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Tuning the energy transfer process for the ensemble of fluorescein with β-cyclodextrin (β-CD) unit and spiropyran with adamantyl (AD) unit: A temperature-gated molecular fluorescence switch

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ABSTRACT

By combining the features of photochromic spiropyran and the host–guest inclusion complex between the adamantyl (AD) and β-cyclodextrin (β-CD) derivatives, we report a temperature-gated molecular fluorescence switch.

1. Introduction

As the basic elements of molecular devices, molecular switches have received a lot of attention in recent years [1]. Most of the molecular switches are based on bistable molecular systems whose reversible structural changes result in the variation of some physical properties (e.g. absorption, fluorescence and redox potential), in response to external signals such as light irradiation and redox reactions. Some of these bistable molecules contain photochromic and redox-active building units. Variation of the photochromic and redox-active units may be used to tune the corresponding photoinduced electron and energy transfer processes, and as a result reversible change of the physical properties such as absorption and fluorescence would occur. As a matter of fact, a number of molecular switches have been developed by employing photoresponsive/electroactive building units [2]. We have recently reported redox molecular fluorescence switches by making use of the unique features of tetrathiafulvalene moiety [3].

If the reversible structural transformation, as a result of the electron/energy transfer process for a given molecular switch, can be influenced by additional external stimulation, an external signal-gated molecular switch can be built. To some extent, an external signal-gated molecular switch is comparable to semiconductor-based field effect transistor in which the current flow between source and drain electrodes is controlled by the gate voltage [4]. Analogues of external signal-gated molecular switch are reported in biological systems [5]. External signal-gated molecular switches are considered as the key components of future molecular circuits. However, to the best of our knowledge, only a few relevant examples of external signal-gated molecular switches were reported. For instance, Lehn and co-workers [6] described proton gated photochromic properties of a diarylethene switch. Willner et al. [7] reported several gated molecular and biomolecular optoelectronic systems via photoisomerizable monolayer electrodes.

Herein we report a temperature-gated molecular switch based on the ensemble of compounds **1** and **2** (Scheme 1). The design rationale is illustrated in Scheme 1: (1) a stable host–guest inclusion complexes can be formed between AD and β-CD derivatives [8]. As a result, a supramolecular spiropyran (SP)-fluorescein dyad can be formed between compounds **1** and **2** [9]; (2) as reported previously [10], the fluorescence of the SP-fluorescein dyad can be reversibly modulated by alternating UV and visible light irradiation since there is spectral overlap between the fluorescence spectrum of fluorescein and the absorption spectrum of merocyanine form of spiropyran (MC); (3) it is known that the photoinduced energy transfer process is dependent on the distance between the energy donor and energy acceptor, and intramolecular energy transfer process is more efficient than the corresponding intermolecular process. This distance in our SP-fluorescein dyad can be modulated by controlling temperature, as the host–guest inclusion complex is dissociatable by increasing the temperature of the solution [11]. Thus, it is reasonable to expect that the energy transfer process between the excited state of fluorescein and MC (merocyanine form of spiropyran) would be attenuated by increasing temper-

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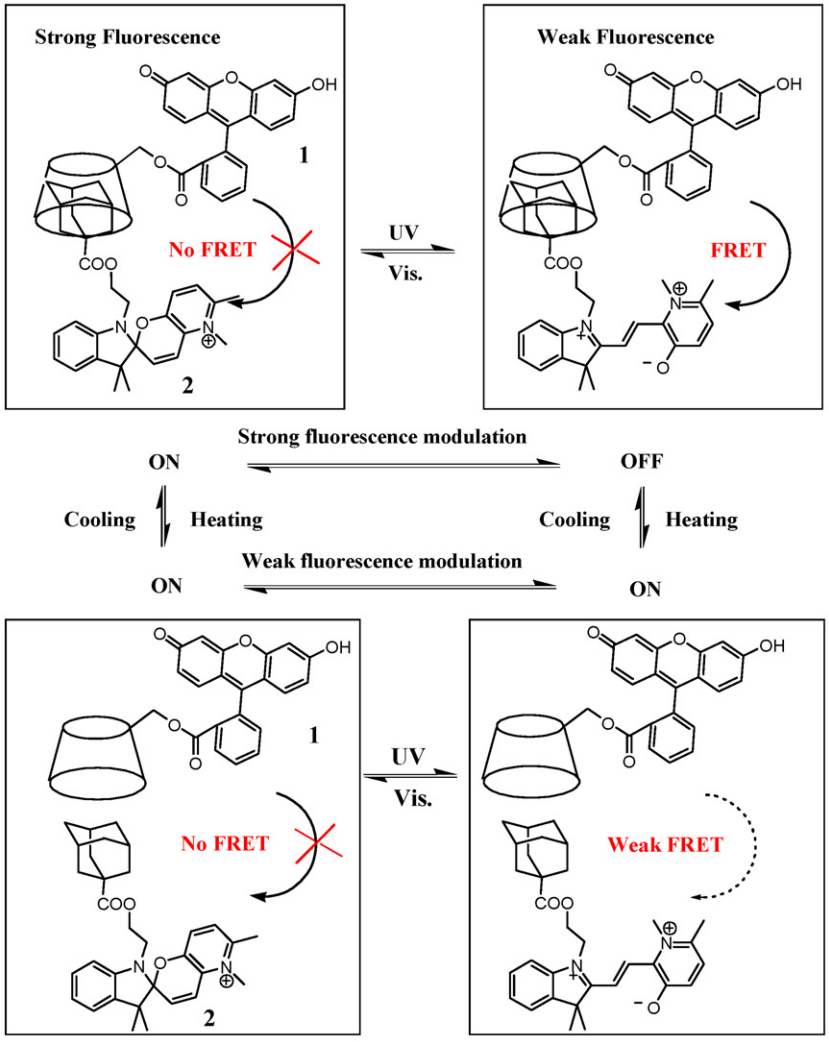


Scheme 1. The design rationale for the temperature-gated molecular fluorescence switch.

ature. As a result, the fluorescence intensity modulation for the ensemble of compounds **1** and **2** upon UV and visible light irradiation would become weaker at higher temperature. Namely, the performance of the molecular fluorescence switch based on the ensemble of **1** and **2** would be influenced by the temperature, leading to a temperature-gated molecular fluorescence switch. Such thermally driven fluorescence switch may be useful as the fluorescence thermometer after further research. The stability of the host–guest inclusion complex (SP-fluorescein dyad) between compounds **1** and **2** is also dependent on the properties of solvents used; the fluorescence variation behavior for the ensemble of **1** and **2** was also investigated in other solvents.

2. Results and discussions

2.1. Synthesis

Compounds **1** [12a] and **3** [12b] were prepared according to the reported methods. Compound **2** was obtained through four reaction steps in 13% yield as shown in Scheme 4. Compound **4** was transformed into compound **5** by sequential reactions with 1,2-dibromoethane and NaOH. The coupling of compound **5** with 3-hydroxy-6-methylpyridine-2-carbaldehyde led to compound **6**, which was converted compound **7** by reaction with 1-adamantanecarboxylic acid in the presence of K_2CO_3. Compound **2** was yielded by further reaction with CH_3I.

Compound **2** shows low solubility in water and as a result the recording of its ^1H NMR in D_2O was rather difficult. However, the ^1H NMR signals due to AD unit were easily observed after addition 1.0 eq. of compound **1** into the solution. Formation of the host–guest complex between **1** and **2** through the inclusion of AD unit into the β-CD unit increases its solubility in water [8].

2.2. Spectral studies

Fig. 1 shows the absorption spectrum of the ensemble of **1** and **2** in aqueous solution and those after UV light (365 nm) and visible light irradiation. After UV light (365 nm) irradiation, a new absorption band around 530 nm was detected, and further visible light irradiation led to the disappearance of this new absorption band. This is obviously due to the reversible transformation between SP form and MC form (merocyanine form of spiropyran) after alternating UV and visible light irradiations as reported previously [10].

Simultaneously, the fluorescence intensity at 526 nm of the ensemble was reduced by ca. 60% upon UV light (365 nm) irradiations shown in Fig. 2, owing to the efficient energy transfer between the excited state of fluorescein and the MC form as reported early [10,13]. Further visible light irradiation induced the transformation

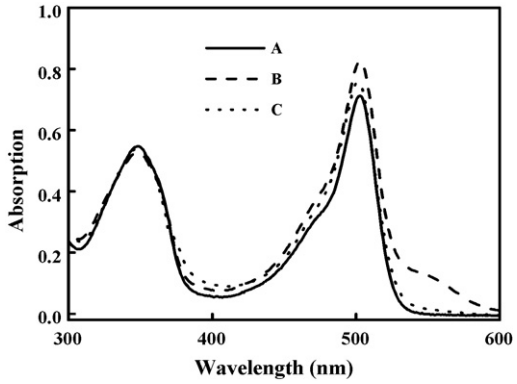


Fig. 1. Absorption spectra of **1** (50 μM) and **2** (50 μM) in aqueous solution at 25 °C (A) before, (B) after irradiation with ultraviolet light (365 nm) for 5.0 min and (C) after further visible light irradiation for 5.0 min.

of MC form into SP form, and as a result the fluorescence of the ensemble was restored. In this way, the fluorescence of the ensemble of **1** and **2** can be reversibly modulated as shown in the inset of Fig. 2 by alternating UV and visible light irradiation. Therefore, the ensemble of **1** and **2** can act as a fluorescence molecular switch. As to be discussed, the fluorescence intensity at 526 nm of the ensemble of **1** and **3** was just reduced by 38% (see Fig. 4) after UV light irradiation under the same condition [14]. Similarly, the fluorescence of the ensemble of **1** and **3** can also be reversibly modulated by alternating UV and visible light irradiations (see Fig. 4).

The fluorescence spectra of **1** in the presence of different amounts of **2** were measured after UV light irradiation at room temperature (see Fig. S1 of SI). The results showed that the fluorescence quenching degree observed for **1** in the presence of **2** under UV light irradiation was dependent on the concentration of **2**. By employing the Stern–Volmer equation, the corresponding fluorescence quenching constant was estimated to be $4.2 \times 10^4\ M^{-1}$. Under the same conditions, the fluorescence spectra of **1** in the presence of different amounts of **3** were also measured after UV light irradiation at room temperature (see Fig. S2 of SI). The corresponding fluorescence quenching constant was estimated to be $2.2 \times 10^4\ M^{-1}$. The results indicate that the fluorescence of **1** was quenched by compound **2** to a larger extent compared to that by compound **3** under the same conditions. This is understandable by considering the fact that **1** and **2** may form host–guest inclusion complex in solution and thus both intramolecular and intermolecular energy transfer processes should contribute to the fluorescence quenching; for compounds **1** and **3**, however, only the intermolecular energy transfer process should be responsible for the fluorescence quenching [14].

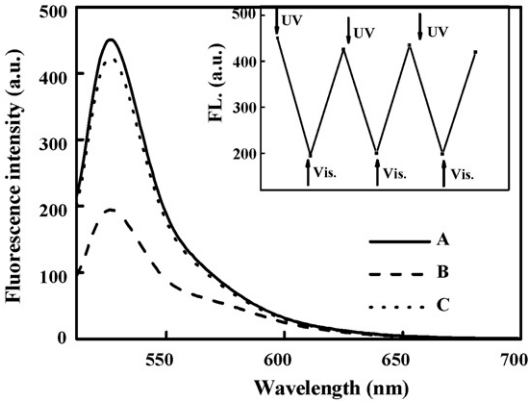


Fig. 2. Fluorescence spectra of the ensemble of **1** (50 μM) and **2** (50 μM) in aqueous solution at 25 °C (A) before and (B) after irradiation with ultraviolet light (365 nm) for 5.0 min and (C) after further irradiation with visible light (>460 nm) for 5.0 min; λ_{ex} = 502 nm; inset shows the reversible variation of the fluorescence intensity at 526 nm after alternating UV/vis light irradiation.

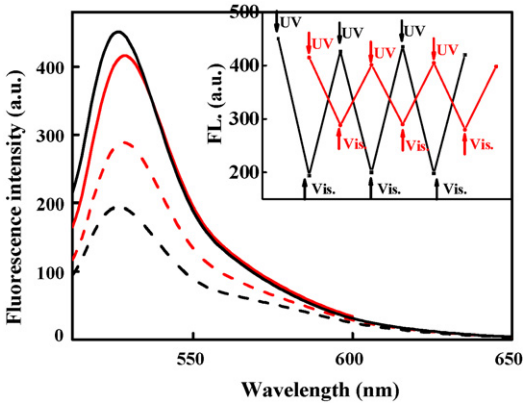
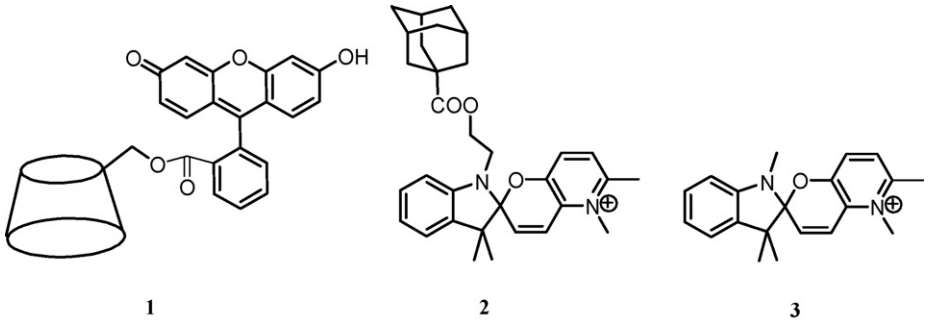


Fig. 3. Fluorescence spectra (λ_{ex} = 502 nm) of the ensemble of **1** (50 μM) and **2** (50 μM) in aqueous solution before (solid line) and after (dash line) irradiation with ultraviolet light (365 nm) for 5.0 min at 25 °C (black) and 50 °C (red); inset shows the reversible variation of the fluorescence intensity at 526 nm of the ensemble of **1** and **2** in aqueous solution at 25 °C (black) and 50 °C (red) under alternating UV/vis light irradiation.

The fluorescence spectra of the ensemble of **1** and **2** were also measured at different temperatures. For example, Fig. 3 shows the fluorescence spectra of the ensemble after UV and visible light irradiation at 50 °C together with those at room temperature for comparison. The fluorescence intensity of the ensemble (before UV light irradiation) was slightly reduced at 50 °C compared to that at room temperature. This is likely due to the acceleration of the nonradiative processes at high temperature. In fact, the fluorescence intensity of compound **1** was also slightly reduced by increasing the temperature of the solution (see Fig. S3 of SI). As expected, the fluorescence intensity at 526 nm of the complex decreased by ca. 30% after UV light irradiation at 50 °C and the fluorescence spectrum could be restored after further visible light irradiation (not shown in Fig. 3). Therefore, we feel justified to say that the fluorescence intensity of the ensemble of **1** and **2** can be reversibly tuned by alternating UV and visible light irradiation. But, the modulation degree for the fluorescence intensity of the complex was obviously reduced at 50 °C compared to that at room temperature as displayed in the inset of Fig. 3. Similar result was obtained for the ensemble at 70 °C and the fluorescence intensity at 526 nm of the ensemble decreased by ca. 28% after UV light irradiation at 70 °C (see Fig. S4 of SI). It should be mentioned that the modulation degree for the fluorescence intensity of the ensemble could be recovered after the hot solution was cooled down to room temperature. The results clearly indicate that our molecular fluorescence switch can be temperature gated.

The temperature gating behavior for the fluorescence modulation of the ensemble of **1** and **2** can be understood as follows. For the ensemble of **1** and **2** there is equilibrium between the host–guest inclusion complex and the free compounds **1** and **2** as shown in Scheme 3. The equilibrium would shift to the left side by increasing the temperature because host–guest inclusion complex due to the hydrophobic interaction between AD and β-CD would be dissociated at high temperature according to previous studies [11]. It is known that the intermolecular energy transfer efficiency is not efficient as the corresponding intramolecular energy transfer. Therefore, it is expected that the energy transfer between the excited state of the fluorescein and MC (merocyanine form of spiropyran) would become less efficient for the ensemble of **1** and



Scheme 2. The chemical structures of compounds **1**, **2** and **3**.

2 after UV light irradiation at high temperature. As a result, the modulation degree for the fluorescence intensity of the ensemble would decrease after alternating UV and visible light irradiation. It should be noted that most of compounds **1** and **2** are not associated in solution; thus it is not unexpected that the decrease of the fluorescence modulation degree is not significant for the ensemble of **1** and **2** after alternating UV and visible light irradiation at high temperature.

Heating would also accelerate the transformation of MC into SP as shown in Scheme 3. This may also contribute to the reduction of the modulation degree for the fluorescence intensity of the ensemble of **1** and **2** by increasing temperature. To minimize the influence of heating on the transformation of MC into SP, the solution was kept exposure to UV light while the solution was heated. In this way the possible effect of the transformation of MC into SP on the fluorescence modulation at high temperature can be neglected as supported by the control experiment with the ensemble of **1** and **3** (Scheme 2). As shown in Fig. 4, the fluorescence of the ensemble of **1** and **3** can also be modulated at room temperature, but the modulation degree is smaller than that for the ensemble of **1** and **2** [14]. The results show that the modulation degree for the fluorescence intensity of the ensemble of **1** and **3** keeps almost constant by increasing the temperature of the solution from room temperature (reduced by 38%) to 50 °C (reduced by 38%) and further to 70 °C (reduced by 38%). Therefore, it may be concluded that the disassociation of the host–guest inclusion complex between **1** and **2** is mainly responsible for the decrease of the fluorescence modulation for the ensemble of **1** and **2** by increasing temperature.

Moreover, the ^{1}H NMR spectra in D_2O recorded at 50 °C and 70 °C also shows that the hydrophobic interaction between AD and β-CD for the ensemble of **1** and **2** becomes weak gradually by increasing temperature as shown in Fig. S5 of SI [11b,c]. Therefore, this result also supports the conclusion that the temperature gating behavior for the fluorescence modulation of the ensemble of **1** and **2** arises mainly from the temperature-dependence of the hydrophobic interaction between AD and β-CD.

The fluorescence spectra of the ensemble of **1** and **2** were also studied in other solvents. For instance, Fig. 5 shows the fluorescent spectra of the ensemble of **1** and **2** in methanol after UV and visible light irradiation and those in aqueous solution for comparison. The fluorescence intensity of the ensemble (before UV light irradiation) was reduced in methanol compared to that in aqueous solution. It is well accepted that the fluorescence of fluorescein derivatives is influenced by the properties of solvents, and thus the reduction of the fluorescence intensity of the ensemble of **1** and **2** in methanol is not unexpected. As expected, the fluorescence intensity of the ensemble of **1** and **2** in methanol can be modulated by alternating UV and visible light irradiation (Fig. 5). But, the modulation degree for the fluorescence intensity of the ensemble of **1** and **2** is small in methanol compared to that for the ensemble in aqueous solution. Similar result was found for the ensemble of **1** and **2** in DMSO (see Fig. S6 of SI). This is probably due to the following two aspects: (1) the host–guest complexes of the AD and β-CD derivatives become unstable in methanol or DMSO, thus the equilibrium between the host–guest inclusion complex and the free compounds **1** and **2** would shift to the left side (see Scheme 3); accordingly, the

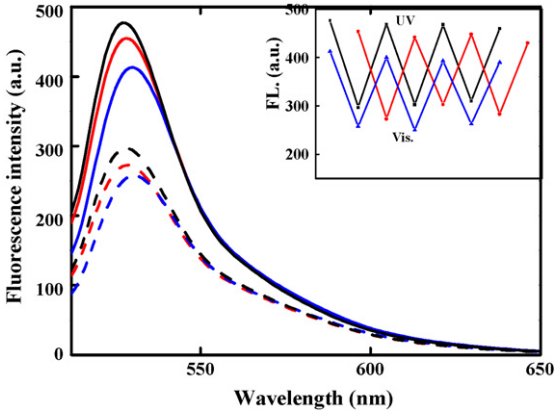


Fig. 4. Fluorescence spectra (λ_{ex} = 502 nm) of the ensemble of **1** (50 μM) and **3** (50 μM) in aqueous solution before (solid line) and after (dash line) UV light irradiation (365 nm) for 5.0 min: 25 °C (black); 50 °C (red); 70 °C (blue); inset shows the reversible variation of the fluorescence intensity at 526 nm for the ensemble of **1** and **3** in aqueous solution: 25 °C (black); 50 °C (red); 70 °C (blue) after alternating UV/vis light irradiations.

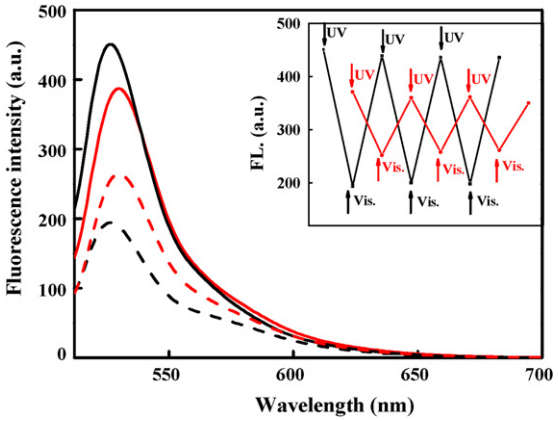
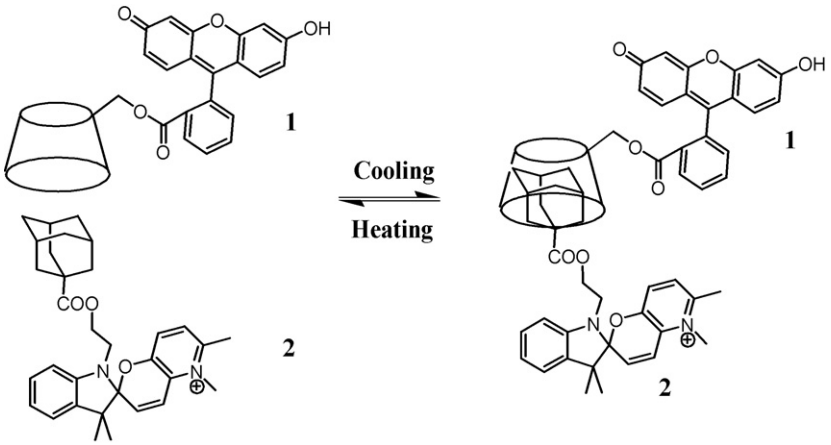
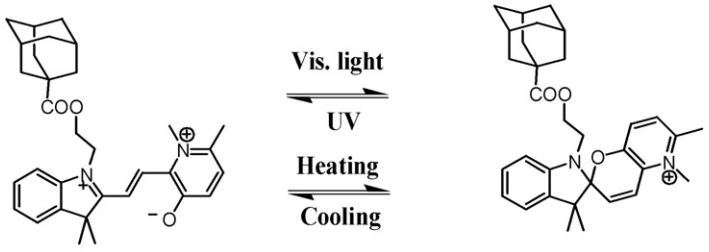


Fig. 5. Fluorescence spectra (λ_{ex} = 502 nm) of the ensemble of **1** (50 μM) and **2** (50 μM) in aqueous solution (black) and methanol (red) before (solid line) and after (dash line) UV light irradiation for 5.0 min at 25 °C; inset shows the reversible variation of the fluorescence intensity at 526 nm of the ensemble of **1** and **2** in aqueous solution (black) and methanol (red) under alternating UV/vis light irradiation.



Equilibrium between the host-guest inclusion complex and the free compounds 1 and 2



Equilibrium between the MC and SP form of compound 2

Scheme 3. The equilibriums existing in the ensemble of **1** and **2**.

energy transfer efficiency between excited state of fluorescein and MC (merocyanine form of spiropyran) is expected to be reduced; (2) the reversible transformation of SP into MC is also affected by the solvent properties. These results indicate that the "performance" of the molecular fluorescence switch based on the ensemble of **1** and **2** is also influenced by the kind of the solvent used.

3. Conclusion

In summary, we design a temperature-gated molecular fluorescence switch by taking advantage of the host–guest interaction between AD and β-CD and the photochromic property of spiropyran. The fluorescence of the ensemble of **1** with β-CD unit and **2** with AD unit can be reversibly modulated. As the stability of this host–guest inclusion complex is dependent on the temperature of the solution, the energy transfer efficiency between the excited state of fluorescein and the open form of spiropyran (MC) can be tuned by varying temperature. As a result, the modulation degree for the fluorescence intensity of the ensemble can be influenced by temperature. Besides, the fluorescence modulation for the ensemble of **1** and **2** is also influenced by the kind of the solvent used. Therefore, we demonstrated how this molecular fluorescence switch can be gated by temperature and solvent.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were recorded on a BRUCK 400 MHz instrument. EI-MS and ESI-MS were determined with AEI-MS 50 and LCMS-2010, respectively. FT-ICRMS spectra were recorded on P-SIMS-Gly of Bruker Daltonics Inc. Fluorescence spectra were recorded on a JASCO FP6000 spectrofluorometer in a 1-cm quartz cell and absorption spectra were recorded on JASCO V-570 UV/VIS/NIR spectrometer. Column chromatography was performed using silica gel (200–300 mesh). Ultrapure water was prepared using a Milli-Q reagent system.

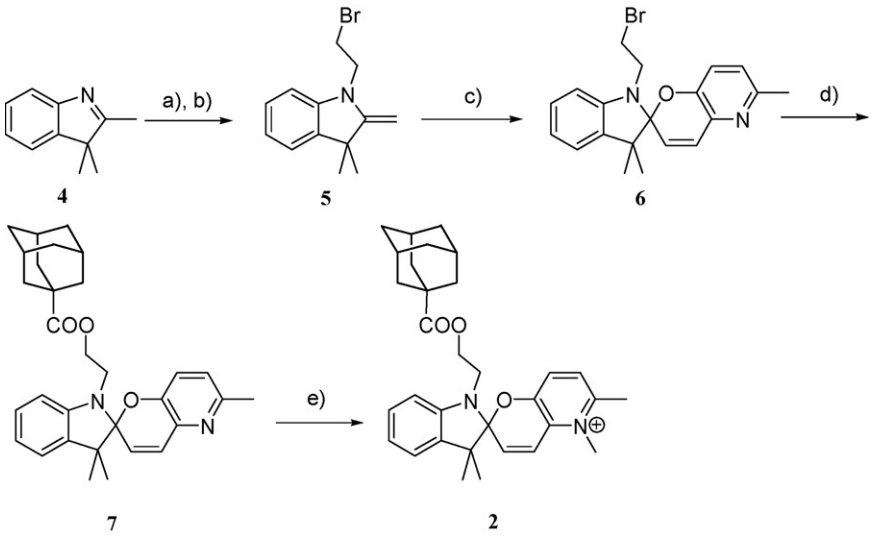
Compound **1** [12a] and **3** [12b] were prepared according to the reported method.

4.2. Synthesis of compound *2* (Scheme 4)

4.2.1. Compound *6*

The mixture of 2,3,3-trimethyl-3*H*-indole (1 ml, 6.2 mmol), 1,2-dibromoethane (2 ml, 24.8 mmol) in 30 ml of acetonitrile was heated under reflux for 3 h. After evaporation of acetonitrile, the residue was washed for several times with petroleum ether to give brown solid. The obtained solid was added into a solution of NaOH (0.25 g, 6.2 mmol) in 30 ml anhydrous ethanol and the mixture was heated under reflux for 1 h. After evaporation of ethanol under reduced pressure, the residue was extracted by *n*-heptane (20 ml × 3). The combined solution was evaporated to give compound **5** (1.1 g), which was used for next step without purification.

3-Hydroxy-6-methylpyridine-2-carbaldehyde (775 mg, 2.9 mmol) and compound **5** (400 mg, 2.9 mmol) were dissolved in 15 ml of ethanol and the mixture was heated under reflux for 3 h. After which the ethanol was removed under reduced pressure and the residue was purified by chromatography column to give **6** as yellow oil (561 mg, 51%).



Scheme 4. Synthetic scheme for compound **2**: (a) $BrCH_2CH_2Br$, CH_3CN, reflux; (b) CH_3CH_2OH, NaOH, reflux; (c) 3-hydroxy-6-methylpyridine-2-carbaldehyde, CH_3CH_2OH, reflux; (d) 1-adamantanecarboxylic acid, K_2CO_3, DMF, 60 °C; (e) CH_3I, THF, reflux.

^{1}H NMR ($CDCl_3$): δ 1.10–1.20 (s, 3H), 1.20–1.30 (s, 3H), 2.41–2.51 (s, 3H), 3.39–3.44 (m, 1H), 3.50–3.60 (m, 2H), 3.65–3.71 (m, 1H), 5.95–6.02 (d, 1H, J = 10.5 Hz), 6.56–6.59 (d, 1H, J = 7.8 Hz), 6.80–6.95 (m, 3H), 7.00–7.07 (d, 1H, J = 10.5 Hz), 7.07–7.12 (d, 1H, J = 7.2 Hz), 7.10–7.25 (t, 1H, J = 7.0 Hz). ^{13}C NMR ($CDCl_3$): δ 20.1, 23.6, 25.9, 30.0, 45.7, 52.8, 104.7, 106.4, 119.9, 122.2, 122.5, 123.8, 124.1, 127.9, 131.8, 136.3, 137.7, 146.3, 148.7, 150.1. EI-MS: m/z 384 (M^+).

4.2.2. Compound **7**

The mixture of compound **6** (173 mg, 0.45 mmol), 1-adamantanecarboxylic acid (85 mg, 0.45 mmol) and K_2CO_3 (125 mg, 0.9 mmol) was stirred in 5 ml of DMF at 60 °C for 7 h, after which it was cooled to room temperature and then treated with 10 ml of cool water. The precipitate appeared in the solution after addition of water was filtered and thoroughly washed with water to give pure compound **7** (157 mg, 72%) as gray solid.

^{1}H NMR ($CDCl_3$): δ 1.10–1.20 (s, 3H), 1.20–1.30 (s, 3H), 1.60–1.72 (m, 6H), 1.80–1.88 (s, 6H), 1.95–2.01 (s, 3H), 2.40–2.50 (s, 3H), 3.35–3.42 (m, 1H), 3.45–3.53 (m, 1H), 4.10–4.25 (m, 2H), 5.92–6.05 (d, 1H, J = 10.1 Hz), 6.62–6.70 (d, 1H, J = 7.4 Hz), 6.80–6.90 (m, 3H), 6.96–7.04 (d, 1H, J = 10.1 Hz), 7.04–7.10 (d, 1H, J = 6.7 Hz), 7.13–7.23 (t, 1H, J = 7.4 Hz). ^{13}C NMR ($CDCl_3$): δ 20.0, 23.4, 25.8, 28.0, 36.5, 38.8, 40.7, 42.4, 52.6, 62.5, 104.8, 106.7, 119.5, 121.7, 122.4, 123.9, 124.1, 127.7, 131.3, 136.0, 137.6, 147.0, 148.9, 149.8, 177.6. ESI MS: m/z 485.4 (M + H). HRMS (EI): Anal. calcd. for ($C_{31}H_{36}N_2O_3$): 484.2726; found: 484.2733.

4.2.3. Compound ***2***

The mixture of 150 mg (0.31 mmol) of compound **7** and 0.5 ml of MeI (10 mmol) was dissolved in 5 ml of THF and refluxed overnight. The solution was then allowed to cool down to room temperature. The yellow precipitate was filtered, washed with THF and dried to give compound **2** (108 mg, 56%).

^{1}H NMR ($CDCl_3$): δ 1.20–1.30 (s, 3H), 1.30–1.39 (s, 3H), 1.62–1.75 (q, 6H), 1.80–1.85 (s, 6H), 1.90–2.01 (s, 3H), 2.85–2.91 (s, 3H), 3.40–3.48 (m, 1H), 3.57–3.65 (m, 1H), 4.13–4.28 (m, 2H), 4.46–4.50 (s, 3H), 6.56–6.61 (d, 1H, J = 11 Hz), 6.70–6.76 (d, 1H, J = 7.8 Hz), 6.89–6.95 (t, 1H, J = 7.4 Hz), 7.00–7.11 (d, 1H, J = 7.2 Hz), 7.18–7.25 (t, 1H, J = 7.8 Hz), 7.49–7.51 (t, 2H, 7.4 Hz), 7.69–7.75 (d, 1H, J = 11 Hz). ^{13}C NMR ($CDCl_3$): δ 20.2, 22.6, 25.6, 27.7, 36.3, 38.7, 40.5, 42.7, 53.7, 62.2, 67.8, 106.5, 107.2, 120.4, 121.6, 122.3, 127.9, 129.2, 130.4, 132.1, 134.4, 134.6, 146.0, 147.4, 151.6, 177.6. ESI MS: m/z 499.5 (M^+). HRMS (P-SIMS-Gly): Anal. calcd. for ($C_{32}H_{39}N_2O_3^+$): 499.2955; found: 499.2951.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2008.01.018.

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[10] This is because the large overlap between the fluorescence spectrum of fluorescein and the absorption spectrum of the open form of SP (MC) result in efficient photoinduced energy transfer and decrease in fluorescence from fluorescein and it is opposite when it comes to SP, see: X.F. Guo, D.Q. Zhang, Y.C. Zhou, D.B. Zhu, J. Org. Chem. 68 (2003) 5681–5687.

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[14] This is simply due to the fact that the intermolecular energy transfer between the excited state of fluorescein and MC is fully responsible for the fluorescence modulation observed for the ensemble of **1** and **3**; for the ensemble of **1** and **2**, however, both the corresponding intramolecular and intermolecular energy transfer processes make contributions to the fluorescence modulation.