

Supporting Information

A fluorescent sensor for thymine based on Bis-BODIPY containing butanediamido bridge

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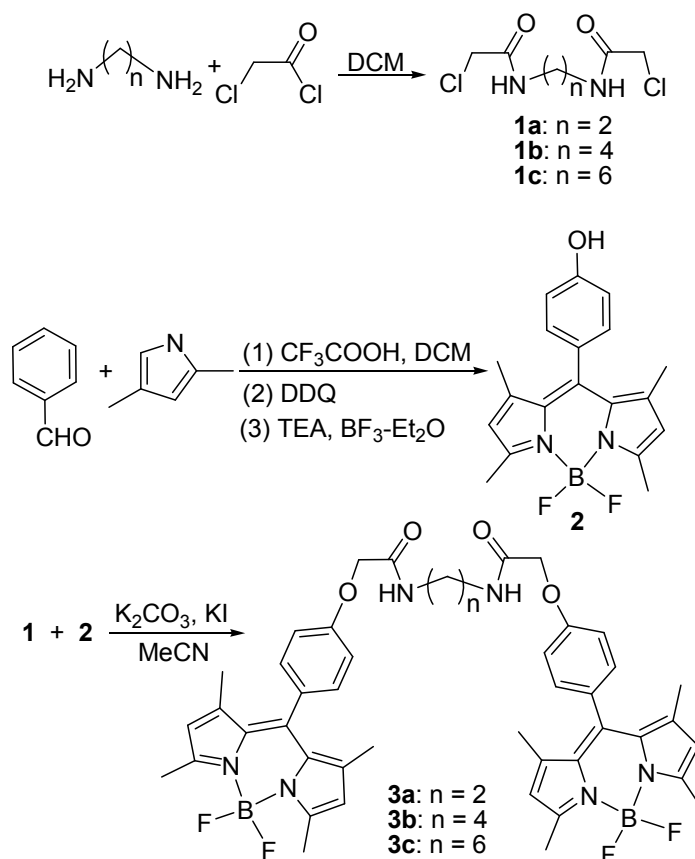
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1. General

All chemical reagents were obtained from commercial suppliers and used without further purification. The other organic solvents and inorganic reagents were purified according to standard anhydrous methods before use. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200-300 mesh). NMR spectra were recorded in CDCl₃ on a Bruker-ARX 600 instrument at 30°C. Chemical shifts are reported in ppm, using tetramethylsilane (TMS) as internal standard. MS spectra were obtained from Bruker mass spectrometer. Elemental analyses were performed at Vario EL III Elemental Analyzer. UV-Vis spectra were recorded on Varian UV-Vis spectrometer. Fluorescence spectra were measured in a conventional quartz cell (10×10×45 nm) at 25 °C on a Hitachi F-4500 spectrometer equipped with a constant-temperature water bath, with excitation and emission slits 10nm wide. The excitation wavelengths were 480 nm. Compound **1a**, **1b** and **1c** were prepared according to the literature (Syntheses and Cations Complexation Properties of Novel Thiocalix[4]-1,3-aza-crown and Bisthiocalix[4]-1,3-aza-crown, Fafu Yang, Fengju Yin, Hongyu Guo, Zhisheng Huang, and Xiaoyi Zhang, J Incl Phenom Macrocycl Chem, 2010, 67, 49-54). Compound **2** was synthesized by reported procedure (Zhenxi Yan, Xiaoru Lin, Hongyu Guo, and Fafu Yang, A novel fluorescence sensor for K⁺ based on bis-Bodipy: The ACQ effect controlled by cation complexation of pseudo crown ether ring, Tetrahedron Letters 58 (2017) 3064–3068).

2. The synthetic process and characteristic spectra.



Scheme S1 The synthetic route for target samples **3a**, **3b** and **3c**

2.1 Synthesis of compounds **3a**, **3b** and **3c**.

Under N_2 atmosphere, the mixture of compound **1a** (**1b** or **1c**, 0.6 mmol), compound **2** (0.41g, 1.2 mmol), dry K_2CO_3 (0.41g, 3 mmol) and KI (0.10g, 0.6 mmol) was stirred and refluxed in 30 mL of dry MeCN for 24 h. TLC detection suggested the disappearance of starting materials. After cooling, 50 mL of HCl solution (1 M) and 60 mL of CH_2Cl_2 were added in reaction system. The obtained mixture was stirred for half an hour and then the organic layer was separated. The organic portion was dried by anhydrous $MgSO_4$ and further concentrated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: CH_2Cl_2 : petroleum ether = 4 : 1). Bis-Bodipy **3a**, **3b** and **3c** were collected as red solid in yield of 74%, 76% and 77%, respectively.

Compound **3a**: 1H NMR (400 MHz, $CDCl_3$) δ ppm: 1.37 (s, 12H, CH_3), 2.51 (s, 12H, CH_3), 3.55 (s, 4H, NCH_2), 4.55 (s, 4H, OCH_2), 5.95 (s, 4H, ArH), 7.05 (d, 4H, $J = 8.0$ Hz, ArH), 7.17 (d, 4H, $J = 8.0$ Hz, ArH), 7.43 (bs, 2H, NH); ^{13}C NMR (100 MHz, $CDCl_3$) δ ppm: 14.34, 29.69, 39.80, 67.15, 115.20, 121.29, 128.42, 129.61, 131.66, 141.33, 142.80, 155.28, 157.68, 168.74; HR-MS(ESI) ($C_{44}H_{46}B_2F_4N_6O_4$) $[M+Na]^+$: Calcd.: 843.3809. found: 843.3829; Anal. calcd for $C_{44}H_{46}B_2F_4N_6O_4$: C 64.41, H 5.65, N 10.24; found C 64.45, H 5.59, N 10.18%.

Compound **3b**: 1H NMR (400 MHz, $CDCl_3$) δ ppm: 1.39 (s, 12H, CH_3), 1.63 (s, 4H, CH_2), 2.54 (s, 12H, CH_3), 3.42 (s, 4H, NCH_2), 4.56 (s, 4H, OCH_2), 5.97 (s, 4H, ArH), 6.83 (bs, 2H, NH), 7.04 (d, 4H, J

= 8.0Hz,ArH), 7.19 (d, 4H, J = 8.0Hz, ArH); ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 15.06, 22.56, 29.52, 38.53, 67.16, 115.54, 121.02, 128.53, 129.65, 131.67, 141.08, 142.62, 155.39, 157.43, 167.91; HR-MS(ESI) ($\text{C}_{46}\text{H}_{50}\text{B}_2\text{F}_4\text{N}_6\text{O}_4$) $[\text{M}+\text{Na}]^+$: Calcd.: 871.4106. found: 871.4142; Anal. calcd for $\text{C}_{46}\text{H}_{50}\text{B}_2\text{F}_4\text{N}_6\text{O}_4$: C 65.11, H 5.94, N 9.90; found C 65.06, H 5.88, N 9.83%.

Compound **3c**: ^1H NMR (400 MHz, CDCl_3) δ ppm: 1.38 (s, 12H, CH_3), 1.57 (s, 4H, CH_2), 2.06 (s, 4H, CH_2), 2.52 (s, 12H, CH_3), 3.35 (bs, 4H, NCH_2), 4.52(s, 4H, OCH_2), 5.96 (s,4H, ArH), 6.72 (bs, 2H, NH), 7.03 (d, 4H, J = 8.0Hz,ArH), 7.20 (d, 4H, J = 8.0Hz, ArH); ^{13}C NMR (100 MHz, CDCl_3) δ ppm: 14.59, 23.30, 26.09, 29.39, 38.79, 67.28, 115.29, 121.29, 128.54, 129.64, 131.68, 141.06, 142.83, 155.51, 157.58, 167.48; HR-MS(ESI) ($\text{C}_{48}\text{H}_{54}\text{B}_2\text{F}_4\text{N}_6\text{O}_4$) $[\text{M}]^+$: Calcd.: 876.4979. found: 876.5011; Anal. calcd for $\text{C}_{48}\text{H}_{54}\text{B}_2\text{F}_4\text{N}_6\text{O}_4$: C 65.77, H 6.21, N 9.59; found C 65.71, H 6.17, N 9.51%.

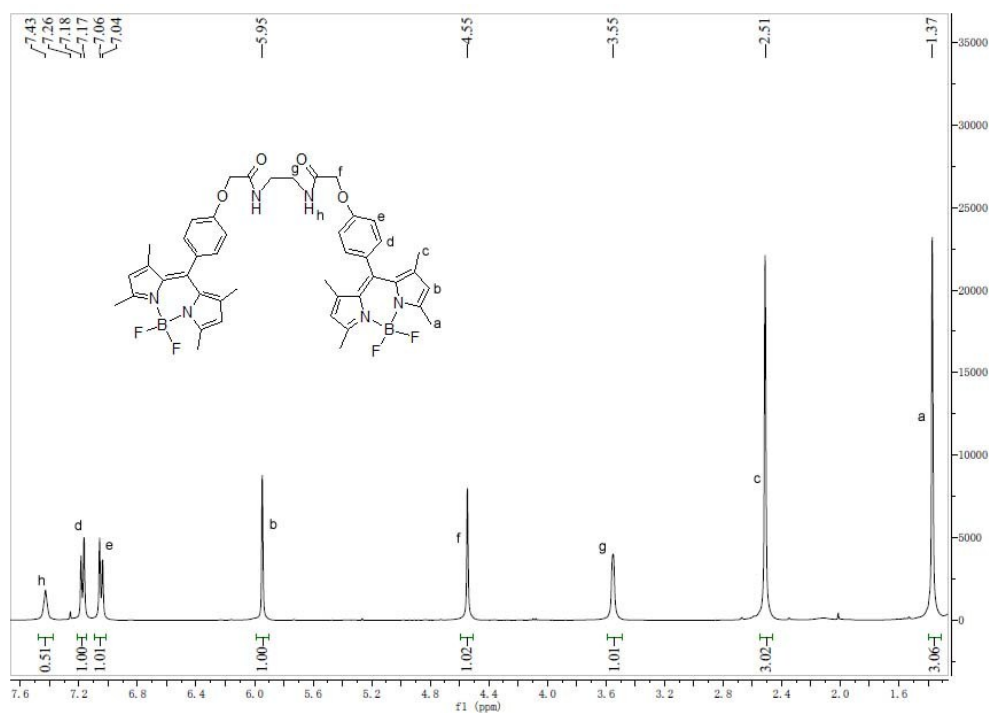


Figure S1. The ^1H NMR spectrum of compound **3a**

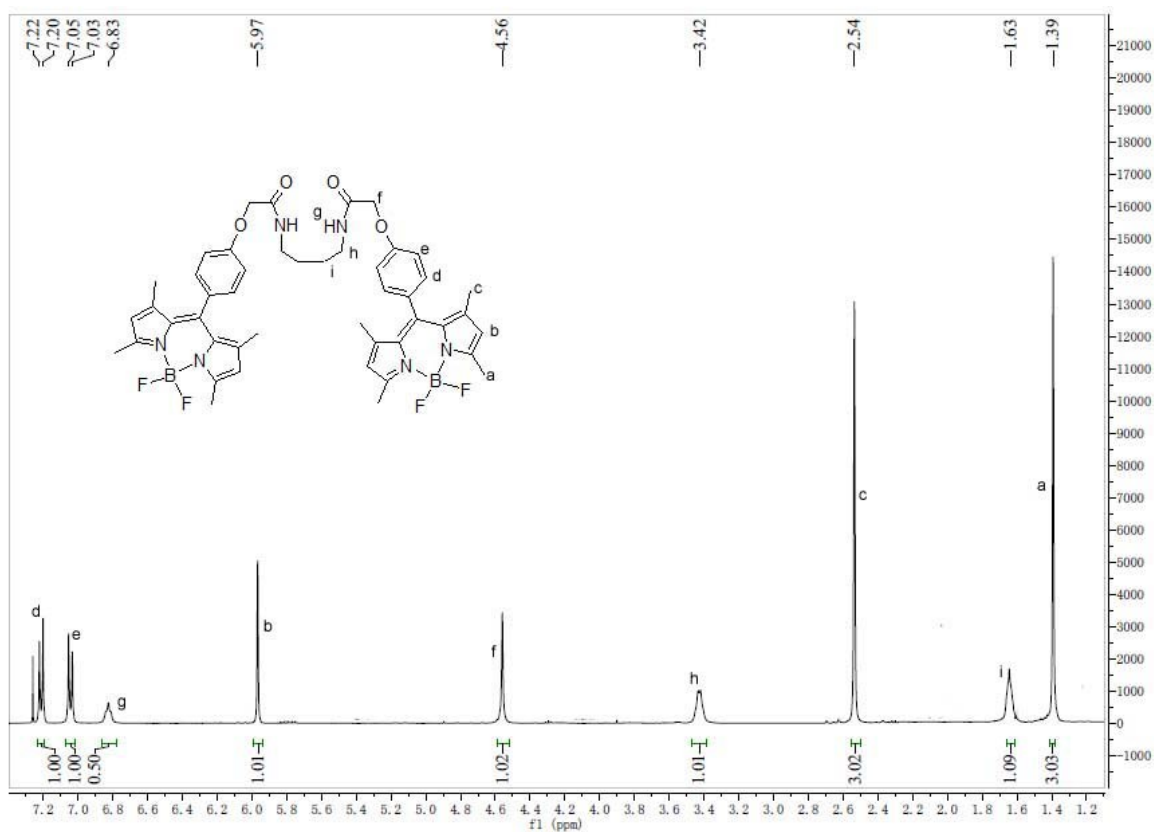


Figure S2. The ^1H NMR spectrum of compound **3b**

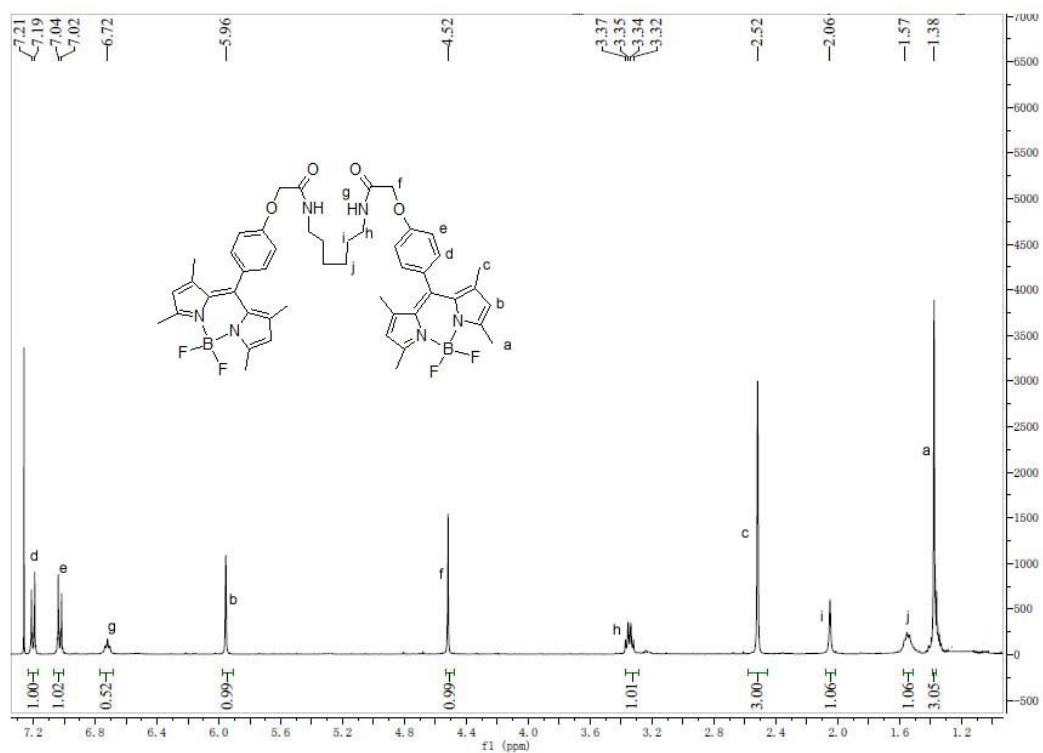


Figure S3. The ^1H NMR spectrum of compound **3c**

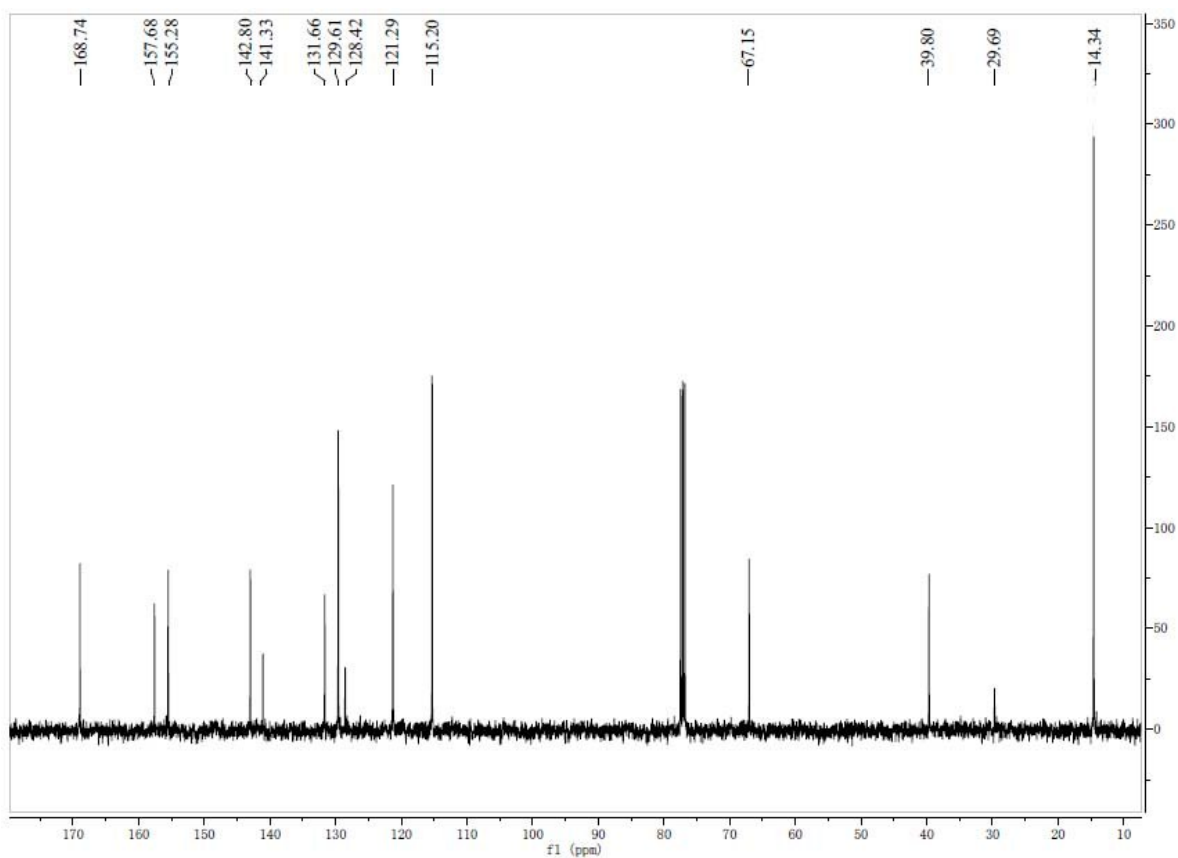


Figure S4. The ^{13}C NMR spectrum of compound **3a**

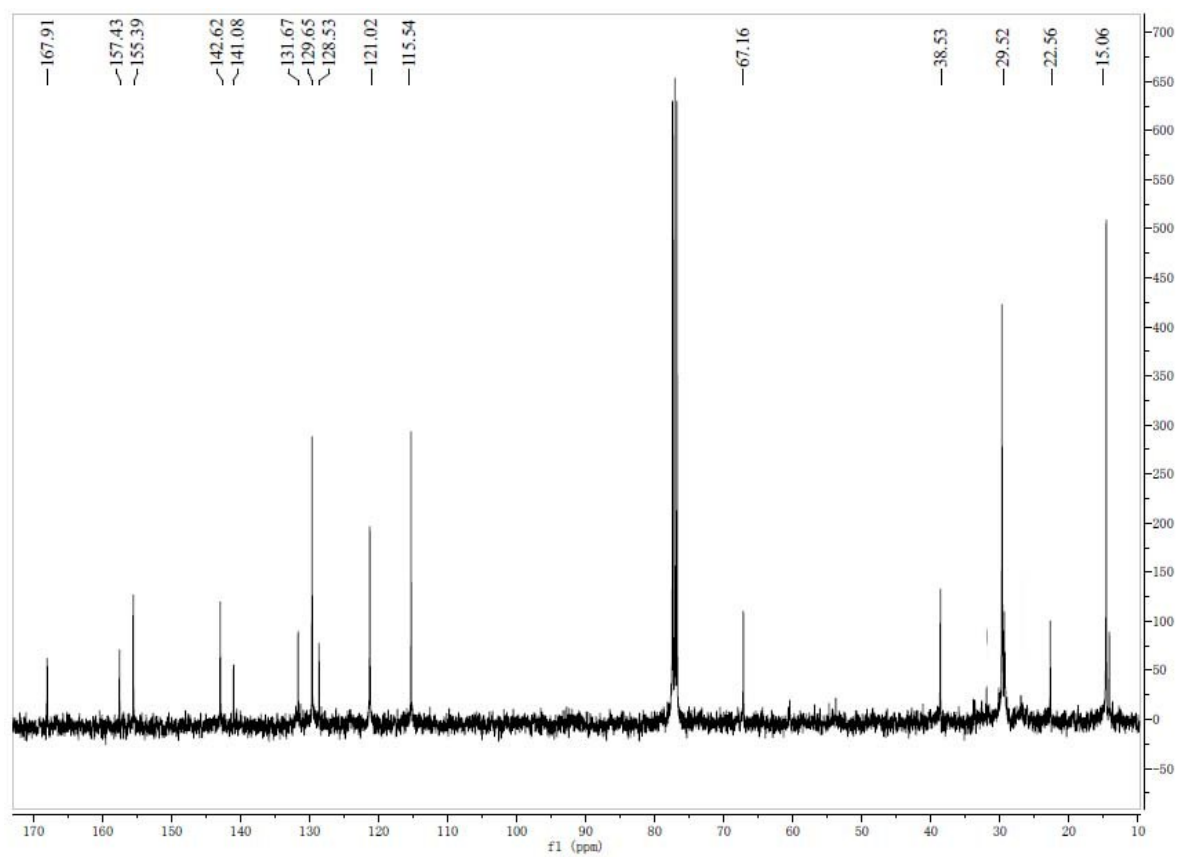


Figure S5. The ^{13}C NMR spectrum of compound **3b**

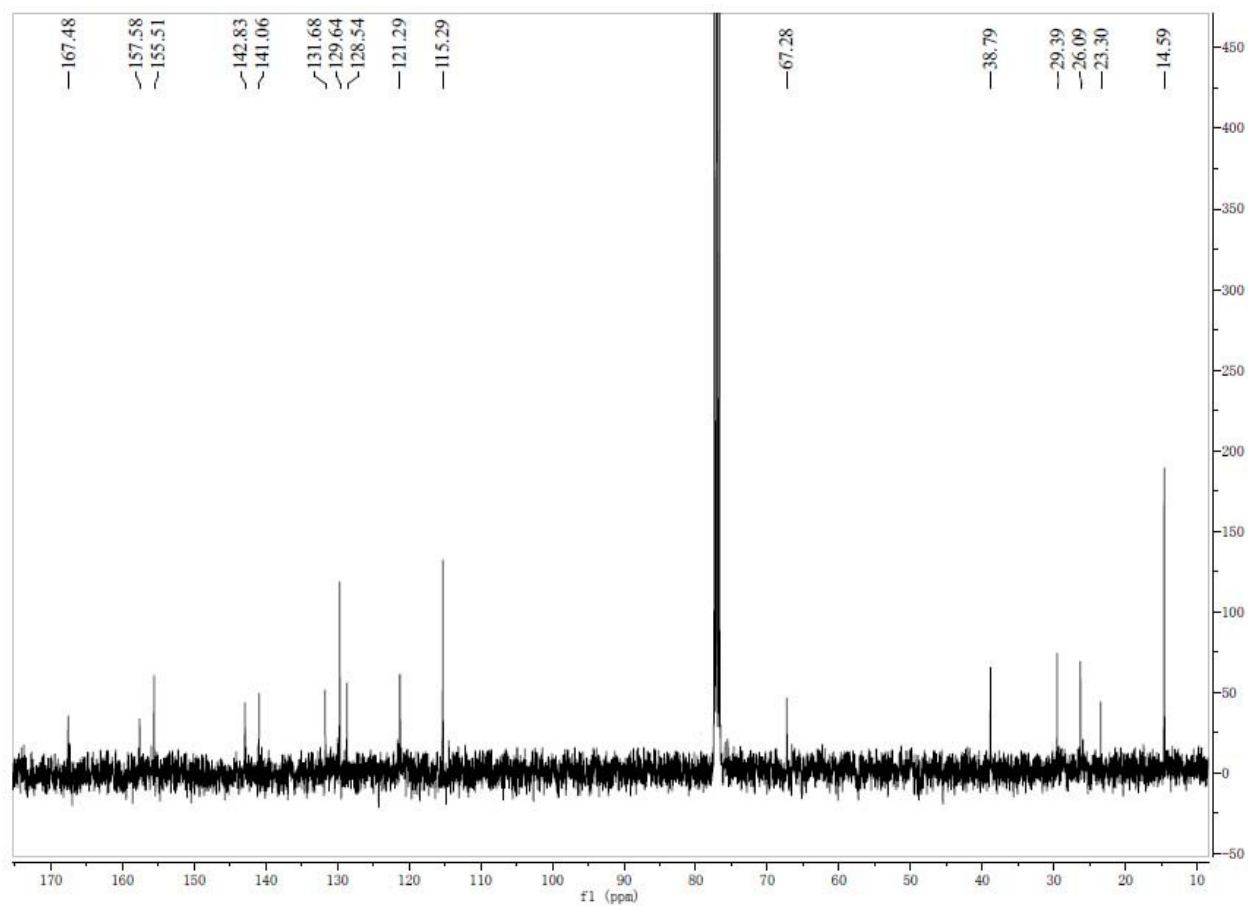


Figure S6. The ^{13}C NMR spectrum of compound **3c**

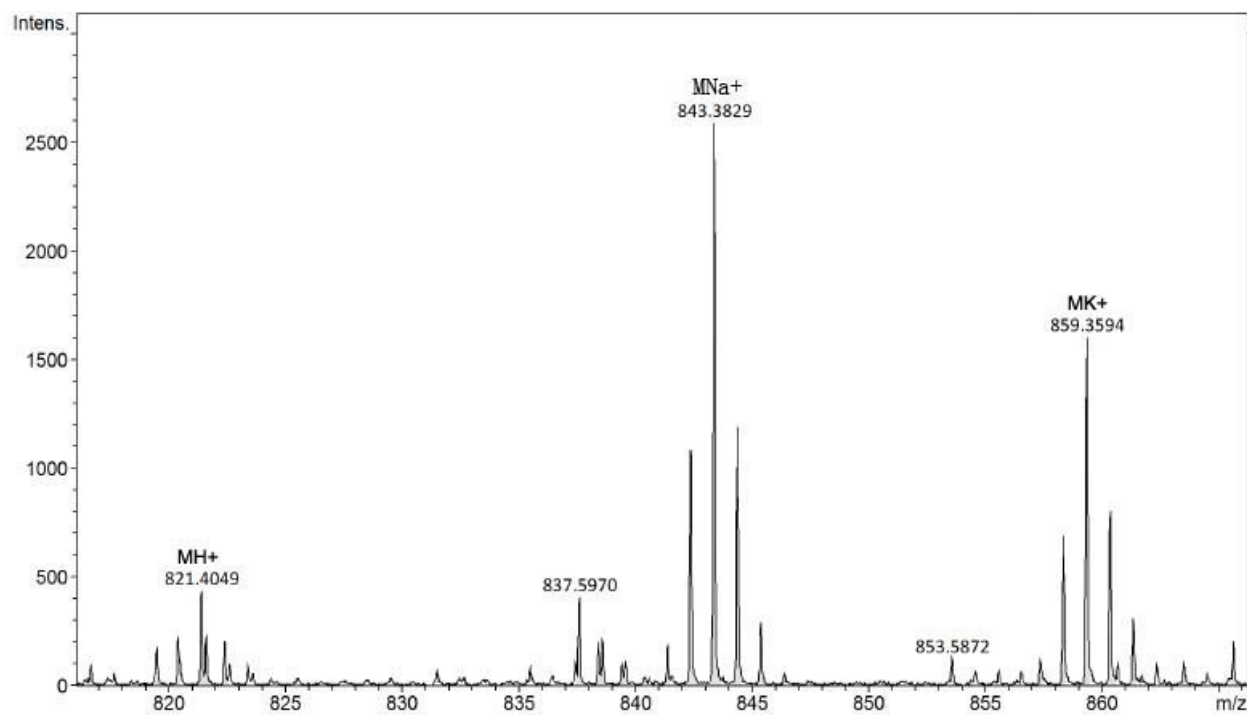


Figure S7. HR-ESI-MS spectrum of compound **3a**

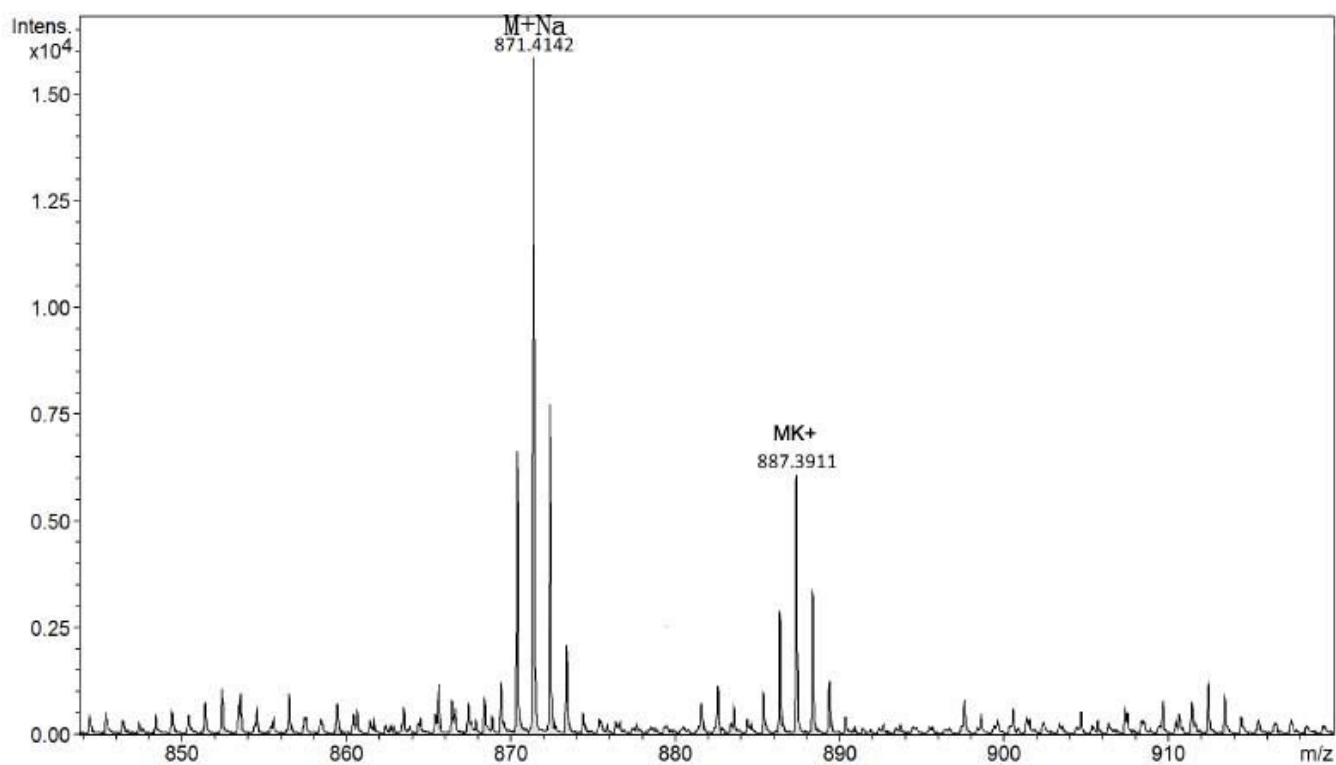


Figure S8. HR-ESI-MS spectrum of compound **3b**

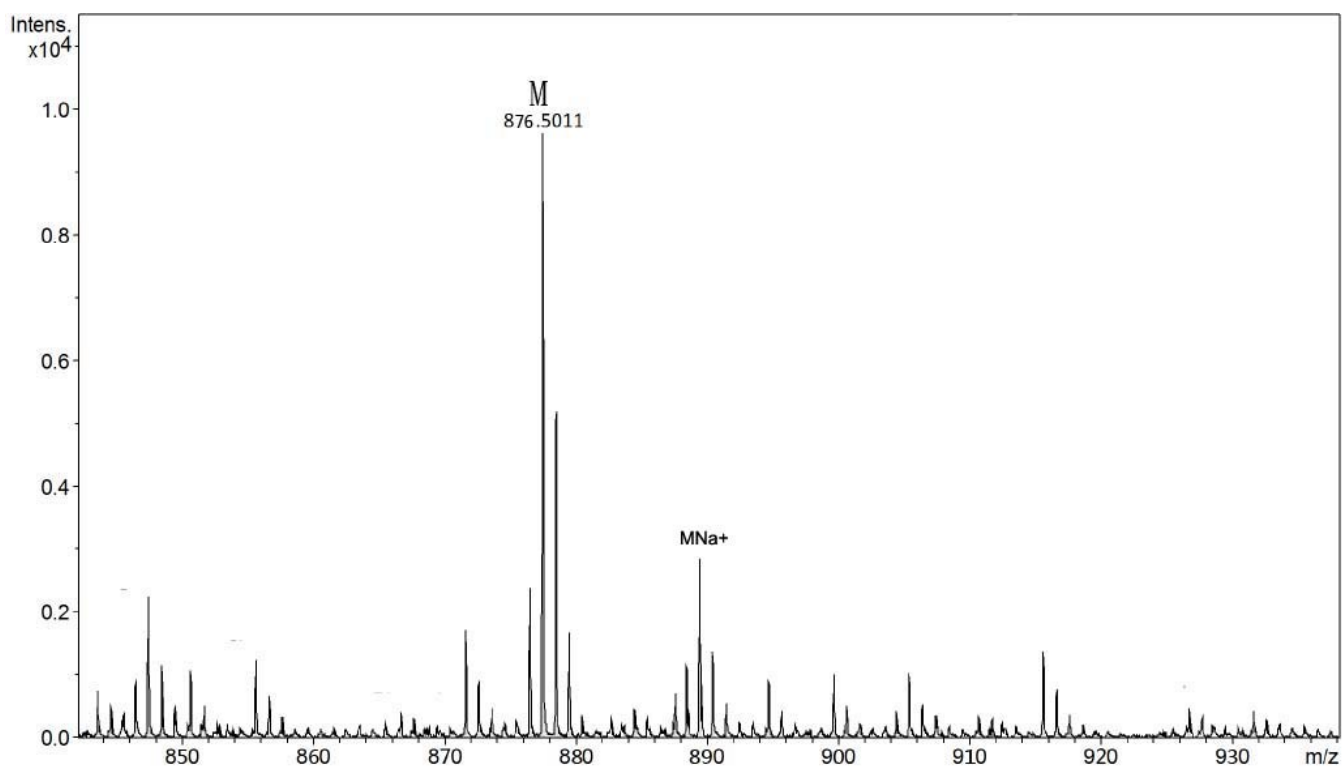


Figure S9. HR-ESI-MS spectrum of compound **3c**

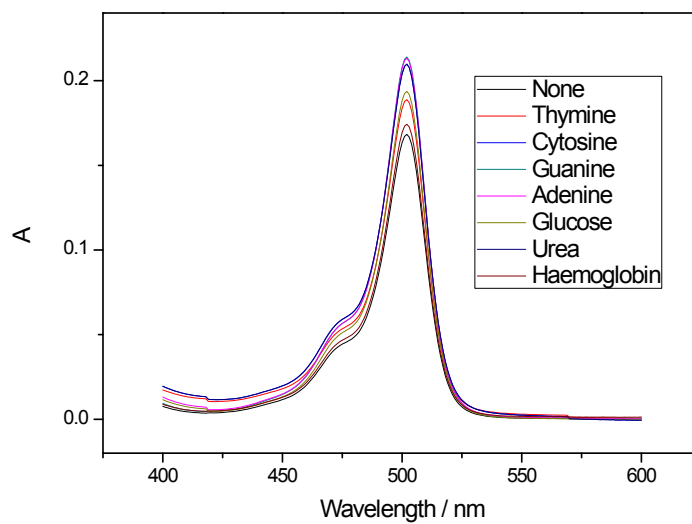


Figure S10 The UV-vis spectra of the compound **3a** (1 μM) with biomolecules in DMSO/H₂O (1:9)

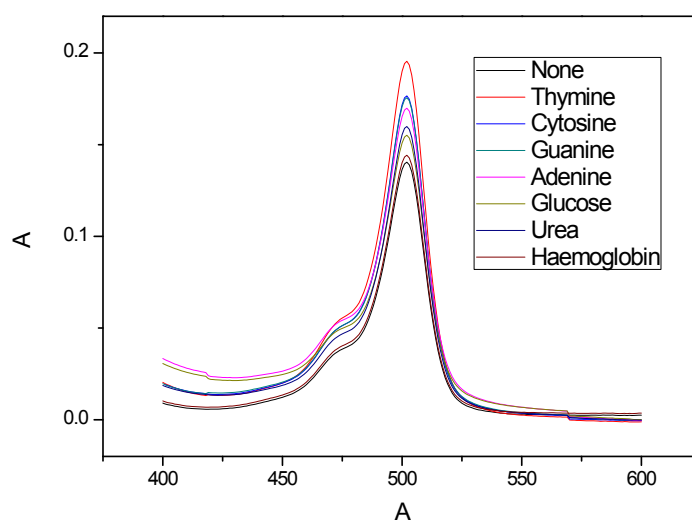


Figure S11 The UV-vis spectra of the compound **3b** (1 μM) with biomolecules in DMSO/H₂O (1:9)

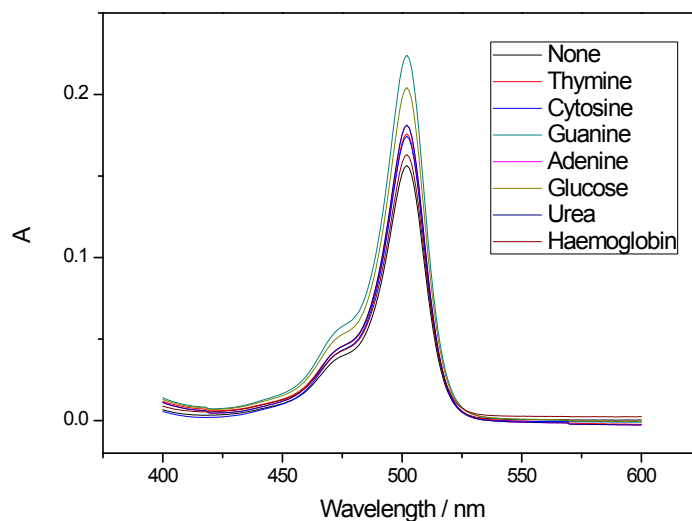


Figure S12 The UV-vis spectra of the compound **3c** ($1 \mu\text{M}$) with biomolecules in DMSO/H₂O (1:9)

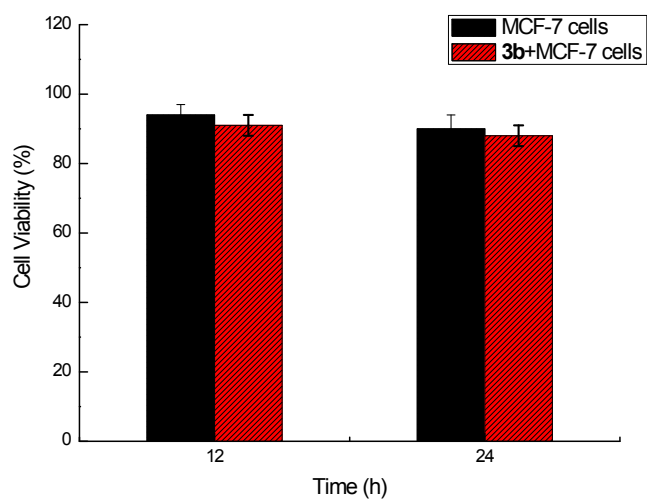


Figure S13 Cell viability of MCF-7 cells before and after incubated with sample **3b** ($1 \mu\text{M}$) for 12 h and 24 h.

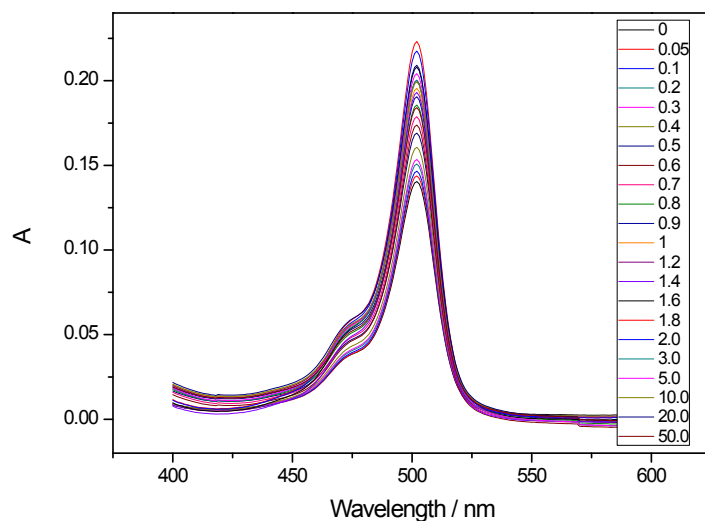


Figure S14 The UV-vis spectra of sample **3b** (1 μM) with thymine in DMSO/H₂O (1:9)

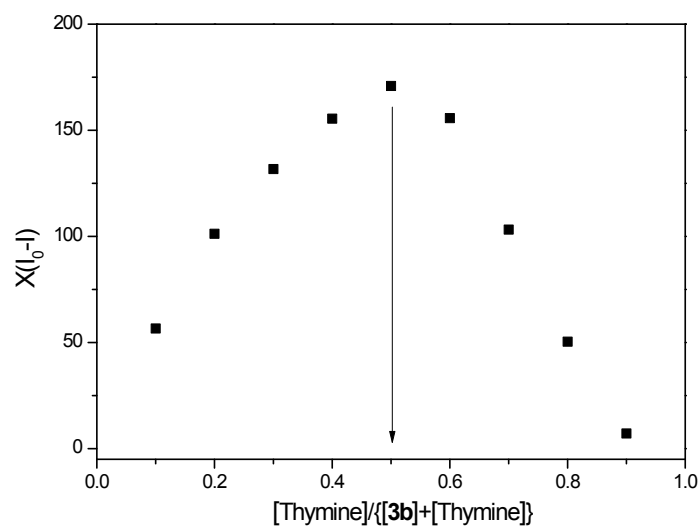


Figure S15 The Job's plot of sample **3b** with thymine in DMSO/H₂O (1:9) (The total concentration was 1 μM , I₀ and I were the fluorescence intensity of sample **3b** before and after binding thymine)

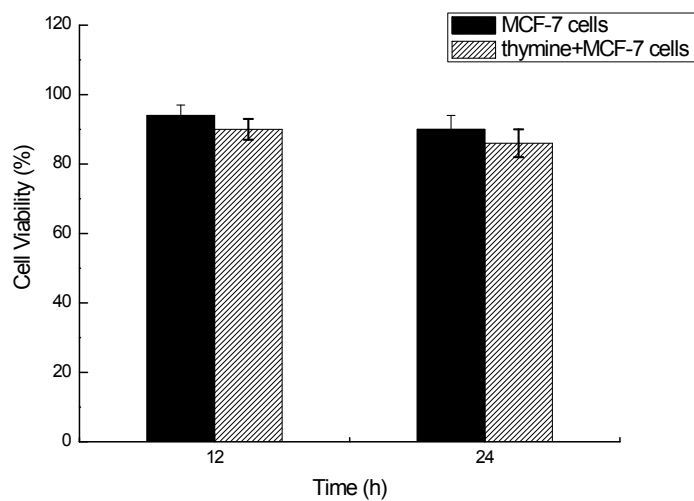


Figure S16 Cell viability of MCF-7 cells before and after incubated with thymine (1 μ M) for 12 h and 24 h.