreases the activation energy for *cis*→*trans* isomerization. This thus results in enhanced SP→MC isomerization.

The above mechanism (iv–vi) involving the formation of transient complexes (**TS4**, **TS5**, and **TS6**) is further confirmed by the activation entropy ($\Delta S^{\neq}$), determined by the kinetic analysis of **1** with different amount of **2a**. As shown in Table 1, the absence of **2a** shows a positive $\Delta S^{\neq}$ value due to the conformational change by *cis*→*trans* rotation.[31] In contrast, addition of **2a** significantly decreases the $\Delta S^{\neq}$ value because the formation of transient complexes decreases the number of molecules and leads to an ordering of the systems.[32] In addition, as shown in Fig. 5, the plots of $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values obtained with different amount of **2a** exhibit a strictly linear relationship, indicating that both $\Delta H^{\neq}$ and $\Delta S^{\neq}$ parameters are affected by a single factor.[33,34] These findings indicate that activation process

is solely affected by the formation of transient complexes between spiropyran and aromatic thiolate.

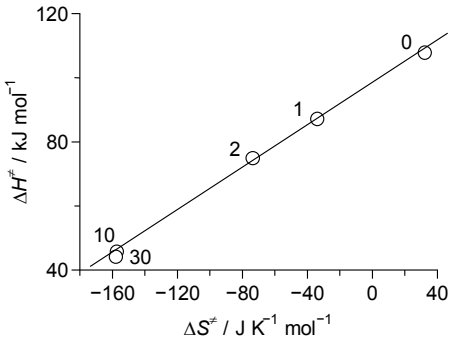


Fig. 5 Relationship between $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the SP → MC isomerization of **1** obtained in the absence and presence of **2a**. The numbers in the figure denote the amount of **2a** added relative to that of **1** (equiv).

In the present system, some factors are important for sensing. As shown in Fig. 2, the SP→MC isomerization of **1** in the presence of amino-substituted benzenethiol (**2c**) is much slower than that of other aromatic thiols, suggesting that the detection of **2c** is difficult by the present sensing system. As reported,[35] the nucleophilic interaction between aromatic thiol and electron-deficient olefin is weakened by the substitution of electron-donating groups onto aromatic thiol. The substitution of electron-donating amino group probably weakens the nucleophilic interaction between the sulfur atom and the olefinic carbon of **1** (Scheme 2, **CCC-2a**) resulting in decreased catalytic effect for isomerization.

Another important factor is the water content of solvent, which strongly affects the colorimetric response of **1** to aromatic thiols. As reported,[17] the standard enthalpy ($\Delta_r H$) for SP→MC isomerization of spiropyran derivatives becomes more negative with an increase in water content (Fig. 3), because water molecules stabilize the MC form via the hydrogen bonding interaction. This means that the decrease in water content shifts the equilibrium to the formation of SP form. Fig. S7 (ESI†) shows the effect of water content on the colorimetric response of **1** to benzenethiol (**2a**). The decreased water content indeed suppresses the SP→MC isomerization. The results clearly indicate that high water content solvent (Fig. 1, 70%) is necessary for colorimetric detection of aromatic thiols.

Conclusions

We found that a spiropyran dye (**1**) is a first example of reusable chemosensor for aromatic thiols. Nucleophilic interaction of aromatic thiolate with the electron-deficient olefinic carbon of ring-opened spiropyran creates transient complexes and significantly decreases the rotational energy. This thus enhances coloration of the solution and facilitates colorimetric detection of aromatic thiols. The basic concept presented here based on the nucleophilic interaction between aromatic thiolate and electron-deficient olefinic carbon might contribute to the design of more efficient chemosensors for aromatic thiols and the creation of new spiropyran dyes for sensory materials.

Experimental

All of the reagents used were purchased from Wako, Aldrich, and Tokyo Kasei, and used without further purification. Water was purified by Milli-Q system. Compound **1** was synthesized according to the procedure described previously.[20] Absorption spectra were measured on an UV-visible photodiode-array spectrophotometer (Shimadzu; Multispec-1500) equipped with a temperature controller using a 10-mm path length quartz cell under aerated condition.[36] Visible light irradiation was carried out with a Xe lamp (300 W; Asahi Spectra Co. Ltd.; Max-302) equipped with 510 nm band-pass filter (LX510; light intensity, 1.10 W m^{-2}).[37]

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Notes and references

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† Electronic Supplementary Information (ESI) available: Details for equilibrium and kinetic analysis and supplementary data (Table S1 and S2, Fig. S1–S7, and Cartesian coordinates). See DOI: 10.1039/b000000x/

1 A. Fersht, *Enzyme Structure and Mechanism*, 2nd ed., Freeman, New York, 1984, pp. 2–4.
2 H. Refsum, P. M. Ueland, O. Nygård and S. E. Vollset, *Annu. Rev. Med.,* 1989, **40**, 31–44.
3 I. Rahman and W. MacNee, *Free Radical Biol. Med.*, 2000, **28**, 1405–1420.
4 K. Shimada and K. Mitamura, *J. Chromatogr. B*, 1994, **659**, 227–241.
5 J. C. Love, L. A. Estroff, J. K. Kriebel, R. G. Nuzzo and G. M. Whitesides, *Chem. Rev.*, 2005, **105**, 1103–1169.
6 A. Eychmüller and A. L. Rogach, *Pure Appl. Chem.*, 2000, **72**, 179–188.
7 G. J. Hathaway and N. H. Proctor, *Proctor and Hughes' Chemical Hazards of the Workplace*, John Wiley & Sons, Inc, New Jersey, 2004.
8 W. Jiang, Q. Fu, H. Fan, J. Ho and W. Wang, *Angew. Chem. Int. Ed.*, 2007, **46**, 8445–8448.
9 W. Jiang, Y. Cao, Y. Lin and W. Wang, *Chem. Commum.*, 2010, **46**, 1944–1946.
10 W. Lin, L. Long and W. Tan, *Chem. Commum.*, 2010, **46**, 1503–1505.
11 C. Zhao, Y. Zhou, Q. Lin, L. Zhu, P. Feng, Y. Zhang and J. Cao, *J. Phy. Chem. B*, 2011, **115**, 642–647.
12 D. Kand, P. K. Mishra, T. Saha, M. Lahiri and P. Talukdar, *Analyst*, 2012, **137**, 3921–3924.
13 Y. Shiraishi, K. Yamamoto, S. Sumiya and T. Hirai, *Chem. Commum*., 2013, **49**, 11680–11682.

14 G. H. Brown, *Photochromism*, Wiley-Interscience, New York, 1971.
15 H. Durr and H. Bouas-Laurent, *Photochromism - Molecules and Systems*, *Elsevier*, Amsterdam, 1990.
16 J. C. Crano and R. J. Guglielmetti, *Organic Photochromic and Thermochromic Compounds*, Plenum Press, New York, 1999.
17 Y. Shiraishi, M. Ito and T. Hirai, *Phys. Chem. Chem. Phys.*, 2010, **12**, 13737–13745.
18 Y. Shiraishi, T. Inoue, S. Sumiya and T. Hirai, *J. Phys. Chem. A*, 2011, **115**, 9083–9090.
19 T. Suzuki, F.-T. Lin, S. Priyadashy and S. G. Weber, *Chem. Commun.*, 1998, **24**, 2685–2686.
20 Y. Shiraishi, K. Adachi, M. Ito and T. Hirai, *Org. Lett.*, 2009, **11**, 3482–3485.
21 J. B. Flannery, Jr., *J. Am. Chem. Soc.*, 1968, **90**, 5660–5671.
22 Y. Sheng, J. Leszczynski, A. A. Garcia, R. Rosario, D. Gust and J. Springer, *J. Phys. Chem. B*, 2004, **108**, 16233–16243.
23 G. Cottone, R. Noto and G. L. Manna, *Chem. Phys. Lett.*, 2004, **388**, 218–222.
24 M. Cossi, V. Barone, R. Cammi and J. Tomasi, *Chem. Phys. Lett.*, 1996, **255**, 327–335.
25 C. Gonzalez and H. B. Schlegel, *J. Phys. Chem.*, 1990, **94**, 5523–5527.
26 J. P. Danehy and C. J. Noel, *J. Am. Chem. Soc.*, 1960, **82**, 2511–2515.
27 H. Hiemstra and H. Wynberg, *J. Am. Chem. Soc.*, 1981, **103**, 417–430.
28 E. H. Krenske, R. C. Petter, Z. Zhu and K. N. Houk, *J. Org. Chem.*, 2011, **76**, 5074–5081.
29 M. Izquierdo, S. Osuna, S. Filippone, A. M.-Domenech, M. Solà and N. Martín, *Eur. J. Org. Chem.*, 2009, 6231–6238.
30 P. R. Conlon and J. M. Sayer, *J. Org. Chem.*, 1979, **44**, 262–267.
31 M. Mammen, E. I. Shakhnovich and G. M. Whitesides, *J. Org. Chem.*, 1998, **63**, 3168–3175.
32 T. B. Phan, C. Nolte, S. Kobayashi, A. R. Ofial and H. Mayr, *J. Am. Chem. Soc.*, 2009, **131**, 11392–11401.
33 J. E. Leffler, *J. Org. Chem.*, 1966, **31**, 533–537.
34 Y. Sueishi, M. Ohcho, S. Yamamoto and N. Nishimura, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 3666–3668.
35 R. Meza, B. Gordillo and M. Galván, *Int. J. Quant. Chem.*, 2005, **104**, 29–37.
36 Y. Shiraishi, K. Tanaka, E. Shirakawa, Y. Sugano, S. Ichikawa, S. Tanaka and T. Hirai, *Angew. Chem. Int. Ed.*, 2013, **52**, 8304–8308.
37 Y. Shiraishi, Y. Matsunaga and T. Hirai, *Chem. Commun.*, 2012, **48**, 5485−5487.