Supporting Information

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1. Experimental Section

General:

Unless otherwise noted, materials were obtained from commercial suppliers and were used without further purification. Thin layer chromatography (TLC) analysis of reaction mixtures was performed on Dynamic adsorbents silica gel F-254 TLC plates. Fluorescence emission spectra were obtained using Shimadzu RF-5301 PC Spectrofluorophotometer. UV-vis absorption spectra were obtained on Beijing purkinje TU-1810. CD spectra recorded on Bio-logic MOS-450 instrument. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were recorded with Bruker Avance-III 600 spectrometers. Chemical shifts were reported in units (ppm) and all coupling constants (*J* values) were reported in Hertz (Hz). High resolution mass spectra were obtained using Bruker micrOTOF-Q instrument with an ESI source. All the experiments were performed at 20℃ unless otherwise noted.

For all the measurements, the solutions of compounds and DNA were freshly prepared before use. DNA concentration was reported as the duplex concentration, unless otherwise specifically notified. For UV-vis, fluorescence, CD and ^{1}H NMR titrations, the stock solutions of target compound were prepared by dissolving them in DMSO (5 mM, 5 mM, 1 mM and 10 mM respectively). UV-vis and fluorescent DNA titrations were carried out in 1 mM PBS buffer (pH=7.3), containing 9 mM KCl, 5% DMSO, 5% methanol. For fluorescence titration, excitation wavelength was 299 nm, slit widths: 3 nm (Ex.), 3 nm (Em.))

. Before the spectra were recorded, the sample solutions were mixed for 2 minute after each addition of DNA. All the experiments were repeated for 3 times at least.

DNA preparation:

All DNA were purchased from General Biosystems, Inc.

For DNA double strand, two complementary strands were dissolved and mixed in PBS buffer(10 mM PBS buffer, 10 mM KCl, pH 7.3), heated to 95℃ for 5 minutes and slowly cooled to room temperature to form the duplex. The volume of the solution was adjusted to a final concentration of 2.0 mM/duplex.

The sequence of DNA, which were studied in this work:

12AT: 5′-AAAAAAAAAAAA-3′; 5′-TTTTTTTTTTTT-3′

12GC: 5′-GGGGGGGGGGGG-3′; 5′-CCCCCCCCCCCC-3′;

DrawAT (6AT base pairs): 5′-CGCGAAATTTCGCG-3′

8AT (8AT base pairs): 5′-CGCGAAAATTTTCGCG-3′

Quantum yield calculation:

The quantum yield of **2** in water by a relative comparison procedure using quinine as standard (Φ = 0.54 in 0.05 M sulfuric acid): Φ = 0.07.

The general equation used in the determination of relative quantum yields is as follows: $\Phi_u = (\Phi_s \times F_u \times A_s \times \eta_u^2)/(F_s \times A_u \times \eta_s^2)$. where Φ is the quantum yields, F is the integrated area under the corrected emission spectrum, A is the absorbance at the excitation wavelength, λ_{ex} is the excitation wavelength, η is the refractive index of the solution and the subscripts 'u' and 's' refer to the unknown and the standard, respectively.

^{1}H-NMR Titration Spectra

Sample preparation: The two complementary strands were dissolved and mixed in 10 mM PBS buffer (pH 7.3) containing 50 mM NaCl, 1 mM EDTA, heated to 95 ^{o}C for 5 minutes and slowly cooled to room temperature to form the duplex. The sample was lyophilized once from water, twice from 99.9% D_2O and then redissolved in 400 μL deuterated solvents (200 μL DMSO-d_6, 40 μL D_2O, 160 μL CD_3OD) and perform the NMR titration at 20^{o}C. For 2D NOESY NMR, T_m is 100 ms.

Binding Association constants

K_a was determined by a nonlinear least-squares analysis of ***Y*** versus ***x*** using the following equation (1) for 1:1 stoichiometry binding[1]:

$$Y = \frac{m \times x}{n + x} \quad (1)$$

Where **x** is guest concentration, $\boldsymbol{K_a}$ is 1/n.

Stern-volmer equation (3): where F and F_0 are the fluorescence intensity of quantum dots in solution without and with a given concentration of guests, respectively.

$$\frac{F}{F_0} = 1 + k \times x \quad (2)$$

Slope is the k.

Molecular Models:

Conformation analyses of **2** was optimized by means of the computer program SPARTAN'14 for windows (V1.1.4, Wavefunction Inc. 18401 Von Karman Avenue, Suite 370 Irvine, CA 92612) on a PC equip with Pentium IV (RAM: 4G).

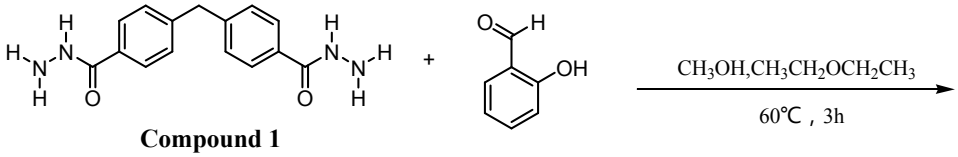
Following the methods[2], conformation search of **2** was carried out using Molecular Mechanics Force Field (MMFF) to give a few optimized low-energy geometries, which were further optimized using the semi-empirical method at PM_3 level. The final optimized low-energy conformation of **2** was listed in **Figure 6.**

CD Titration Spectra

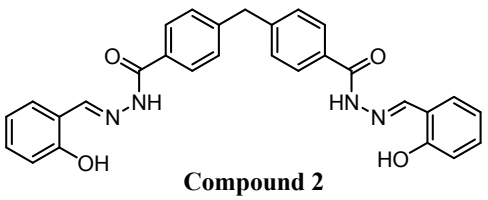
The measurements were performed at 25 °C (1 mM PBS buffer, 9 mM KCl, 5% DMSO, 5% methanol, pH 7.3). The CD spectrum of 12AT (20 μM) and its complexes with **2** were scanned from 200 to 400 nm, respectively.

Synthesis method：

Synthesis of Compound **2** and the control compound (monomer)：



Compound 1



Compound 2

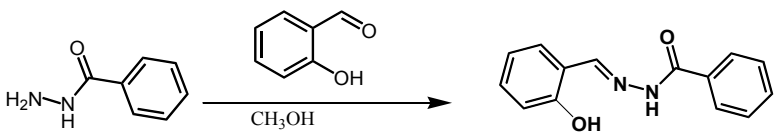
Compound 2： 13 mg compound **1** and 22.3 mg salicylaldehyde were dissolved in 4 mL methanol and 4 mL aether and then heated at 80℃ for 3 h. Afterwards, the mixture was cooled and washed with methanol，DCM and petroleum ether for 2 times.，to give 16.5 mg **2**. White solid, Yield 73.5%.

^{1}H NMR (600 MHz, DMSO-d_6) δ 12.05 (s, 1H), 11.30 (s, 1H), 8.63 (s, 1H), 7.89 (d, J = 8.1 Hz, 2H), 7.54 (d, J = 7.5 Hz, 1H), 7.44 (d, J = 7.9 Hz, 2H), 7.30 (t, J = 7.7 Hz, 1H), 6.94 (d, J = 8.1 Hz, 2H), 6.92 (d, J = 7.5 Hz, 1H), 4.13 (s, 1H)；

^{13}C NMR (151 MHz, DMSO-d_6) δ 163.0, 157.8, 148.5, 145.3, 131.7, 131.1, 129.8, 129.3, 128.3, 119.7, 119.0, 116.7, 41.0；

HRMS(ESI): m/z :$[M+Na]^+$ calc.:515.1690;found:515.1695.

The control compound (monomer):



Control Compound
(Monosalicylaldehyde hydrazone)

This control compound is not new and it was synthesized based on the literature[3]

^{1}H NMR (600 MHz, DMSO-d_6) δ 12.11 (s, 1H), 11.29 (s, 1H), 8.65 (s, 1H), 7.95-7.94 (d, J = 6 Hz, 2H), 7.63-7.60 (t, J_1 =J_2= 6 Hz 1H), 7.55 (sbr, J = 7.9 Hz, 2H), 7.32-7.30 (t, J_1 =J_2= 6 Hz, 1H), 6.95-6.92 (m, 2H), 6.92 (d, J = 7.5 Hz, 1H);

2. Various Spectra

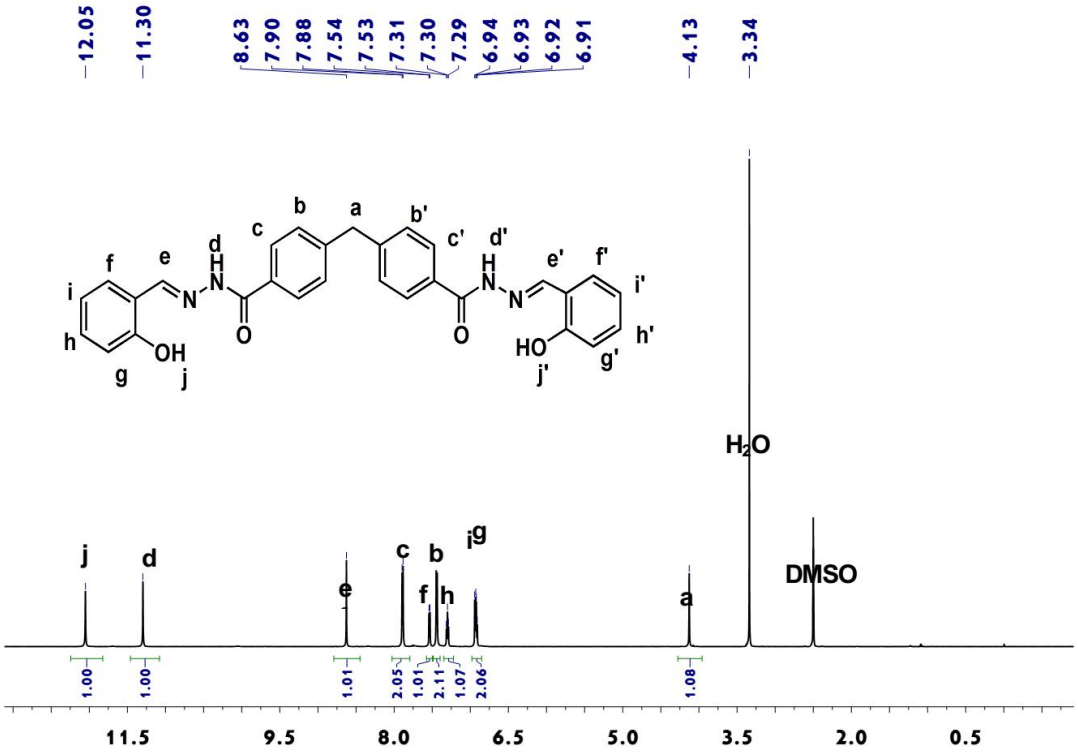


Figure S1. ^{1}H NMR of **Compound 2**(600 MHz, DMSO-d_6) at 20 ^{o}C

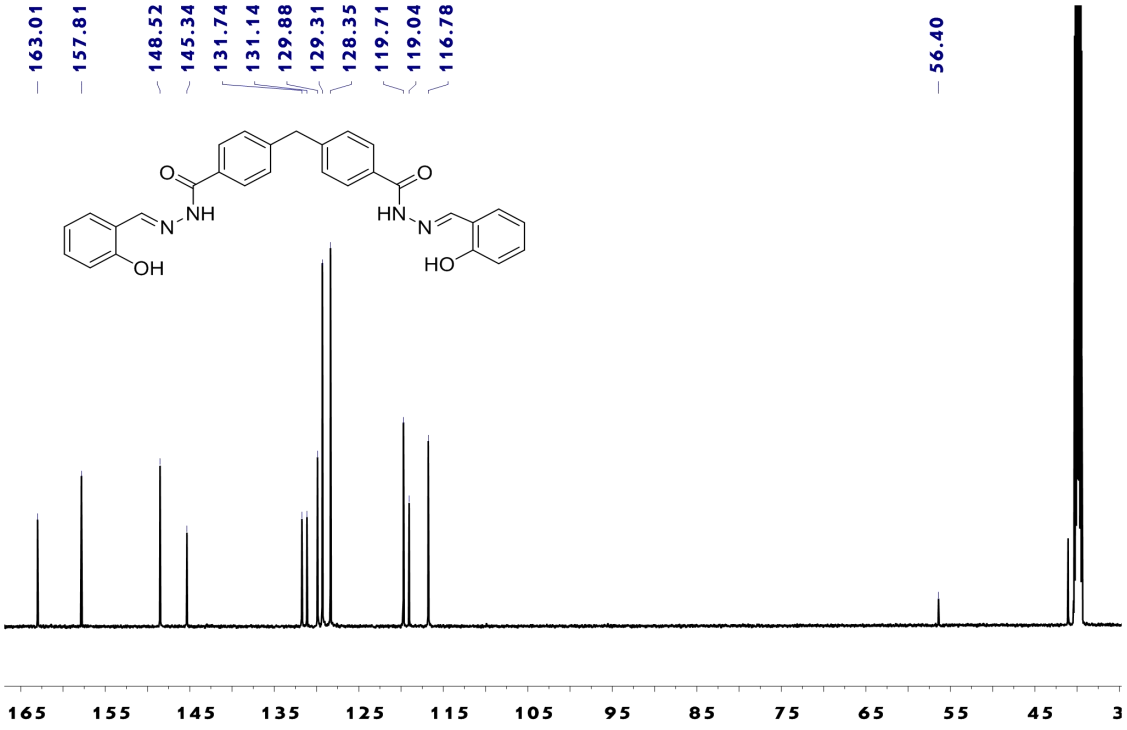


Figure S2. ^{13}C NMR of **Compound 2** (150 MHz, DMSO-d_6) at 20 ºC

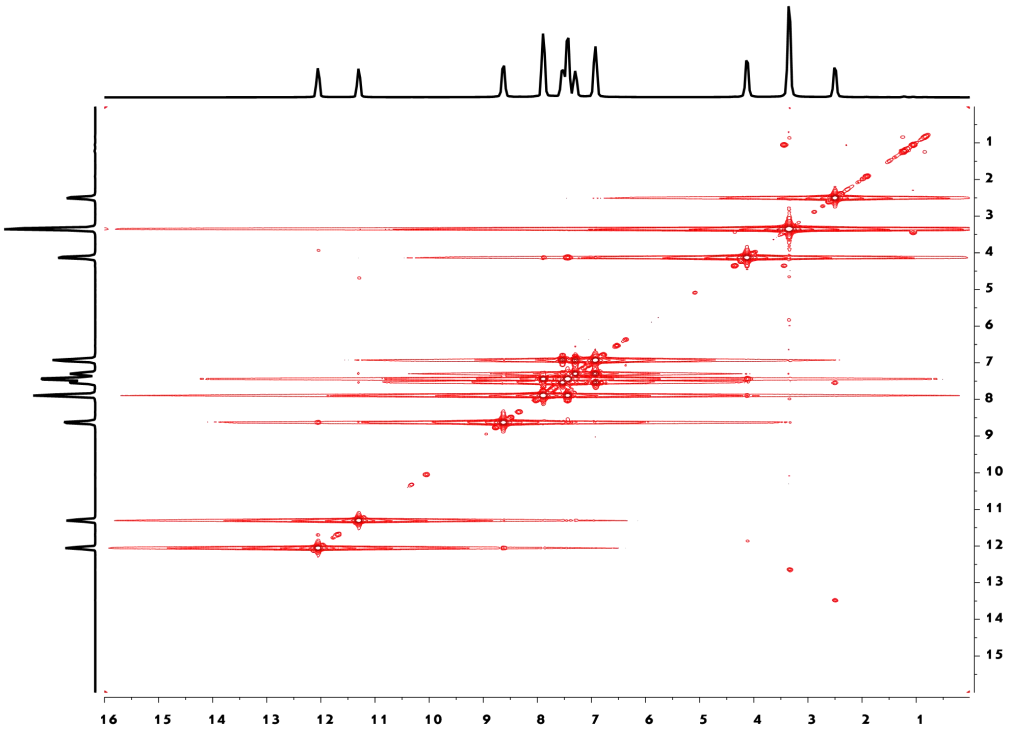


Figure S3. 2D COSY spectrum of **2** (600 MHz, DMSO-d*6*,20℃)

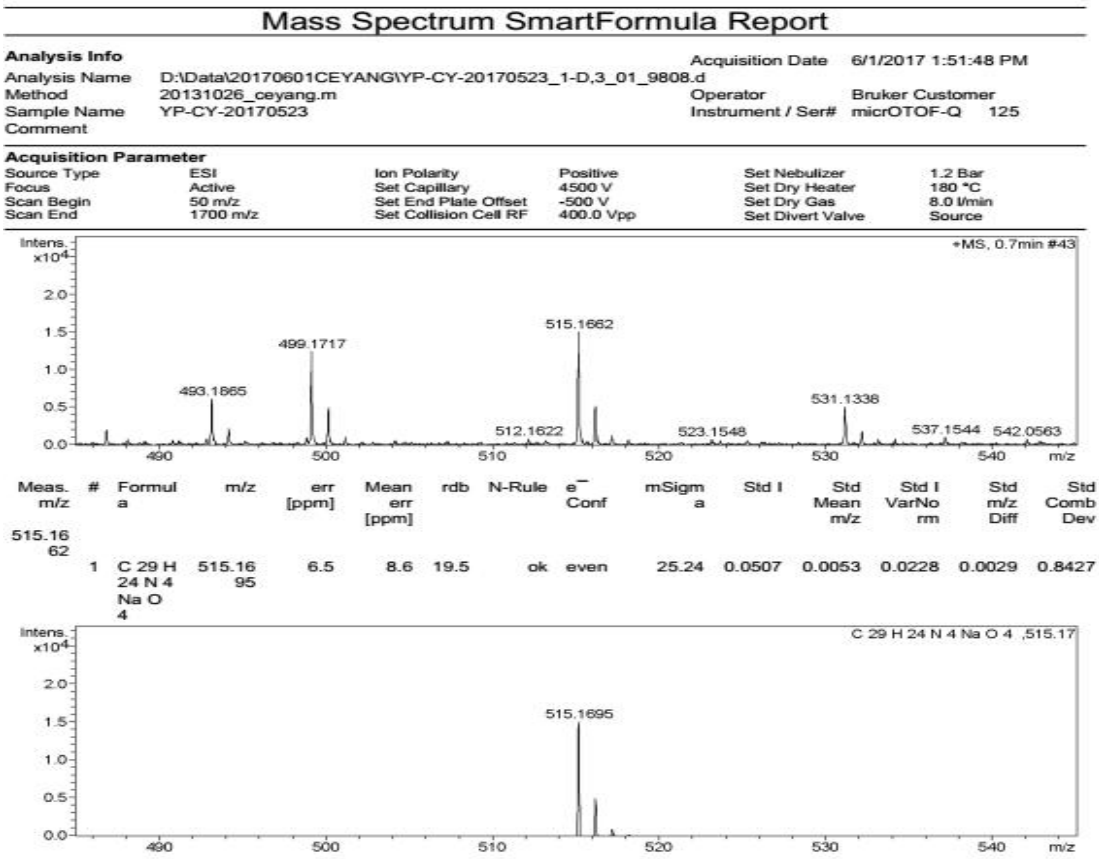


Figure S4. HRMS of **Compound 2**

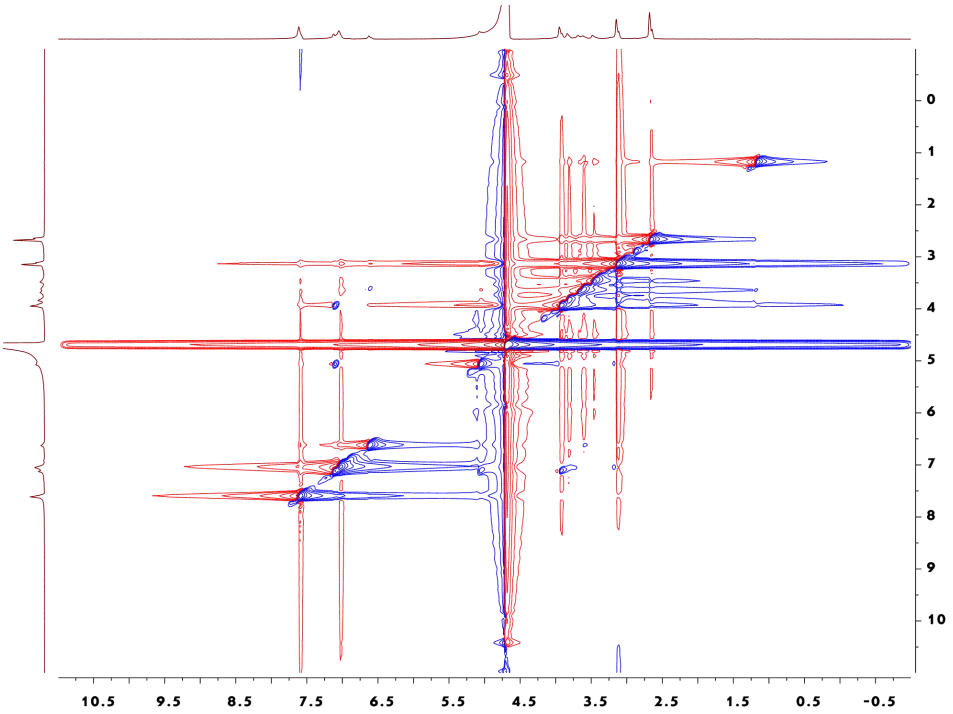


Figure S5. 2D NOESY spectrum of calix[4]carbazole/**1** complexes(600 MHz, DMSO-*d6*/D_2O/CD_3OD = 3/1/5, *V*/*V*/*V*, 20 ℃)

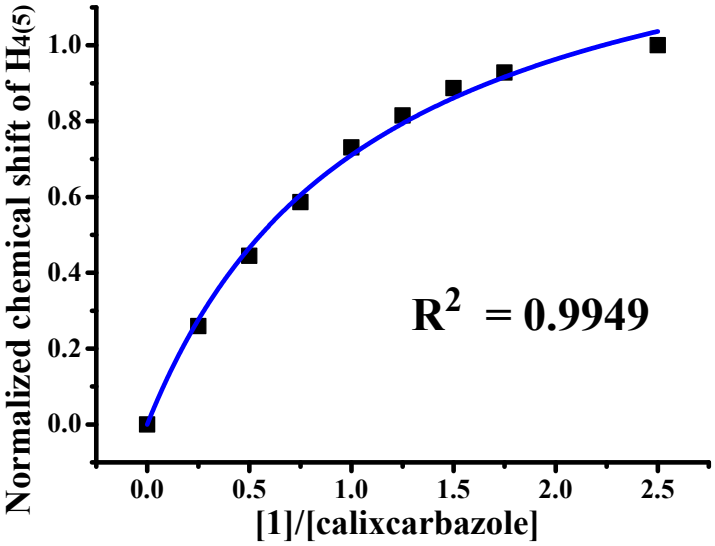


Figure S6 Fitted curve of the normalized chemical shift of $\mathbf{H_{4(5)}}$ as a function of [**1**]/[**calix4carbazole**]

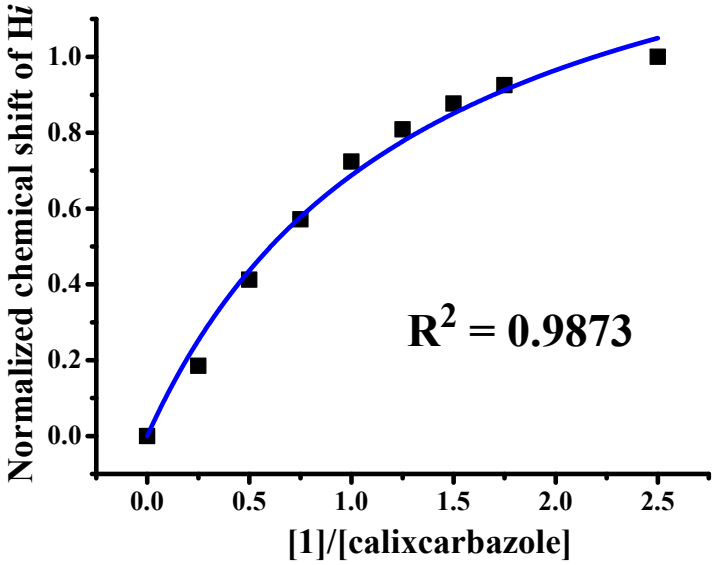


Figure S7 Fitted curve of the normalized chemical shift of $\mathbf{H}_i$ as a function of [**1**]/[**calix4carbazole**]

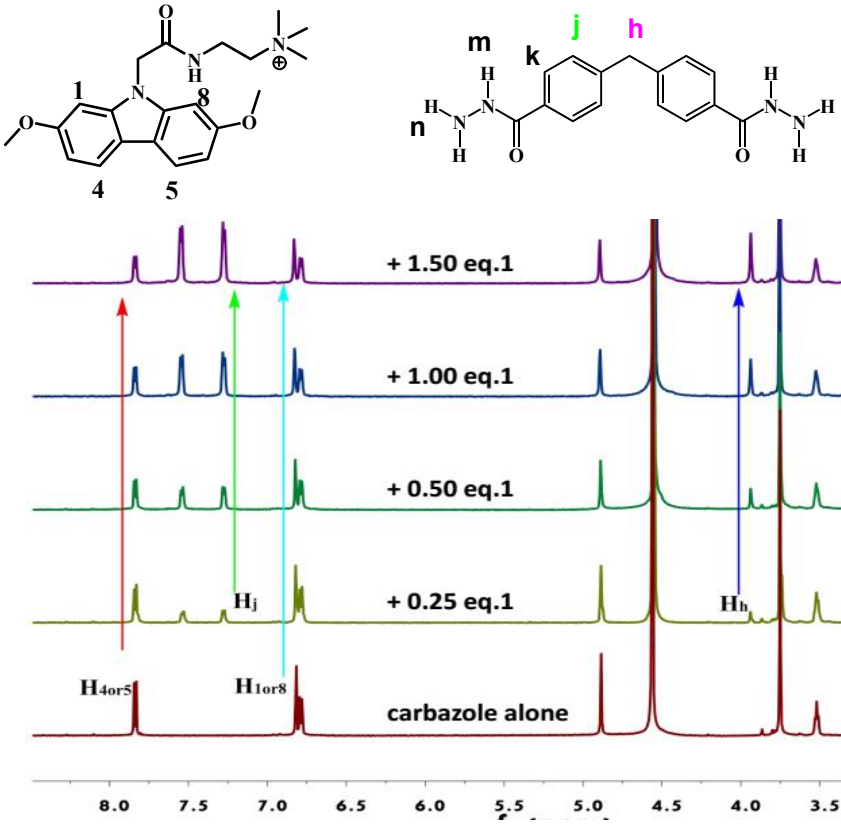


Figure S8. [1]HNMR spectra of carbazole monomer upon addition of **1**

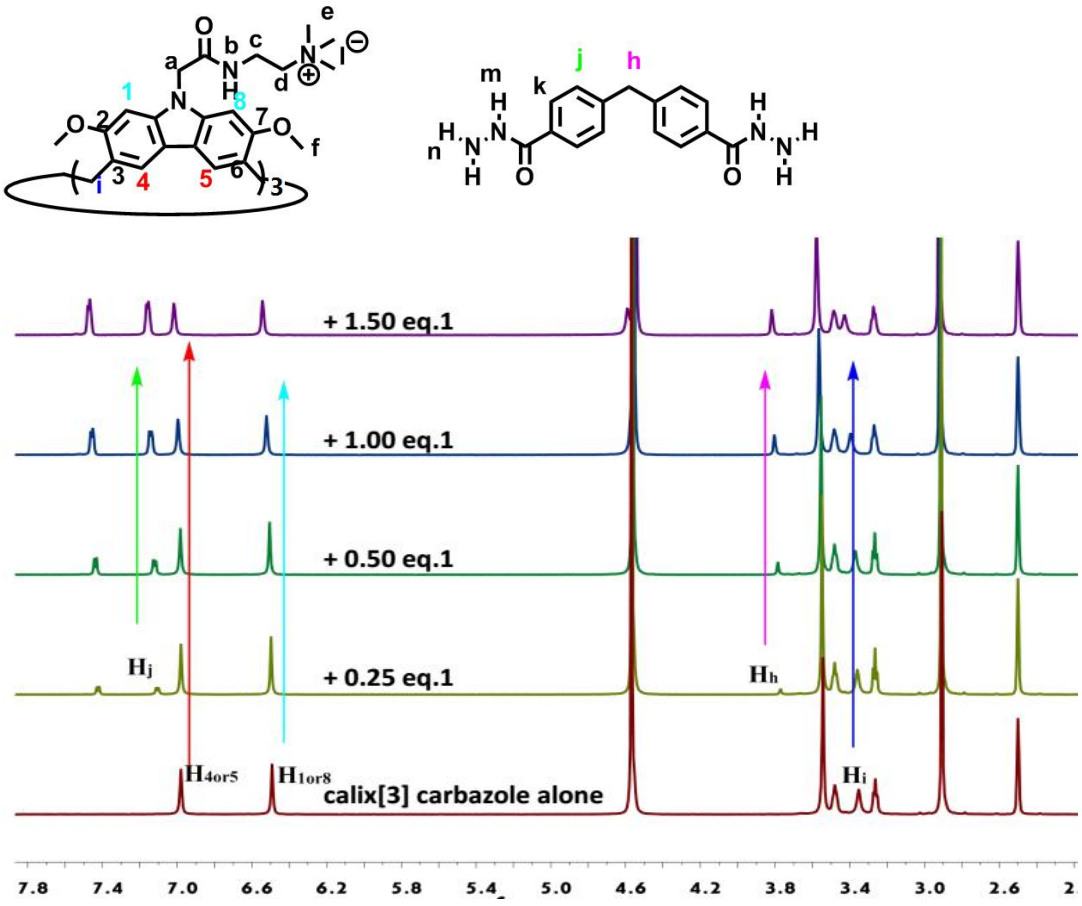


Figure S9.[1]HNMR spectra of calix[3]carbazole upon addition of **1**

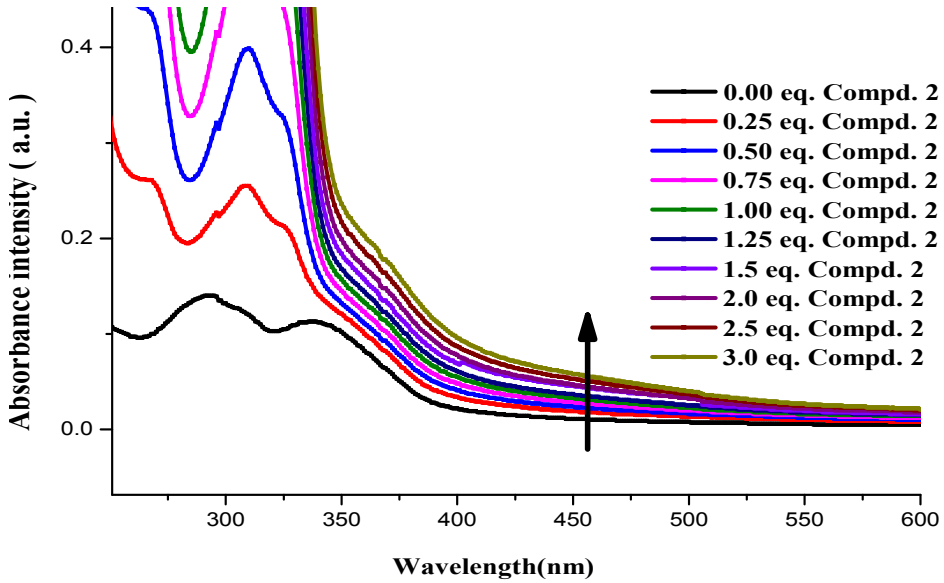


Figure S10. UV-vis spectra of calix[4]carbazole (10 μM) upon addition of **2** in 10 mM PBS buffer, DMSO<1%, pH=7.35

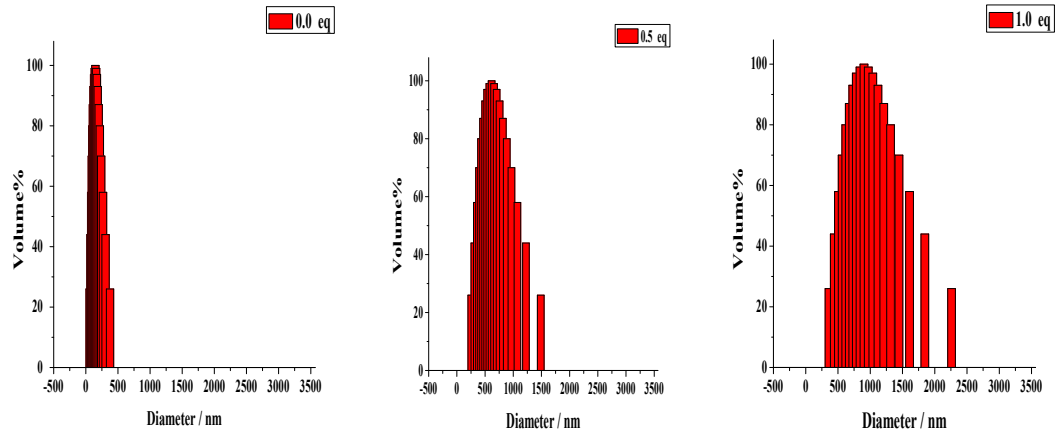


Figure S11 DLS titration of calix[4]carbazole (20 μM) upon addition of **2** in 10 mM PBS buffer, DMSO<1%, pH=7.35

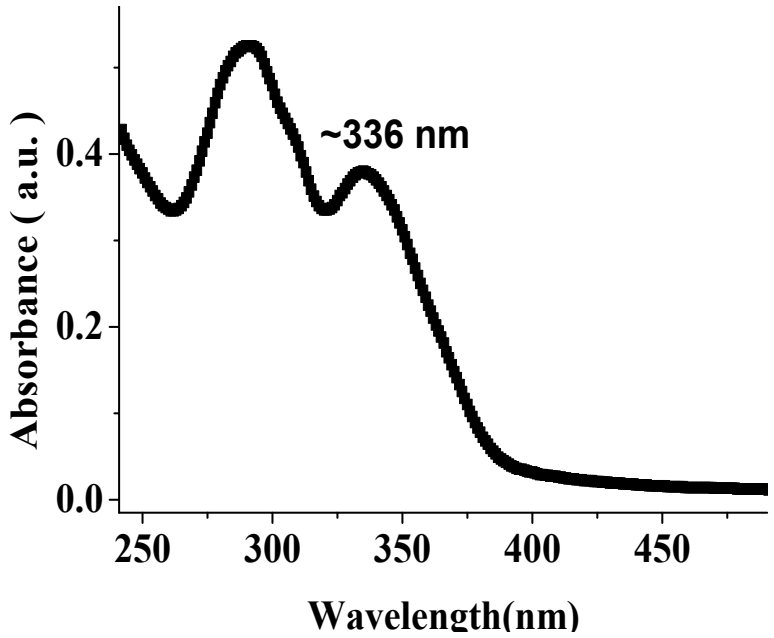


Figure S12 UV-vis spectrum of **2** (20 μM) (1 mM PBS buffer, 9 mM KCl, 5% DMSO,5% methanol, pH=7.3);

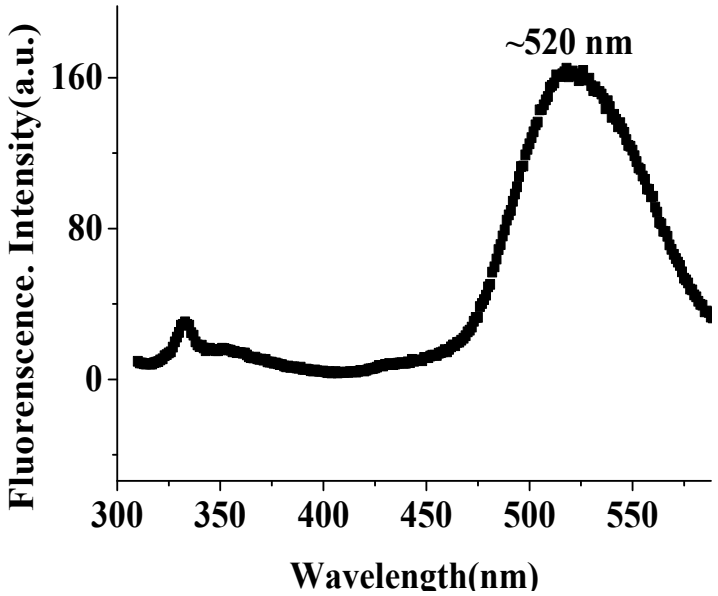


Figure S13 Fluorescence spectrum of **2** (5 μM) (1 mM PBS buffer, 9 mM KCl, 5% DMSO,5% methanol, pH=7.3);

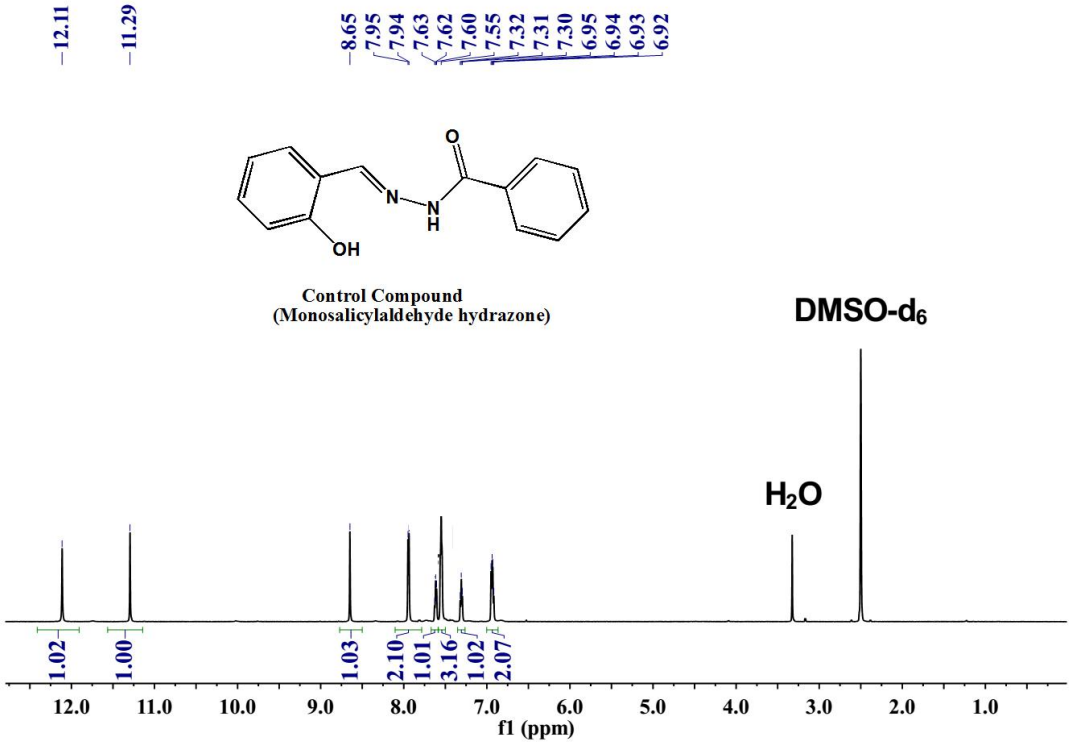


Figure S14. ^{1}H NMR of control compound (600 MHz, DMSO-*d6*) at 20 ^{o}C

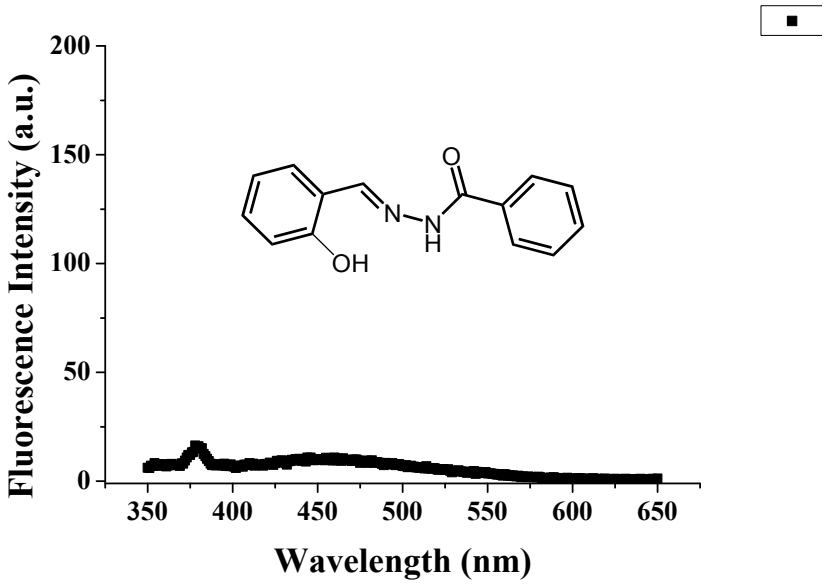


Figure S15. Fluorescence spectrum of the control compound

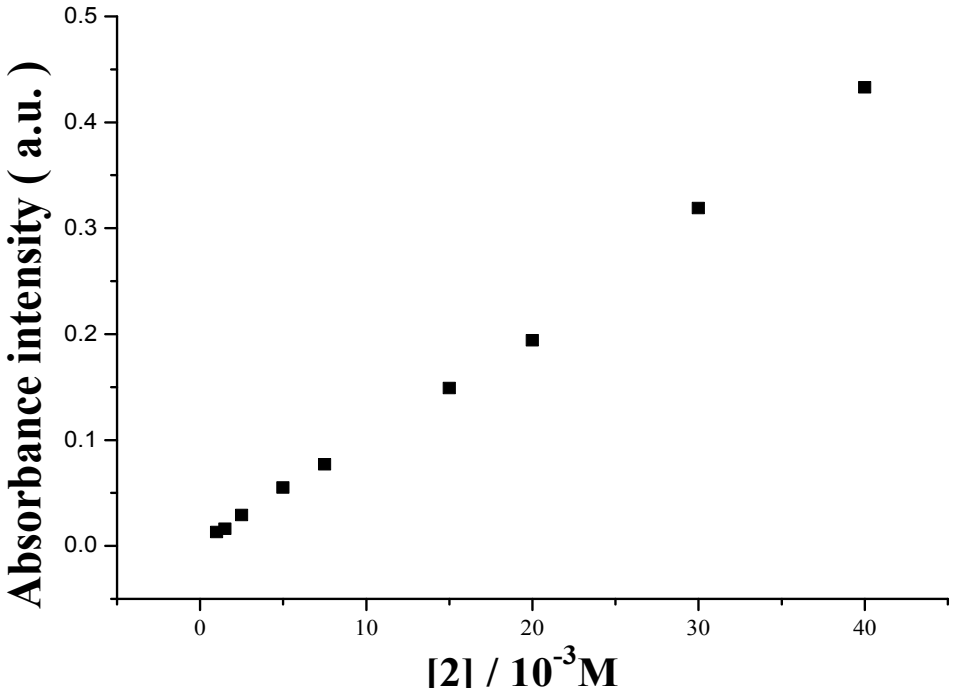


Figure S16. Concentration-dependent absorbance of **2**

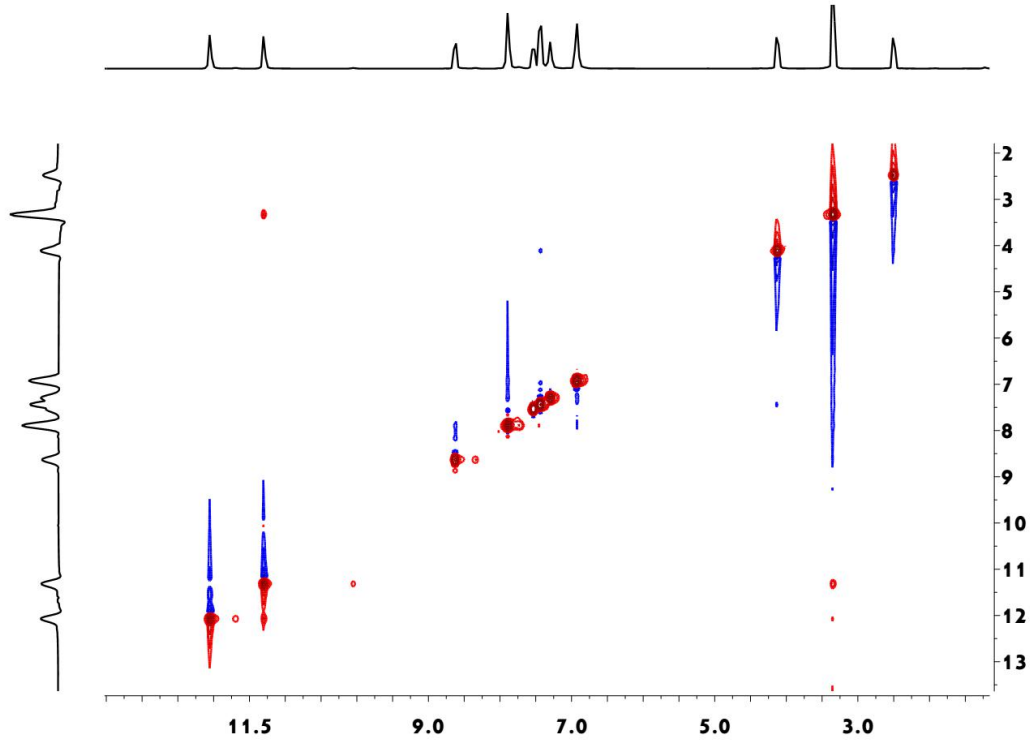


Figure S17. 2D NOESY of **2** (600 MHz, DMSO-d*6*,20℃)

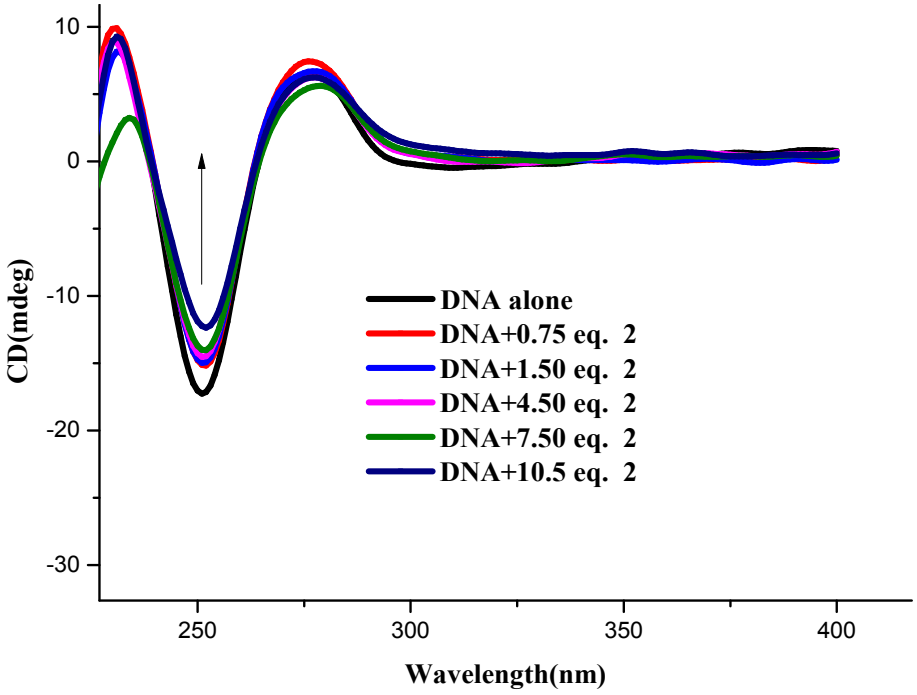


Figure S18. CD spectra of 12AT (20 μM) upon addition of **2** (1 mM PBS,5% DMSO，5% methanol，9 mM KCl, pH = 7.3).

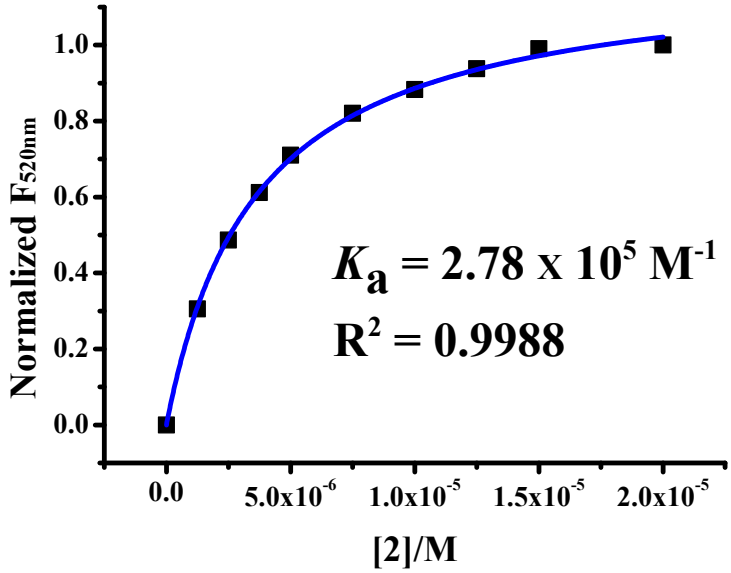


Figure S19 Fitted curve of the normalized F_{520nm} as a function of [**2**].

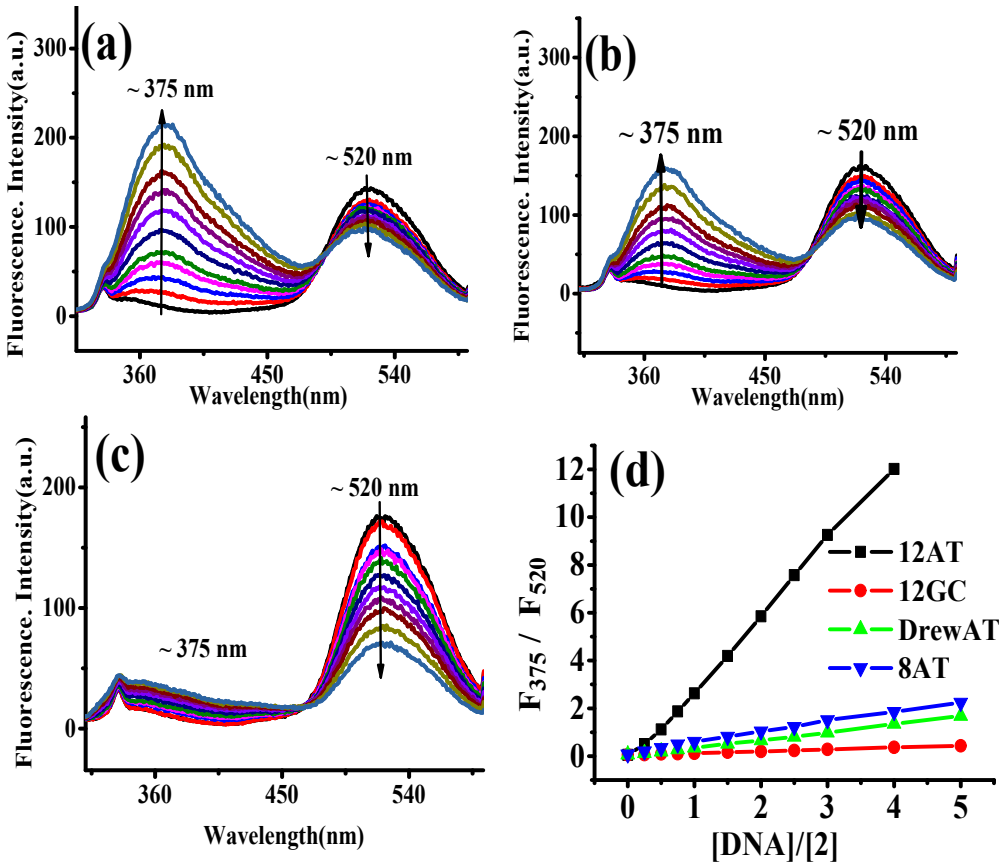


Figure S20. Fluorescence of **2** (5 μM) upon addition of (a) 8AT; (b)drewAT; (c)12GC;(DNA/**2** ratio: 0.25, 0.50, 0.75,1.0, 1.50, 2.0, 2.5, 3.0, 4.0) (d)plotted curve using F_{375}/F_{520nm} as a function of the ratio of [DNA]/[**2**].

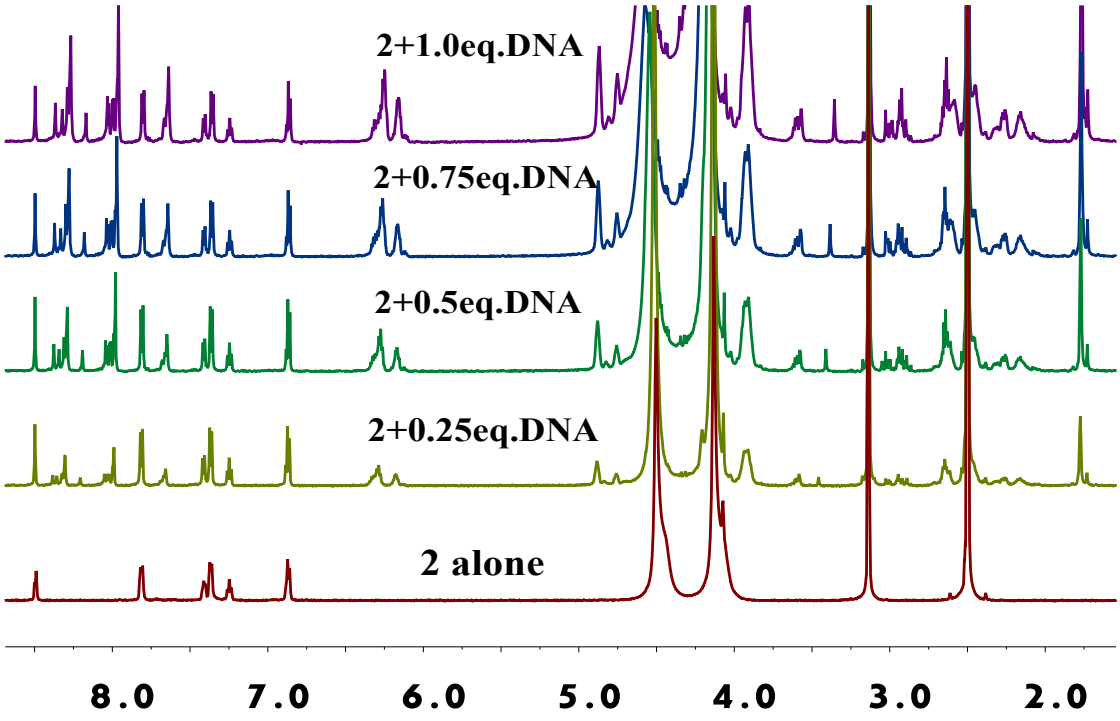


Figure S21. Full ^{1}HNMR spectra of **2** (1 mM) upon binding to 12AT (600 MHz, DMSO-*d6*/D_2O/CD_3OD = 5/1/4, *V*/*V*/*V*, 20 °C)

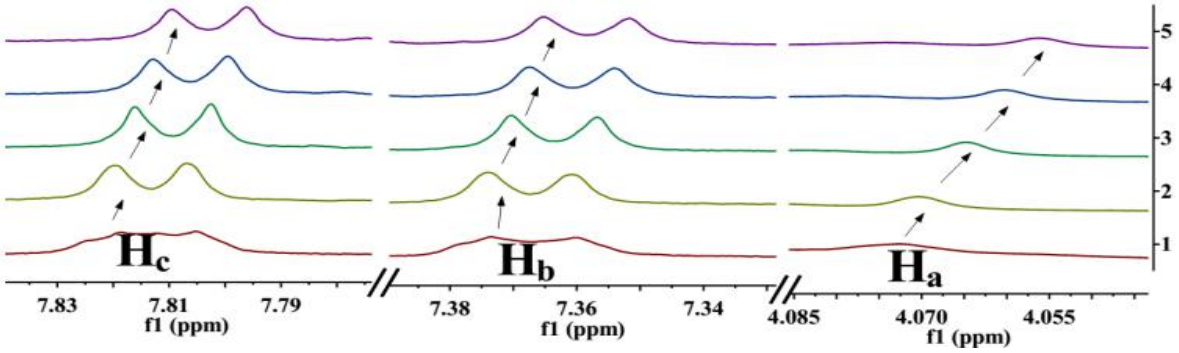


Figure S22. Partial ^{1}HNMR spectra of **2** upon addition of 12AT (Line 1: **2** alone; Line 2: **2**+0.25eq.DNA; Line 3: **2**+0.5eqDNA; Line 4 **2**:+0.75eq.DNA; Line 5: **2**+1.0eq.DNA)

3. References:

1. Connors, A. *Binding Constants*, Wiley, New York, **1987**.
2. (a) Kamieth, M.; Klärner, F.-G.; Diederich, F. *Angew. Chem. Int. Ed.* **1998**, *37*, 3303; (b) Yakovenko A. V.; Boyko, V. I.; Kalchenko, V. I.; Baldini, L.; Casnati, A.; Sansone, F.; Ungaroand, R. *J. Org. Chem.* **2007**, *72*, 3223. (c) Nishimura, N.; Yoza, K.; Kobayashi, K. *J. Am. Chem. Soc.* **2010**, *132*, 777
3. Johnson, D. K.; Murphy, T. B.; Rose, N. J.; Goodwin, W. H.; Pickart, L. *Inorg. Chim. Acta* **1982**, *67*, 159−165.