

## Supporting Information

### Recognition-Gated Azobenzene Photoswitch

Yu Ouyang, Ziyong Yuan, Jiaobing Wang\*

School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, China

e-mail: wangjb5@mail.sysu.edu.cn

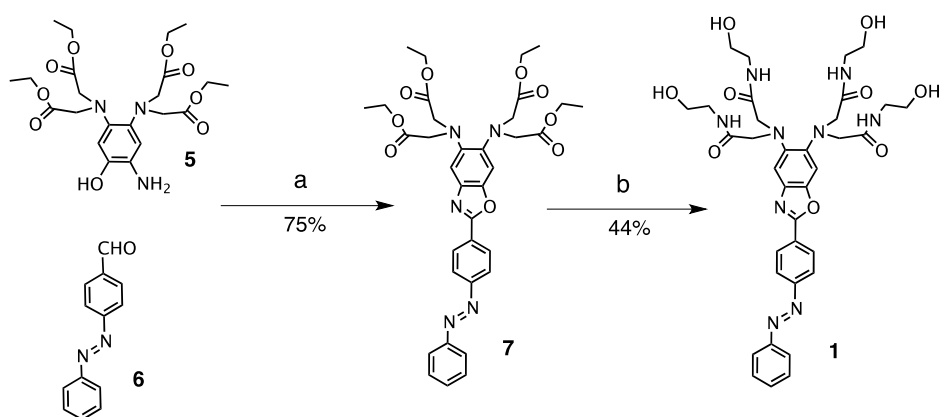
#### General remarks

Chemicals were purchased from Aldrich, J&K Chemical or Energy Chemical and were used without further purification. Freshly distilled tetrahydrofuran (THF), dichloromethane (DCM), and toluene were used for synthesis. Acetonitrile was dried using molecular sieve. Qingdao Haiyang silica gel (200-300 mesh) was used in flash chromatography. Technical grade solvents were used for extraction and chromatography. NMR spectra were obtained using a Bruker Avance 400 spectrometer (400 MHz). UV/Vis measurements were performed on a SHIMADZU UV-2600 spectrophotometer. Irradiation experiments were carried out using the monochromated (20 nm bandwidth) output of the Xe lamp of the SHIMADZU RF-5301 PC spectrophotometer or projector with a 440 nm filter as a light source. Mass spectra were measured on a Trace GC Ultra-DSQ LC-MS spectrometer. High-resolution mass spectra (HRMS) (ESI) were recorded on a Bruker Daltonics ESI-Q-TOF maXis 4G spectrometer.

#### Contents:

|  |     |
|--|-----|
| Synthesis.....   | S2  |
| Photoswitching of <i>trans</i> - <b>2</b> .....  | S4  |
| Thermoisomerization of <i>cis</i> - <b>1</b> and complex <i>cis</i> - <b>1</b> -Hg <sup>2+</sup> ..... | S5  |
| Photoswitching of compound <b>3</b> and its mercury complex.....                                       | S6  |
| DFT calculation .....  | S8  |
| <sup>1</sup> H-NMR and <sup>13</sup> C-NMR spectra.....  | S10 |

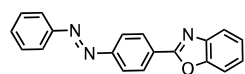
## Synthesis



Scheme S1. Synthesis of switch **1**: (a) **6**, BaMnO<sub>4</sub>, toluene, N<sub>2</sub>, 80 °C, 2h; (b) 2-aminoethanol, MeCN, N<sub>2</sub>, 80 °C, 2 h.

**7.** To a solution of compound **5** (*ref* 1) (0.27 g, 0.54 mmol) in 15 mL dry THF was added aldehyde **6** (*ref* 2) (0.23 g, 1.1 mmol) and acetic acid (0.5 mL). The solution was stirred at room temperature under a nitrogen atmosphere for 5 min. After this time, the solvent was removed under vacuum to obtain a brown oil and dry toluene (30 mL) and BaMnO<sub>4</sub> (0.24 g, 0.93 mmol) was added. The mixture was heated at 80 °C in a sealed flask under N<sub>2</sub> for 3h, then cooled and concentrated under vacuum to remove the solvent. The residue was purified by silica gel column chromatography using ethyl acetate/petroleum ether (1/3, v/v) as the eluant affording 0.14 g (0.21 mmol) of **7** (75%) as a red oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 8.32 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 7.96 (d, *J* = 7.2 Hz, 2H), 7.53 (m, 3H), 7.49 (s, 1H), 7.34 (s, 1H), 4.40 (s, 4H), 4.33 (s, 4H), 4.12 (m, 8H), 1.21 (t, *J* = 6.8 Hz, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 170.7, 162.1, 153.7, 152.6, 147.5, 141.3, 140.3, 137.8, 131.5, 129.3, 129.1, 128.0, 123.4, 123.0, 112.3, 103.5, 60.7, 60.6, 53.5, 53.3, 14.2. MS: *m/z* calcd for C<sub>35</sub>H<sub>39</sub>N<sub>5</sub>O<sub>9</sub>Na [M+Na]<sup>+</sup>: 696.7; found: 696.2.

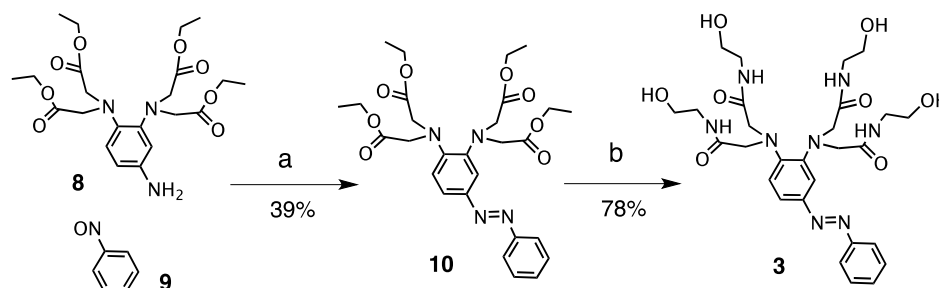
*trans*-**1.** Compound **7** (110 mg, 0.16 mmol) was added to a solution of dry acetonitrile (10 mL) and 2-aminoethanol (15 mL). The mixture was heated at 80 °C under N<sub>2</sub> for 2h. After cooling down to room temperature, the solvent and 2-aminoethanol were removed under vacuum. The residue was recrystallized in ethanol/ether to obtain compound **1** (44%) as a red solid. mp: 89-91 °C. <sup>1</sup>H NMR (DMSO-D<sub>6</sub>) δ 8.34 (d, *J* = 8.4 Hz, 2H), 8.19 (br, 4 H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.97 (d, *J* = 7.2 Hz, 2H), 7.63 (m, 3H), 7.37 (s, 1H), 7.34 (s, 1H), 4.66 (br, 4H), 4.12 (s, 4H), 4.04 (s, 4H), 3.30 (m, 8H), 3.09 (m, 8H); <sup>13</sup>C NMR (DMSO-D<sub>6</sub>) δ 170.5, 161.1, 153.4, 152.3, 147.3, 142.7, 141.3, 137.1, 132.5, 130.0, 129.4, 128.4, 123.9, 123.2, 111.5, 103.1, 60.1, 55.9, 41.8. HRMS: *m/z* calcd for C<sub>35</sub>H<sub>43</sub>N<sub>9</sub>O<sub>9</sub>Na [M+Na]<sup>+</sup>: 756.3081; found: 756.3080.



*trans*-**2.** 2-Aminophenol (180 mg, 1.29 mmol) and aldehyde **6** (180 mg, 0.86 mmol) were added to a solution of dry toluene (20 mL) and acetic acid (2 mL).

The mixture was stirred at room temperature for 10 min. After this time, BaMnO<sub>4</sub> (0.14 g, 0.54 mmol) was added and the mixture was heated at 80 °C under N<sub>2</sub> for 4h. After cooling down to room temperature, the solvent was removed under vacuum. The residue was purified by silica gel column

chromatography using DCM/petroleum ether (1/3, v/v) as the eluant affording 70 mg (0.23 mmol) of **2** (27%) as a yellow solid. mp: 135-137 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 8.46 (d, *J* = 8.4 Hz, 2H), 8.10 (d, *J* = 8.4 Hz, 2H), 8.00 (d, *J* = 7.2 Hz, 2H), 7.83 (m, 1H), 7.65 (m, 1H), 7.57 (m, 3H), 7.42 (m, 2H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 162.4, 154.2, 152.6, 151.0, 142.2, 131.7, 129.2, 129.1, 128.6, 125.5, 124.8, 123.4, 123.2, 120.2, 110.7. HRMS: *m/z* calcd for C<sub>19</sub>H<sub>14</sub>N<sub>3</sub>O [M+H]<sup>+</sup>: 300.1137; found: 300.1135.



Scheme S2. Synthesis of switch **3**: (a) **9**, THF, N<sub>2</sub>, rt, 18h; (b) 2-aminoethanol, MeCN, N<sub>2</sub>, 80 °C, 2.5 h.

**10**. Compound **8** (ref 3) (310 mg, 0.64 mmol) and nitrosobenzene **9** (200 mg, 1.87 mmol) were added to a solution of dry THF (15 mL) and acetic acid (1.5 mL). The mixture was stirred at room temperature under nitrogen for 18 h. Then the mixture was poured into 100 mL water and extracted with DCM (2 ×100 mL). The combined organic phase was dried and the solvent was removed under vacuum. The residue was purified by silica gel column chromatography using pentane/ethyl acetate (3/1, v/v) as the eluant affording 140 mg (39%) of compound **10** as a red oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 7.88 (d, *J* = 7.6 Hz, 2H), 7.72 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.52 (m, 3H), 7.16 (d, *J* = 8.4 Hz, 1H), 4.43 (s, 4H), 4.37 (s, 4H), 4.16 (m, 8H), 1.25 (t, *J* = 6.8 Hz, 12H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 170.7, 170.6, 152.8, 148.2, 144.4, 141.6, 130.3, 129.0, 122.6, 121.1, 119.2, 115.9, 60.7, 60.6, 52.4, 52.3, 14.2. MS: *m/z* calcd for C<sub>28</sub>H<sub>36</sub>N<sub>4</sub>O<sub>8</sub> [M+Na]<sup>+</sup>: 579.2; found: 579.1.

*trans*-**3**. Compound **10** (130 mg, 0.23 mmol) was added to a solution of dry acetonitrile (7 mL) and 2-aminoethanol (15 mL). The mixture was heated at 80 °C under N<sub>2</sub> for 2.5 h. After cooling down to room temperature, the solvent and 2-aminoethanol were removed under vacuum. The residue was purified by silica gel column chromatography using methanol/DCM (1/4, v/v) as the eluant affording 110 mg (78%) of compound **3** as a red oil. <sup>1</sup>H NMR (DMSO-D<sub>6</sub>) δ 8.27 (br, 2H), 8.21 (br, 2H), 8.19 (br, 4H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.58 (t, *J* = 8.0 Hz, 2H), 7.47 (m, 3H), 7.00 (d, *J* = 8.4 Hz 1H), 4.63 (br, 4H), 4.16 (s, 4H), 4.04 (s, 4H), 3.30 (m, 8H), 3.08 (m, 8H); <sup>13</sup>C NMR (DMSO-D<sub>6</sub>) δ 170.2, 152.6, 147.1, 145.3, 141.7, 131.0, 129.8, 122.6, 120.4, 118.7, 115.0, 60.1, 55.0, 54.6, 41.8, 41.7. HRMS: *m/z* calcd for C<sub>28</sub>H<sub>41</sub>N<sub>8</sub>O<sub>8</sub>Na [M+H]<sup>+</sup>: 617.3047; found: 617.3048.

## Photoswitching of *trans*-2

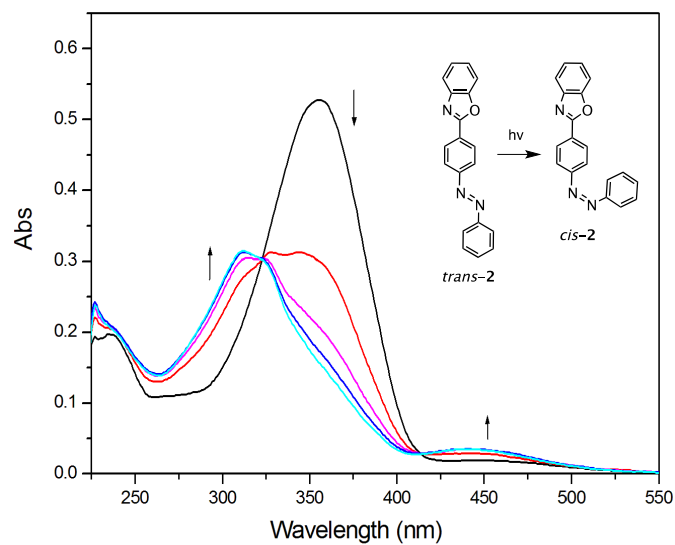


Fig. S1 UV-vis absorption spectral changes of *trans*-2 (15  $\mu$ M, DCM) upon irradiation at 365 nm.

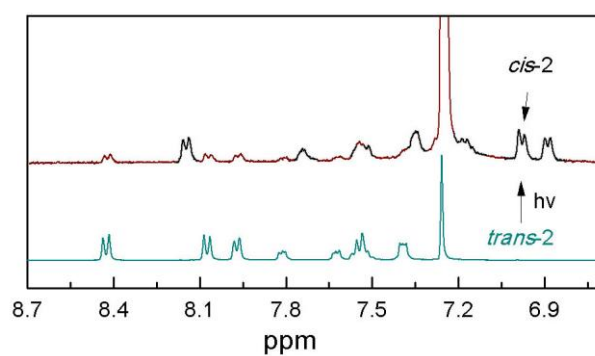


Fig. S2  $^1\text{H-NMR}$  (400 MHz) spectral changes of *trans*-2 (1 mM,  $\text{CDCl}_3$ ) upon irradiation at 365 nm. Resonance signals of *cis*-2 are marked in black.

## Thermoisomerization of *cis*-1 and complex *cis*-1-Hg<sup>2+</sup>

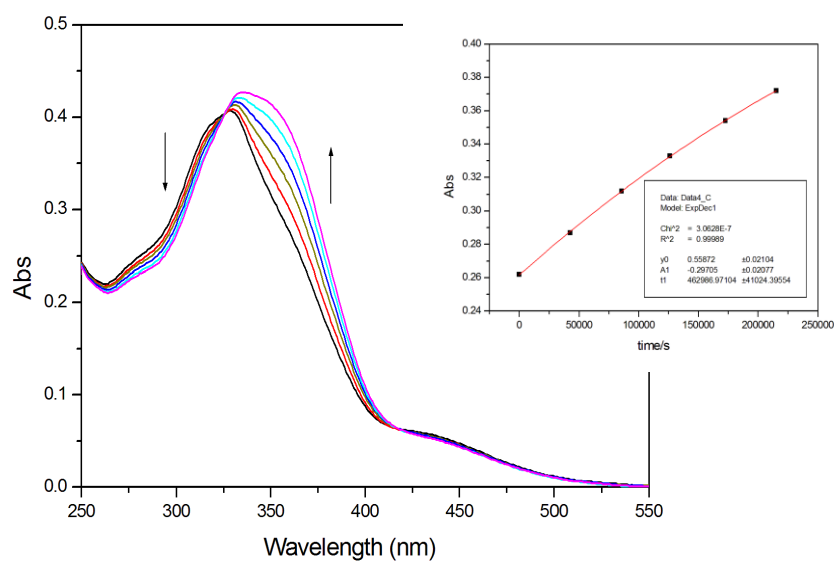


Fig. S3 Thermo *cis*-to-*trans* transformation of *cis*-1-Hg<sup>2+</sup> in phosphate (8.0 mM) buffered H<sub>2</sub>O/ethanol solution (v/v, 8/2, pH = 7.5) at 25 °C. Inset: time dependent absorption changes at 365 nm ( $t_{1/2} = 89$  h).

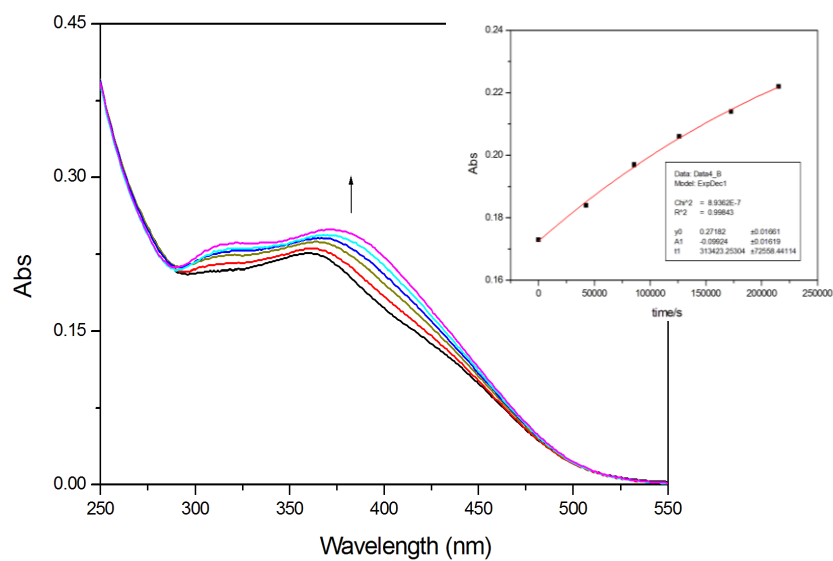


Fig. S4 Thermo *cis*-to-*trans* transformation of *cis*-1 in phosphate (8.0 mM) buffered H<sub>2</sub>O/ethanol solution (v/v, 8/2, pH = 7.5) at 25 °C. Excess of EDTA (200 eq of **1**) was added to the *cis*-1-Hg<sup>2+</sup> solution to yield *cis*-1. Inset: time dependent absorption changes at 400 nm ( $t_{1/2} = 60$  h).

## Photoswitching of compound 3 and its mercury complex

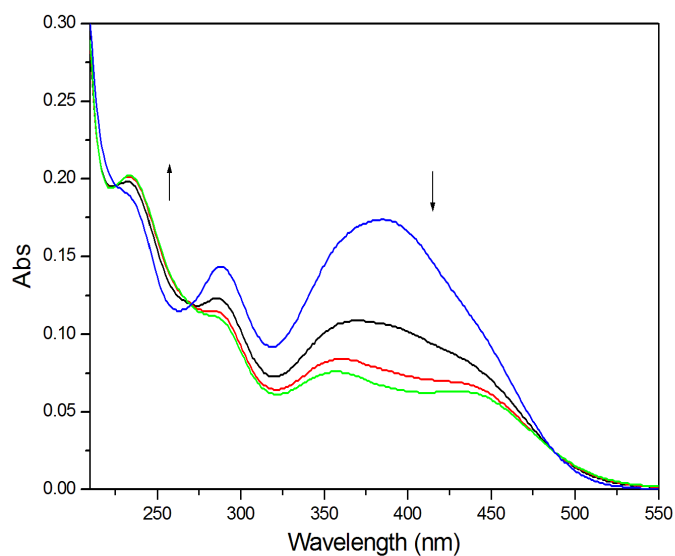


Fig. S5 UV-vis absorption spectral changes of *trans*-3 (26 μM) in H<sub>2</sub>O/ethanol solution (v/v, 8/2) upon irradiation at 400 nm.

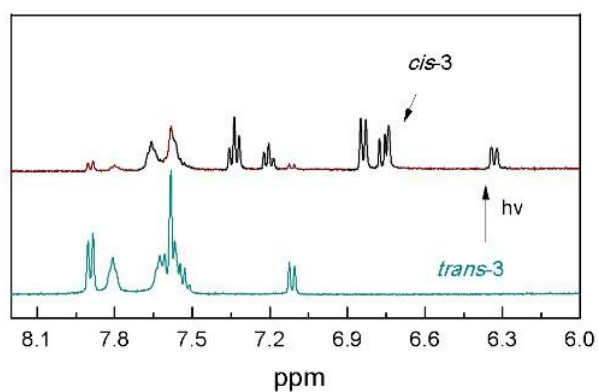


Fig. S6 <sup>1</sup>H-NMR (400 MHz) spectral changes of *trans*-3 (1 mM, CD<sub>3</sub>CN) upon irradiation at 400 nm. Resonance signals of *cis*-3 are marked in black.

Note: Half-life for thermo *cis*-to-*trans* isomerization of *cis*-3 in H<sub>2</sub>O/ethanol solution (v/v, 8/2) at 25 °C was determined to be 5.6 min (spectral data not shown). In acetonitrile, the half-life is significantly longer ( $t_{1/2} = 9.6$  h). It is known that thermo *cis*-to-*trans* isomerization of 4-dimethylaminoazobenzene derivative is faster than unmodified azobenzene (~ 2 days) and more sensitive to the polarity and pH of the solution (ref 4, 5).

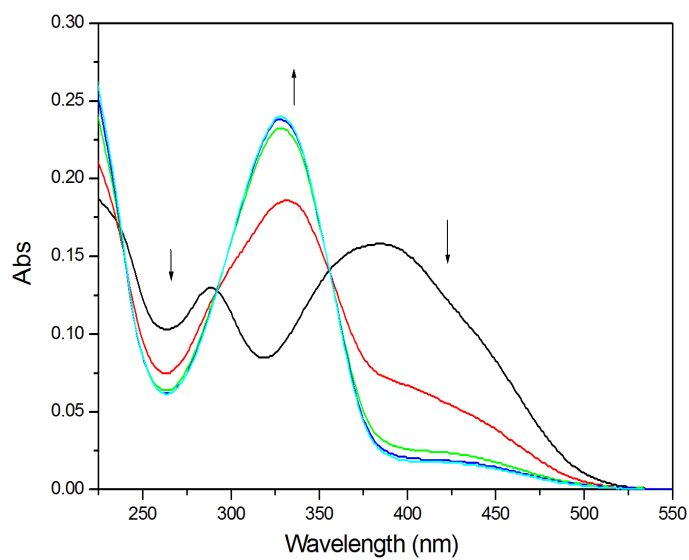


Fig. S7 UV-vis absorption spectral changes of *trans-3* (25  $\mu\text{M}$ ) in  $\text{H}_2\text{O}$ /ethanol solution (v/v, 8/2) upon titration with  $\text{Hg}^{2+}$  ion (4 eq).

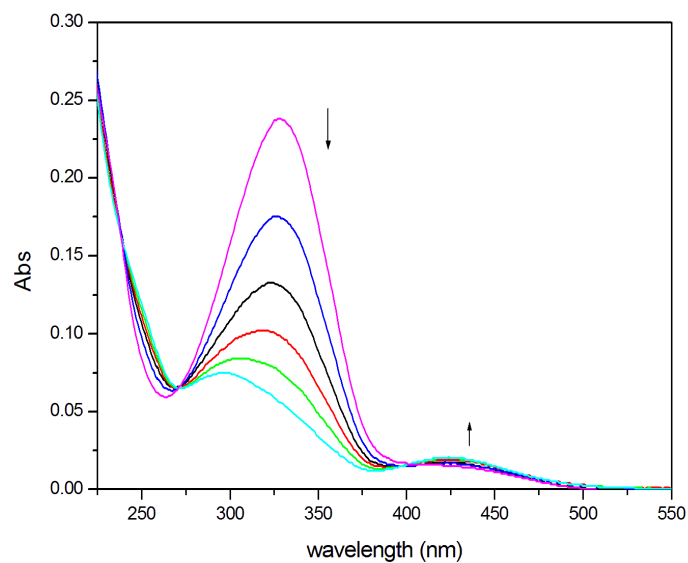


Fig. S8 UV-vis absorption spectral changes of complex *trans-3*- $\text{Hg}^{2+}$  (25  $\mu\text{M}$ , 4 eq of  $\text{Hg}^{2+}$  added) in  $\text{H}_2\text{O}$ /ethanol solution (v/v, 8/2) upon irradiation at 320 nm.

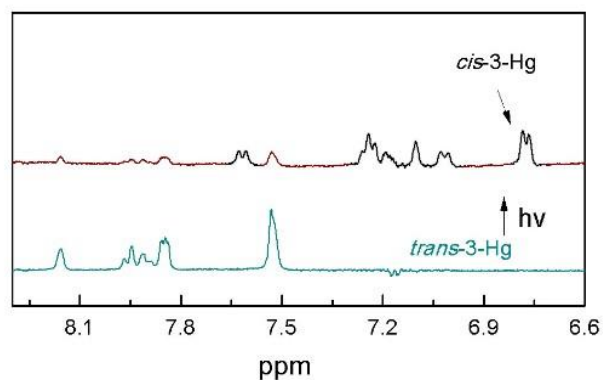


Fig. S9  $^1\text{H-NMR}$  (400 MHz) spectral changes of complex  $\text{trans-3-Hg}^{2+}$  (0.5 mM,  $\text{D}_2\text{O/ethanol-D}_6$ , v/v, 8/2) upon irradiation at 400 nm. Resonance signals of complex  $\text{cis-3-Hg}^{2+}$  are marked in black. Excess of  $\text{Hg}^{2+}$  ion (8 eq) was added to obtain the complex.

### DFT calculations

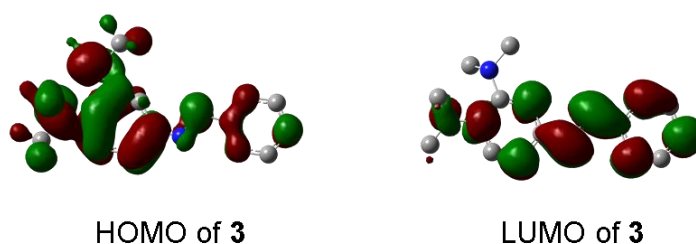


Fig. S10 Kohm-Sham frontier orbitals of **3** calculated at the B3LYP/6-31G\* level of theory (isovalue = 0.02). The receptor of **3** was simplified as tetramethyl-1,2-diamino benzene.

Note: compared with switch **1** (see Figure 5 in main text), the HOMO-LUMO orbitals of  $\text{trans-3}$  were less separated in space, suggesting a substantial contribution of  $\pi\text{-}\pi^*$  excitation to the electronic transitions.

**Table S1.** Summary of TD-DFT calculation for switch **1** and **2** at the  $S_0$  structure at the CAM-B3LYP/6-31G\* level.

| Compound | Transition       | Calculation     |             |                     |
|----------|------------------|-----------------|-------------|---------------------|
|          |                  | Wavelength (nm) | Energy (eV) | Oscillator strength |
| 1        | $S_0\text{-}S_1$ | 457.56          | 2.7097      | 0.0000              |
|          | $S_0\text{-}S_2$ | 352.65          | 3.5158      | 1.5065              |
|          | $S_0\text{-}S_3$ | 289.20          | 4.2871      | 0.1488              |
|          | $S_0\text{-}S_4$ | 272.51          | 4.5498      | 0.0103              |
|          | $S_0\text{-}S_5$ | 266.93          | 4.6448      | 0.0143              |
| 2        | $S_0\text{-}S_1$ | 459.00          | 2.7012      | 0.0000              |



|                                |        |        |        |
|--------------------------------|--------|--------|--------|
| S <sub>0</sub> -S <sub>2</sub> | 327.28 | 3.7883 | 1.5336 |
| S <sub>0</sub> -S <sub>3</sub> | 267.60 | 4.6331 | 0.0152 |
| S <sub>0</sub> -S <sub>4</sub> | 263.72 | 4.7013 | 0.0143 |
| S <sub>0</sub> -S <sub>5</sub> | 257.68 | 4.8115 | 0.0076 |

| Compound | Transition                     | Coefficient of orbital |            |            |            |            |            |           |
|----------|--------------------------------|------------------------|------------|------------|------------|------------|------------|-----------|
| 1        | S <sub>0</sub> -S <sub>1</sub> | HOMO-3                 | HOMO-3     | HOMO-3     |            |            |            |           |
|          |                                | ->LUMO                 | ->LUMO+1   | ->LUMO+6   |            |            |            |           |
|          |                                | (0.66449)              | (0.18688)  | (-0.13794) |            |            |            |           |
|          | S <sub>0</sub> -S <sub>2</sub> | HOMO-2                 | HOMO-1     | HOMO       | HOMO       |            |            |           |
|          |                                | ->LUMO                 | ->LUMO     | ->LUMO     | ->LUMO+1   |            |            |           |
|          |                                | (-0.27378)             | (0.12144)  | (0.60155)  | (-0.18025) |            |            |           |
|          | S <sub>0</sub> -S <sub>3</sub> | HOMO-2                 | HOMO-1     | HOMO-1     | HOMO       | HOMO       | HOMO       |           |
|          |                                | ->LUMO                 | ->LUMO     | ->LUMO+1   | ->LUMO     | ->LUMO+1   | ->LUMO+4   |           |
|          |                                | (0.43862)              | (-0.37846) | (0.11672)  | (0.20517)  | (-0.23086) | (-0.11751) |           |
|          | S <sub>0</sub> -S <sub>4</sub> | HOMO-6                 | HOMO-4     | HOMO-2     | HOMO-1     | HOMO-1     | HOMO       |           |
|          |                                | ->LUMO                 | ->LUMO     | ->LUMO     | ->LUMO     | ->LUMO+1   | ->LUMO+4   |           |
|          |                                | (-0.19996)             | (-0.18795) | (0.37362)  | (0.40767)  | (-0.22653) | (0.11353)  |           |
|          | S <sub>0</sub> -S <sub>5</sub> | HOMO-7                 | HOMO-6     | HOMO-2     | HOMO-2     | HOMO-1     | HOMO-1     | HOMO      |
|          |                                | ->LUMO                 | ->LUMO     | ->LUMO     | ->LUMO+2   | ->LUMO     | ->LUMO+1   | ->LUMO+2  |
|          |                                | (-0.13097)             | (0.56100)  | (0.13343)  | (-0.16951) | (0.17180)  | (-0.11787) | (0.15868) |
| 2        | S <sub>0</sub> -S <sub>1</sub> | HOMO-1                 | HOMO-1     | HOMO-1     |            |            |            |           |
|          |                                | ->LUMO                 | ->LUMO+1   | ->LUMO+6   |            |            |            |           |
|          |                                | (0.66071)              | (0.20111)  | (-0.13858) |            |            |            |           |
|          | S <sub>0</sub> -S <sub>2</sub> | HOMO-2                 | HOMO-2     | HOMO       |            |            |            |           |
|          |                                | ->LUMO                 | ->LUMO+1   | ->LUMO     |            |            |            |           |
|          |                                | (0.16053)              | (0.10064)  | (0.66084)  |            |            |            |           |
|          | S <sub>0</sub> -S <sub>3</sub> | HOMO-6                 | HOMO-5     | HOMO-2     | HOMO       |            |            |           |
|          |                                | ->LUMO+2               | ->LUMO     | ->LUMO     | ->LUMO+2   |            |            |           |
|          |                                | (0.12463)              | (0.61959)  | (0.11568)  | (0.23897)  |            |            |           |
|          | S <sub>0</sub> -S <sub>4</sub> | HOMO-4                 | HOMO-4     | HOMO-2     | HOMO       |            |            |           |
|          |                                | ->LUMO                 | ->LUMO+1   | ->LUMO+3   | ->LUMO+3   |            |            |           |
|          |                                | (0.60870)              | (0.20346)  | (-0.13076) | (-0.12744) |            |            |           |
|          | S <sub>0</sub> -S <sub>5</sub> | HOMO-4                 | HOMO-3     | HOMO-2     | HOMO       | HOMO       |            |           |
|          |                                | ->LUMO                 | ->LUMO     | ->LUMO     | ->LUMO     | ->LUMO+1   |            |           |
|          |                                | (-0.12463)             | (-0.38906) | (0.42875)  | (-0.11883) | (0.28362)  |            |           |

## Reference

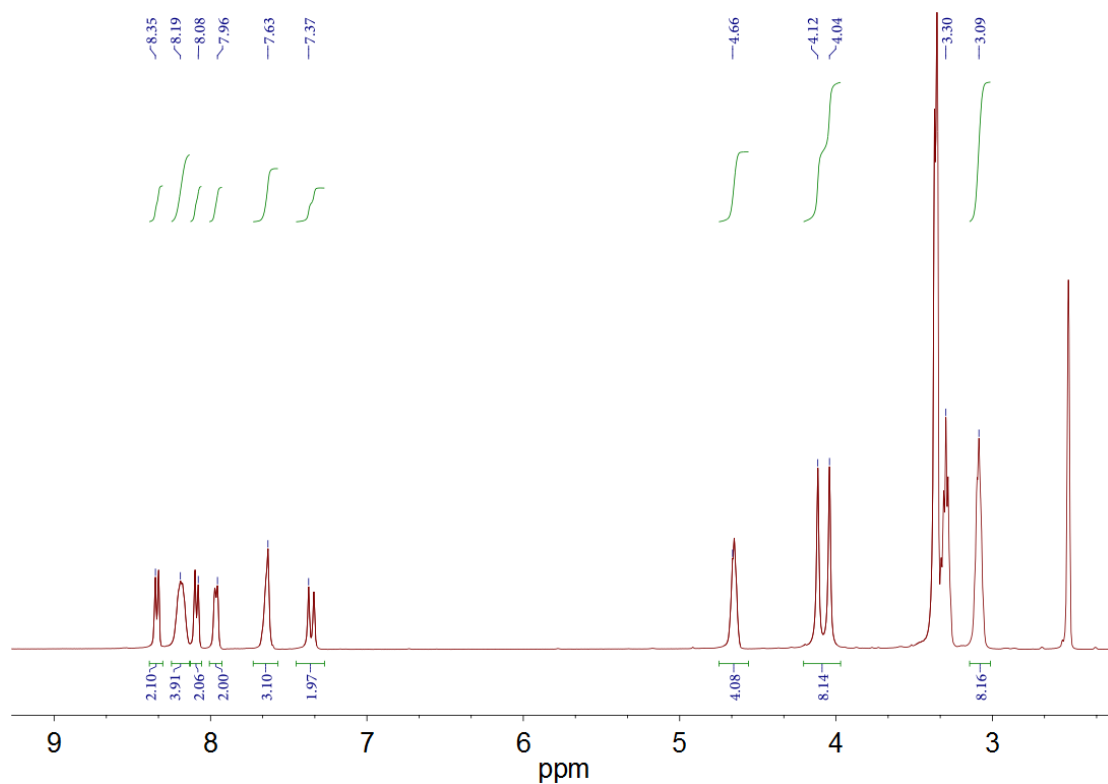
- (1) J. Wang, X. Qian, J. Qian and Y. Xu *Chem. Eur. J.* 2007, **13**, 7543.
- (2) Y. Kim, M. Koh, D.-K. Kim, H.-S. Choi and S. B. Park, *J. Comb. Chem.* 2009, **11**, 928.
- (3) Y. Liu, X. Dong, J. Sun, C. Zhong, B. Li, X. You, B. Liu and Z. Liu, *Analyst* 2012, **137**, 1837.

(4) H. M. D. Bandara and S. C. Burdette, *Chem. Soc. Rev.* 2012, **41**, 1809.

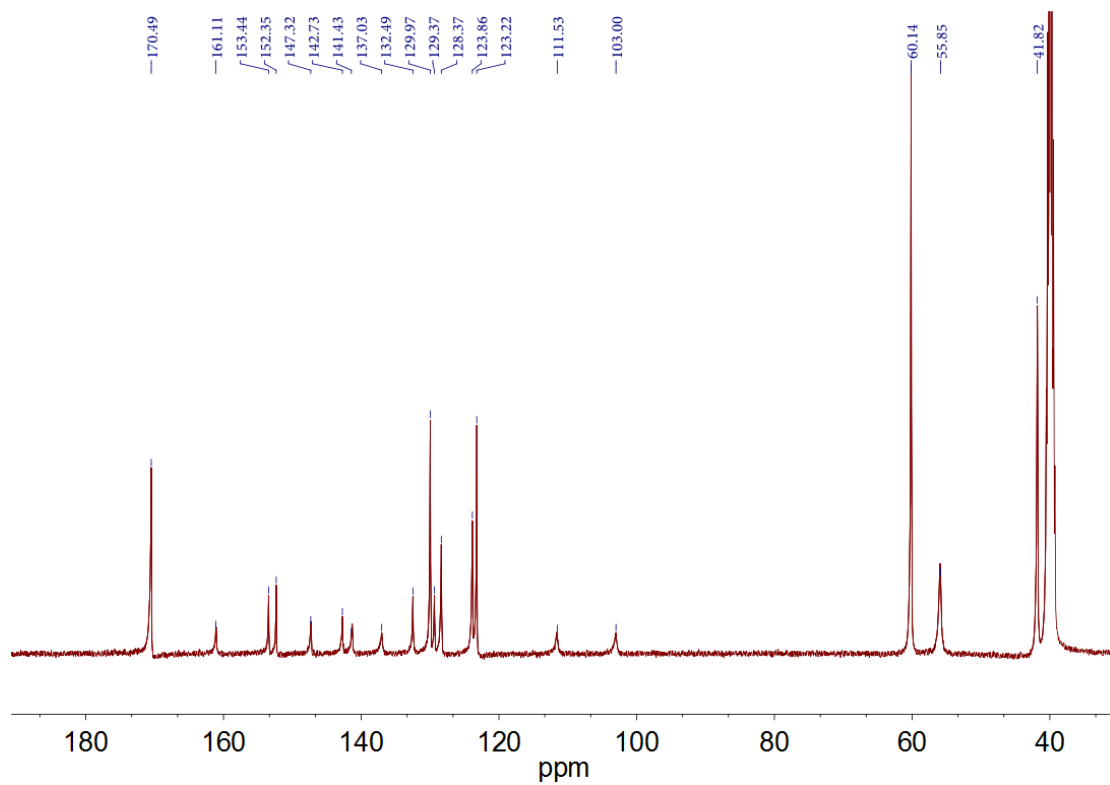
(5) E. Fischer and Y. Frei, *J. Chem. Phys.* 1957, **27**, 328.

## NMR Spectra

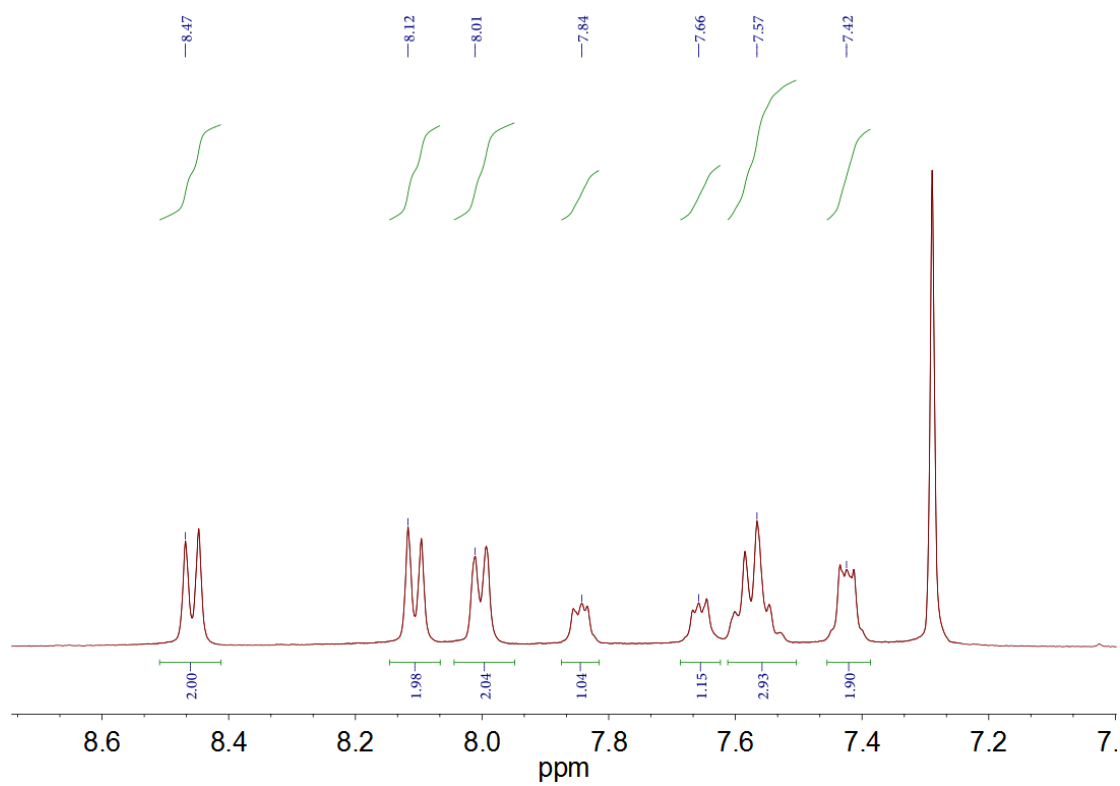
$^1\text{H}$  NMR spectrum of *trans*-**1**



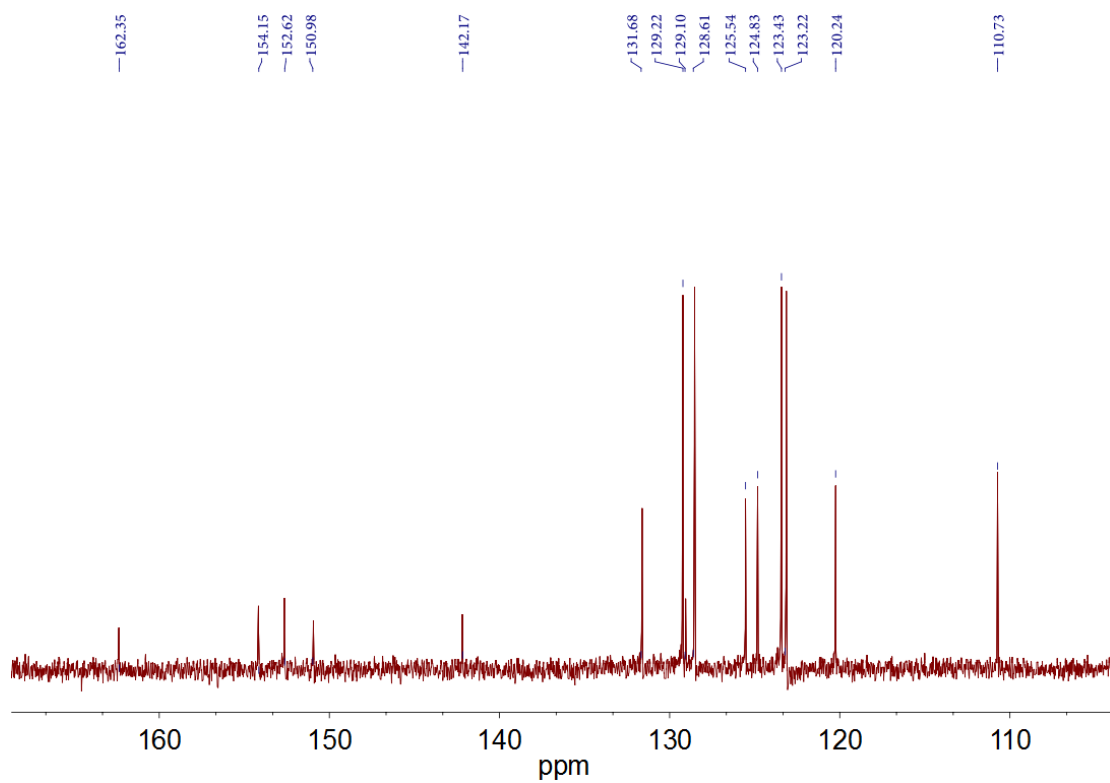
$^{13}\text{C}$  NMR spectrum of *trans*-**1**



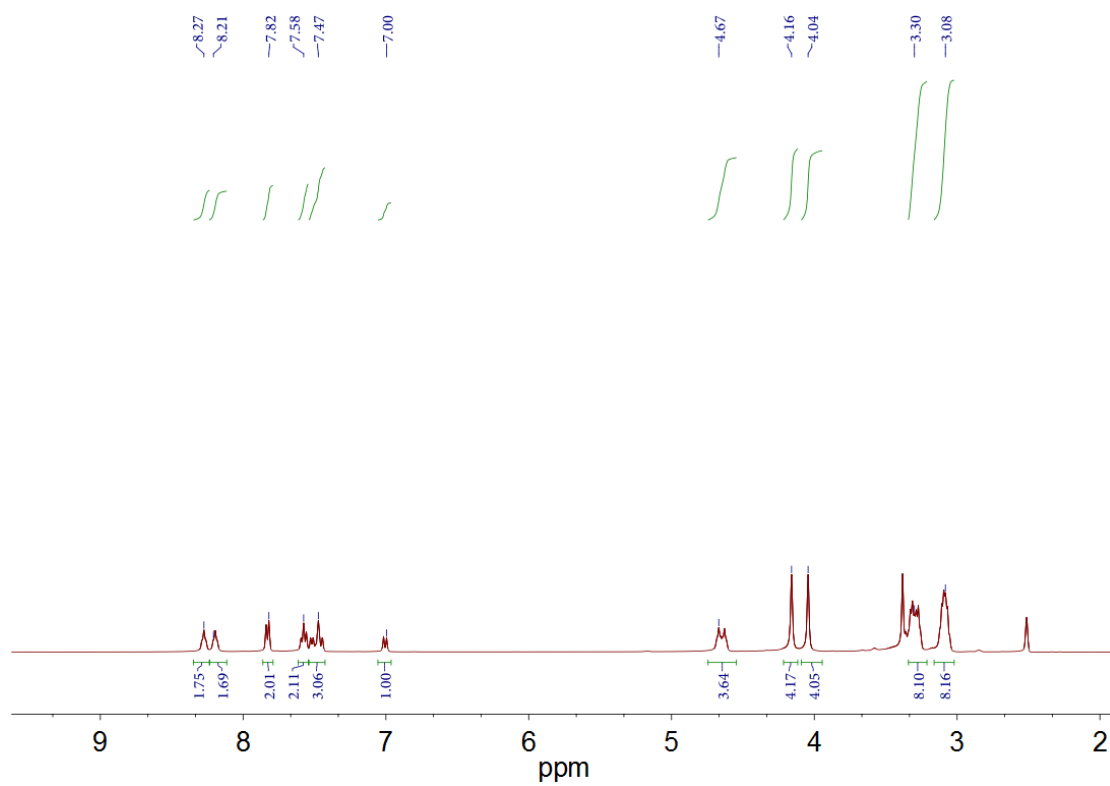
<sup>1</sup>H NMR spectrum of *trans*-2



<sup>13</sup>C NMR spectrum of *trans*-2



$^1\text{H}$  NMR spectrum of *trans*-3



$^{13}\text{C}$  NMR spectrum of *trans*-3

