Supporting Information

Controlling Binding Affinities for Anions by a Photoswitchable Foldamer

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1. General Information.

All starting materials were purchased from Alfa Aesar except trimethylsilylacetylene from J&K CHEMICA and used as received unless otherwise noted. Common solvents including dichloromethane (DCM), ethyl acetate (EA), methanol (MeOH), tetrahydrofuran (THF), acetone and petroleum ether (PE) were purchased from Beijing Chemical Factory (Beijing, China). Without specification, all solvents were used as received with no further purification. Anhydrous tetrahydrofuran was obtained after being distilled over sodium wires with benzophenone as indicator under inert gas until the blue colour forms. Diisopropylamine ($i\text{Pr}_2\text{NH}$) was used after been distilled over CaH_2 under Ar. Proton Nuclear Magnetic Resonance (^1H NMR) spectra and carbon NMR (^{13}C NMR) spectra were obtained on a Bruker AVANCE-400 (400 MHz). 2D NMR experiments were taken on a Bruker AVANCE-600 (600 MHz) spectrometer at ambient temperature (298 K). Chemical shifts are expressed in parts per million (δ) using residual solvent protons as internal standards (^1H : $\delta(\text{CHCl}_3) = 7.26$ ppm, $\delta(\text{CH}_3\text{COCH}_3) = 2.05$ ppm; ^{13}C : $\delta(\text{CHCl}_3) = 77.16$ ppm, $\delta(\text{CH}_3\text{COCH}_3) = 29.84, 206.26$ ppm). Mass spectra (EI, ESI, MALDI-TOF, ESI-HRMS) were obtained on a GCT, Waters-QTOF, Autotlex III spectrometer and Bruker APEX IV FTMS spectrometer, respectively. Photo irradiation experiments were carried on a UV lamp (for 365 nm light) or filament lamp with UV filters (for visible light). The distance between the lamp and the sample was 5 cm.

2 Synthesis of Compound 1

3,5-Dibromophenol, (3). Aluminum chloride (3.35g, 25 mmol) was added to the solution of pentabromophenol (**2**, 2.4 g, 5 mmol) in anhydrous benzene (20ml). The reaction mixture was heated to reflux under N₂ for over 3 hours, and then poured into a mixture of concd HCl and ice water. The organic layer was separated and the water layer was extracted with diethyl ether for 3 times. The combined organic layer was washed with 10% NaOH aqueous solution for 3 times. The pH value of the combined water solution was adjusted to strong acidity with concd HCl then the water solution was extracted with CH₂Cl₂. The organic layer was washed with water, dried over sodium sulfate and concentrated in vacuo to give brown solid. The crude product was re-crystallized with petroleum ether to give compound **3** (1.0 g, 82%) as a needle.

1,3-dibromo-5-(2-(2-methoxyethoxy)ethoxy)benzene, (4). To the mixture of **3** (500 mg, 2 mmol), triphenylphosphine (576 mg, 2.2 mmol) and 2-(2-methoxyethoxy)ethanol (283 μ L, 2.4 mmol) in N₂ atmosphere, anhydrous THF (10 mL) was added. While the mixture was cooled and stirred under 0°C, Diisopropyl azodicarboxylate (430 μ L, 2.2 mmol) was added dropwise and the mixture was stirred at 0°C for 30 min, then at room temperature for 2 h. The solvent was evaporated. The product was purified by silica gel flash column chromatography (DCM/PE, 0/100, 30/70) to yield 510 mg (72.4%) as a pale yellow oil. ¹H-NMR (CDCl₃, 400 MHz), δ = 7.24 (t, 1H, *J* = 1.4 Hz), 7.02 (d, 2H, *J* = 1.5 Hz), 4.10 (t, 2H, *J* = 4.6 Hz), 3.83 (t, 2H, *J* = 4.9 Hz), 3.70 (t, 2H, *J* = 4.4 Hz), 3.57 (q, 2H, *J*₁ = 1.9 Hz, *J*₂ = 1.9 Hz), 3.39 (s, 3H). ¹³C-NMR (CDCl₃, 100 MHz), δ = 160.1, 126.7, 123.1, 117.2, 72.0, 70.9, 69.5, 68.1, 59.2. EI-MS (*m/z*), calcd. for C₁₁H₁₄Br₂O₃ (M) 354.2, found 354.

1-azido-3-bromo-5-(2-(2-methoxyethoxy)ethoxy)benzene, (5). Compound **4** (500 g, 1.41 mmol) was dissolved in anhydrous THF (10 ml). The solution was cooled to -78 °C in acetone bath under N₂. *n*BuLi (0.88 ml, 1.48 mmol) was added during 10 min via

a syringe. After complete, the mixture solution was allowed to slowly warm to -30 °C to react for another 45 min. When the solution was cooled back to -78 °C, a solution of 4-methylbenzenesulfonyl azide (TsN₃, 340 mg in 3 ml anhydrous THF, 1.72 mmol) was slowly added. The reaction was then warmed to room temperature and stirred for over 2 hours. The solvent was removed in vacuo, and the residue was re-dissolved in EA. The solution was washed with brine, dried over sodium sulfate and concentrated in vacuo. The residue was purified on silica gel flash column chromatography (DCM/PE, 80/20) to give the product (360 mg, 80.7 %) as a pale yellow oil. ¹H-NMR (CDCl₃, 400 MHz), δ = 6.85 (s, 1H), 6.78 (s, 1H), 6.51 (s, 1H), 4.11(t, 2H, *J* = 4.6 Hz), 3.84 (t, 2H, *J* = 4.9 Hz), 3.70 (t, 2H, *J* = 4.9 Hz), 3.57 (t, 2H, *J* = 4.9 Hz), 3.39 (s, 3H). ¹³C-NMR (CDCl₃, 100 MHz), δ = 160.5, 142.5, 123.5, 114.8, 114.7, 104.9, 72.0, 70.9, 69.6, 68.0, 59.2. EI-MS (*m/z*), calcd. for C₁₁H₁₄BrN₃O₃ (M) 316.2, found 316.

3-bromo-5-(2-(2-methoxyethoxy)ethoxy)aniline, (6). Compound **5** (1.1 g, 3.48 mmol) was dissolved in 40 ml MeOH. The mixture was warmed to 40 °C. To this solution, NaBH₄ (1.32 g, 34.8 mmol) was added in 5 portions within 20 min at room temperature with stirring. A great deal of bubble formatted in this process accompanied with the temperature increase of the mixture solution. Upon completion, the reaction was quenched with careful dropwise addition of H₂O and then the solution was poured into plenty of H₂O and extracted with EA. The combined organic layers were washed with brine, dried over sodium sulfate and concentrated in vacuo. The residue was purified on silica gel flash column chromatography (MeOH/DCM, 0/100, 1/100) to give the product (0.95 g, 95%) as a pale yellow oil. ¹H-NMR (CDCl₃, 400 MHz), δ = 6.47 (t, 1H, *J* = 1.7 Hz), 6.44 (t, 1H, *J* = 1.7 Hz), 6.16 (t, 1H, *J* = 2.0 Hz), 4.07 (t, 2H, *J* = 4.7 Hz), 3.82 (t, 2H, *J* = 5.0 Hz), 3.70 (t, 2H, *J* = 4.4 Hz), 3.57 (t, 2H, *J* = 4.4 Hz), 3.39 (s, 1H). ¹³C-NMR (CDCl₃, 100 MHz), δ = 160.5, 148.7, 123.3, 111.2, 108.2, 100.6, 72.1, 70.9, 69.7, 67.6, 59.2. ESI-MS (*m/z*), calcd. for C₁₁H₁₆BrN₁O₃ (M) 289.0, found 290.1 (M+H⁺)

3-(2-(2-methoxyethoxy)ethoxy)-5-((trimethylsilyl)ethynyl)aniline, (7). To the mixture of Compound **6** (590 mg, 2.04 mmol), copper(I) iodide (CuI) (8 mg, 0.042 mmol) and tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (50 mg, 0.043 mmol) in anhydrous and degassed diisopropylamine (*i*Pr₂NH, 15 ml), trimethylsilylacetylene (0.35 mL, 2.45 mmol) was added. The flask was sealed and heated to 78 °C for 72 hours. The solution was evaporated in vacuo and the residue was re-dissolved with EA. Organic solution was washed with water, 0.5 M HCl and brine, respectively, dried over sodium sulfate and evaporated in vacuo to dryness. The crude product was purified by silica gel flash column chromatography (MeOH/DCM, 0/100, 1/100) to give the product (432 mg, 69%) as pale yellow oil. ¹H-NMR (CDCl₃, 400 MHz), δ = 6.43 (s, 1H), 6.42 (s, 1H), 6.23 (s, 1H), 4.08 (t, 2H, *J* = 4.7 Hz), 3.82 (t, 2H, *J* = 5.0 Hz), 3.70 (t, 2H, *J* = 4.3 Hz), 3.63 (s, 2H), 3.57 (t, 2H, *J* = 5.0 Hz), 3.39 (s, 3H), 0.23 (s, 9H). ¹³C-NMR (CDCl₃, 100 MHz), δ = 159.6, 147.5, 124.4, 111.9, 107.9, 105.4, 103.2, 93.2, 72.1, 70.9, 69.8, 67.5, 59.2, 0.1. ESI-MS (*m/z*), calcd. for C₁₆H₂₅NO₃Si (M) 307.2, found 330.1 (M+Na⁺)

Azobenzene Bis(ethynyl-TMS), (8). Compound **7** (980 mg, 3.2 mmol) was dissolved in pyridine (30 mL) then CuI (3.04 mg, 16 mmol) was added and the reaction mixture was stirred at room temperature for 72 hours. The reaction mixture was evaporated in vacuo and the residue was re-dissolved with EA. The mixture solution was filtered, subsequently washed with water, brine, 1 N HCl, and again with water and brine, then dried over sodium sulfate and evaporated in vacuo to dryness. The crude product was purified by silica gel flash column chromatography (EA/DCM, 2/100, 9/100) to give the product (180 mg, 18.4%) as bright orange oil. ¹H-NMR (CDCl₃, 400 MHz), δ = 7.64 (s, 2H), 7.42 (d, 2H, *J* = 1.7 Hz), 7.14 (s, 2H), 4.22 (t, 4H, *J* = 4.6 Hz), 3.39 (t, 4H, *J* = 5.2 Hz), 3.74 (t, 4H, *J* = 4.3 Hz), 3.59 (t, 4H, *J* = 4.4 Hz), 0.26 (s, 18H). ¹³C-NMR (CDCl₃, 100 MHz), δ = 159.3, 153.3, 124.8, 121.0, 120.7, 108.6, 104.2, 95.2, 72.1, 71.0, 69.7, 68.0, 59.3, 0.0. ESI-MS (*m/z*), calcd. for C₃₂H₄₆N₂O₆Si₂ (M) 610.3, found 633.4 (M+Na⁺). HRMS-ESI (*m/z*), calcd. for C₃₂H₄₇N₂O₆Si₂ (M+H⁺) 611.2964, found 611.2967

Azobenzene Bis-ethyne, (9). To the solution of Compound **8** (135 mg, 0.22 mmol) in DCM (3 mL), Tetrabutylammonium fluoride (TBAF, 83.8 mg, 0.27 mmol) was added. The reaction mixture was stirred at room temperature for 10 min and then washed with brine, dried over sodium sulfate and evaporated in vacuo to dryness to give the compound **9** (97.1 mg, 94.1%) as an orange oil. $^1\text{H-NMR}$ (CDCl_3 , 400 MHz), δ = 7.67 (s, 1H), 7.46 (s, 1H), 7.18 (s, 1H), 4.23 (t, J = 4.2 Hz, 2H), 3.90 (t, J = 4.3 Hz, 2H), 3.74 (t, J = 4.0 Hz, 2H), 3.59 (t, J = 4.3 Hz, 2H), 3.40 (s, 3H), 3.12 (s, 1H). $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz), δ = 159.4, 153.4, 123.8, 121.6, 121.0, 108.5, 108.5, 82.8, 72.1, 71.0, 69.7, 68.1, 59.2. ESI-MS (m/z), calcd. for $\text{C}_{26}\text{H}_{30}\text{N}_2\text{O}_6$ (M) 466.2, found 467.3 ($\text{M}+\text{H}^+$). HRMS-ESI (m/z), calcd. for $\text{C}_{26}\text{H}_{31}\text{N}_2\text{O}_6$ ($\text{M}+\text{H}^+$) 467.2177, found 467.2171

Phenyl-triazole-Azobenzene, (1). Compound **9** (91.7 mg, 0.2 mmol) and compound **5** (144 mg, 0.44 mmol) was dissolved in 6 ml 5:1 *t*-BuOH/ H_2O . Sodium ascorbate (8 mg, 0.04 mmol) was added as a solid, followed by the addition of CuSO_4 (3 mg, 0.02 mmol). The reaction mixture was degassed and stirred overnight under Ar at 32 °C with being protected from light. Silica gel powder was added to the mixture. The crude mixture was concentrated and purified directly by silica gel flash column chromatography (MeOH/DCM, 0/100, 1/100) to give the product (177 mg, 82.2%) as a bright orange oil that solidified under -18 °C. $^1\text{H-NMR}$ (d_6 -Acetone, 400 MHz), δ = 9.27 (s, 2H), 8.21 (s, 2H), 7.80 (s, 2H), 7.77 (s, 2H), 7.63 (s, 2H), 7.53 (s, 2H), 7.30 (s, 2H), 4.33 (m, 8H), 3.92-3.87 (8H), 3.72-3.67 (8H), 3.54 (m, 8H), 3.32 (s, 3H), 3.30 (s, 3H). $^{13}\text{C-NMR}$ (d_6 -Acetone, 150 MHz), δ = 160.7, 160.0, 153.7, 147.1, 138.7, 132.4, 123.1, 119.3, 117.5, 114.8, 114.6, 114.4, 106.1, 105.3, 71.9, 71.8, 70.5, 70.4, 69.4, 69.2, 68.5, 67.9, 58.0. MALDI-TOF-MS (m/z), calcd. for $\text{C}_{48}\text{H}_{58}\text{Br}_2\text{N}_8\text{O}_{12}$ (M) 1096.2, found 1118.7 ($\text{M}+\text{Na}^+$). HRMS-ESI (m/z), calcd. for $\text{C}_{48}\text{H}_{59}\text{Br}_2\text{N}_8\text{O}_{12}$ ($\text{M}+\text{H}^+$) 1097.2614, found 1097.2597

3. UV/vis Study on Photoresponsive Properties of **1**

Figure S1. UV/vis spectra of (a) **1**_{trans} (30 μ M, Acetone, 298 K); (b) Irradiation with 365 nm light for 5 min. (c) then irradiation with visible light for 8 min. The insert figure reflects the changes of the absorbance at 339 nm upon alternate irradiation with UV and visible light.

4. NMR Studies on Photoresponsive Properties of **1**

Figure S2. Partial NOESY spectrum (600MHz, *d*₆-Acetone, 298K) of **1**_{trans}.

Figure S3. Partial TOCSY spectrum (600MHz, *d*₆-Acetone, 298K) of **1_{trans}**.

Figure S4. Partial HSQC spectrum (600MHz, *d*₆-Acetone, 298K) of **1_{trans}**.

Figure S5. Partial ^1H - ^1H COSY spectrum (600MHz, d_6 -Acetone, 298K) of **1_{trans}**.

Figure S6. Partial HMBC spectrum (600MHz, d_6 -Acetone, 298K) of **1_{trans}**. The signals which were not assigned came from the **1_{cis}**.

Figure S7. Partial ¹H-¹H NOESY spectrum (600MHz, *d*₆-Acetone, 298K) of **1_{cis}**. The signals which were not assigned came from the **1_{trans}**.

Figure S8. Partial TOCSY spectrum (600MHz, *d*₆-Acetone, 298K) of **1_{cis}**. The signals which were not assigned came from the **1_{trans}**.

Figure S9. Partial HSQC spectrum (600MHz, *d*₆-Acetone, 298K) of **1_{cis}**. The signals which were not assigned came from the **1_{trans}**.

Figure S10. Partial HMBC spectrum (600MHz, *d*₆-Acetone, 298K) of **1_{cis}**. The signals which were not assigned came from the **1_{trans}**.

Figure S11. Partial ^1H - ^1H COSY spectrum (600MHz, d_6 -Acetone, 298K) of **1**_{cis}. The signals which were not assigned came from the **1**_{trans}.

Figure S12. Partial ^1H NMR spectra (400 MHz, d_6 -acetone, 298 K) of (a) **1**_{trans}; (b) Irradiation with 365 nm for over 40 min until a photostationary state of **1** was reached; (c) then kept the above solution in dark at ambient temperature for over 10 days. The initial concentration of **1**_{trans} was 2 mM.

5. UV/vis Studies of Anions-binding Properties of **1_{trans}** and **1_{cis}**

Figure S13. There is no Changes of the UV/vis spectra of **1_{trans}** (30 μM) in acetone upon addition of $n\text{Bu}_4\text{N}^+\text{Cl}^-$.

Figure S14. Changes of the UV/vis spectra of **1_{cis}** (30 μM) in acetone upon addition of $n\text{Bu}_4\text{N}^+\text{Cl}^-$.

6. ^1H NMR Binding Experiments with $\mathbf{1}_{trans}$

Figure S15. Partial ^1H NMR spectra changes of $\mathbf{1}_{trans}$ in d_6 -Acetone upon addition of $n\text{Bu}_4\text{N}^+\text{Cl}^-$. $[\mathbf{1}_{trans}] = 2 \text{ mM}$. The measurements were taken at ambient temperature.

Figure S16. Changes in the triazole (H_d) ^1H chemical shift of $\mathbf{1}_{trans}$ in d_6 -Acetone with increasing chloride ions at ambient temperature. The data (■) were curve-fitted to 1:1 binding model (fitting-curve was represented by line). $[\mathbf{1}_{trans}] = 2 \text{ mM}$.

Figure S17. Job's Plot for complexation of **1_{trans}** in *d*₆-Acetone with Bu₄N⁺Cl⁻ by NMR spectroscopy, in which the chemical shift of triazole (H_d) was monitored. [**1_{trans}**] + [Cl⁻] = 2 mM.

Figure S18. Partial ¹H NMR spectra changes of **1_{trans}** in *d*₆-Acetone upon addition of *n*Bu₄N⁺Br⁻. [**1_{trans}**] = 2 mM. The measurements were taken at ambient temperature.

Figure S19. Change in ^1H chemical shift of $\mathbf{1}_{trans}$ in d_6 -Acetone with increasing concentration of bromide ions. $[\mathbf{1}_{trans}] = 2 \text{ mM}$.

Figure S20. Changes in the triazole (H_d) ^1H chemical shift of $\mathbf{1}_{trans}$ in d_6 -Acetone with increasing bromide ions at ambient temperature. The data (■) were curve-fitted to 1:1 binding model (fitting-curve was represented by line). $[\mathbf{1}_{trans}] = 2 \text{ mM}$.

Figure S21. Partial ^1H NMR spectra changes of $\mathbf{1}_{trans}$ in d_6 -Acetone upon addition of $n\text{Bu}_4\text{N}^+\text{I}^-$. $[\mathbf{1}_{trans}] = 2 \text{ mM}$. The measurements were taken at ambient temperature.

Figure S22. Change in ^1H chemical shift of $\mathbf{1}_{trans}$ in d_6 -Acetone with increasing concentration of iodide ions. $[\mathbf{1}_{trans}] = 2 \text{ mM}$.

Figure S23. Changes in the triazole (H_d) 1H chemical shift of **1_{trans}** in d_6 -Acetone with increasing iodide ions at ambient temperature. The data (■) were curve-fitted to 1:1 binding model (fitting-curve was represented by line). [**1_{trans}**] = 2 mM.

Figure S24. Partial 1H NMR spectra changes of **1_{trans}** in d_6 -Acetone upon addition of $nBu_4N^+HSO_4^-$. [**1_{trans}**] = 2 mM. The measurements were taken at ambient temperature.

Figure S25. Change in ^1H chemical shift of $\mathbf{1}_{trans}$ in d_6 -Acetone with increasing concentration of hydrogen sulfate ions. $[\mathbf{1}_{trans}] = 2\text{ mM}$.

Figure S26. Changes in the triazole (H_d) ^1H chemical shift of $\mathbf{1}_{trans}$ in d_6 -Acetone with increasing hydrogen sulfate ions at ambient temperature. The data (■) were curve-fitted to 1:1 binding model (fitting-curve was represented by line). $[\mathbf{1}_{trans}] = 2\text{ mM}$.

Figure S27. Partial ^1H NMR spectra changes of $\mathbf{1}_{trans}$ in d_6 -Acetone upon addition of $n\text{Bu}_4\text{N}^+\text{NO}_3^-$. $[\mathbf{1}_{trans}] = 2 \text{ mM}$. The measurements were taken at ambient temperature.

Figure S28. Change in ^1H chemical shift of $\mathbf{1}_{trans}$ in d_6 -Acetone with increasing concentration of nitrate ions. $[\mathbf{1}_{trans}] = 2 \text{ mM}$.

Figure S29. Changes in the triazole (H_d) ¹H chemical shift of **1**_{trans} in *d*₆-Acetone with increasing nitrate ions at ambient temperature. The data (■) were curve-fitted to 1:1 binding model (fitting-curve was represented by line). [**1**_{trans}] = 2 mM.

7. ¹H NMR Binding Experiments with **1**_{cis}

Figure S30. Partial ¹H NMR spectra changes of **1**_{cis} in *d*₆-Acetone upon addition of *n*Bu₄N⁺Cl⁻. [**1**_{cis}] = 2 mM. The measurements were taken at ambient temperature.

Figure S31. Changes in the triazole (H_d) 1H chemical shift of 1_{cis} in d_6 -Acetone with increasing chloride ions at ambient temperature. The data (■) were curve-fitted to 1:1 binding model (fitting-curve was represented by line). $[1_{cis}] = 2$ mM.

Figure S32. Job's Plot for complexation of 1_{cis} in d_6 -Acetone with chloride by NMR spectroscopy, in which the chemical shift of triazole (H_d) was monitored. $[1_{cis}] + [Cl^-] = 2$ mM.

Figure S33. Partial ^1H NMR spectra changes of $\mathbf{1}_{cis}$ in d_6 -Acetone upon addition of $n\text{Bu}_4\text{N}^+\text{Br}^-$. $[\mathbf{1}_{cis}] = 2 \text{ mM}$. The measurements were taken at ambient temperature.

Figure S34. Change in ^1H chemical shift of $\mathbf{1}_{cis}$ in d_6 -Acetone with increasing concentration of bromide ions. $[\mathbf{1}_{cis}] = 2 \text{ mM}$.

Figure S35. Changes in the triazole (H_d) 1H chemical shift of 1_{cis} in d_6 -Acetone with increasing bromide ions at ambient temperature. The data (■) were curve-fitted to 1:1 binding model (fitting-curve was represented by line). $[1_{cis}] = 2$ mM.

Figure S36. Partial 1H NMR spectra changes of 1_{cis} in d_6 -Acetone upon addition of $nBu_4N^+I^-$. $[1_{cis}] = 2$ mM. The measurements were taken at ambient temperature.

Figure S37. Changes in ^1H chemical shift of $\mathbf{1}_{cis}$ in d_6 -Acetone with increasing concentration of iodide ions. $[\mathbf{1}_{cis}] = 2 \text{ mM}$.

Figure S38. Changes in the triazole (H_d) ^1H chemical shift of $\mathbf{1}_{cis}$ in d_6 -Acetone with increasing iodide ions at ambient temperature. The data (■) were curve-fitted to 1:1 binding model (fitting-curve was represented by line). $[\mathbf{1}_{cis}] = 2 \text{ mM}$.

Figure S39. Partial ^1H NMR spectra changes of $\mathbf{1}_{cis}$ in d_6 -Acetone upon addition of $n\text{Bu}_4\text{N}^+\text{HSO}_4^-$. $[\mathbf{1}_{cis}] = 2$ mM. The measurements were taken at ambient temperature.

Figure S40. Change in ^1H chemical shift of $\mathbf{1}_{cis}$ in d_6 -Acetone with increasing concentration of hydrogen sulfate ions. $[\mathbf{1}_{cis}] = 2$ mM.

Figure S41. Changes in the triazole (H_d) ^1H chemical shift of $\mathbf{1}_{cis}$ in d_6 -Acetone with increasing hydrogen sulfate ions at ambient temperature. The data (■) were curve-fitted to 1:1 binding model (fitting-curve was represented by line). $[\mathbf{1}_{cis}] = 2 \text{ mM}$.

Figure S42. Partial ^1H NMR spectra changes of $\mathbf{1}_{cis}$ in d_6 -Acetone upon addition of $n\text{Bu}_4\text{N}^+\text{NO}_3^-$. $[\mathbf{1}_{cis}] = 2 \text{ mM}$. The measurements were taken at ambient temperature.

Figure S43. Change in ^1H chemical shift of $\mathbf{1}_{cis}$ in d_6 -Acetone with increasing concentration of nitrate ions. $[\mathbf{1}_{cis}] = 2 \text{ mM}$.

Figure S44. Changes in the triazole (H_d) ^1H chemical shift of $\mathbf{1}_{cis}$ in d_6 -Acetone with increasing nitrate ions at ambient temperature. The data (■) were curve-fitted to 1:1 binding model (fitting-curve was represented by line). $[\mathbf{1}_{cis}] = 2 \text{ mM}$.

8. Study on the transformation between **1**_{trans} and **1**_{cis} in the presence of anions

Figure S45. UV/vis spectra of (a) **1**_{trans} (30 μM, Acetone, 298 K) in the presence of 40 equivalent chloride ions. (b) Irradiation with 365 nm light for 5 min. (c) then irradiation with visible light for 8 min. The insert figure reflects the changes of the absorbance at 339 nm upon alternate irradiation with UV and visible light.

Figure S46. ¹H NMR spectra of (a) **1**_{trans} (*d*₆-Acetone, 2mM, 298 K) in the presence of 4 equivalent chloride ions; (b) Irradiation with 365 nm light for 40 min to reach the photostationary state of **1**; (c) then the solution was further stored in dark at the ambient temperature for over 14 days.

9. ^1H and ^{13}C NMR Spectra of Compounds 4-9 and 1_{trans}

Figure S47. ^1H -NMR spectra of 4

Figure S48. ^{13}C -NMR spectra of 4

Figure S49. ¹H-NMR spectra of **5**

Figure S50. ¹³C-NMR spectra of **5**

Figure S51. ¹H-NMR spectra of **6**

Figure S52. ¹³C-NMR spectra of **6**

Figure S53. ¹H-NMR spectra of 7

Figure S54. ¹³C-NMR spectra of 7

Figure S55. ¹H-NMR spectra of **8**

Figure S56. ¹³C-NMR spectra of **8**

Figure S57. ¹H-NMR spectra of **9**

Figure S58. ¹³C-NMR spectra of **9**

Figure S59. ¹H-NMR spectra of **1_{trans}**

Figure S60. ¹³C-NMR spectra of **1_{trans}**