Supporting Information

A fluorescent sensor for folic acid based on crown ether-bridged bis-tetraphenylethylene

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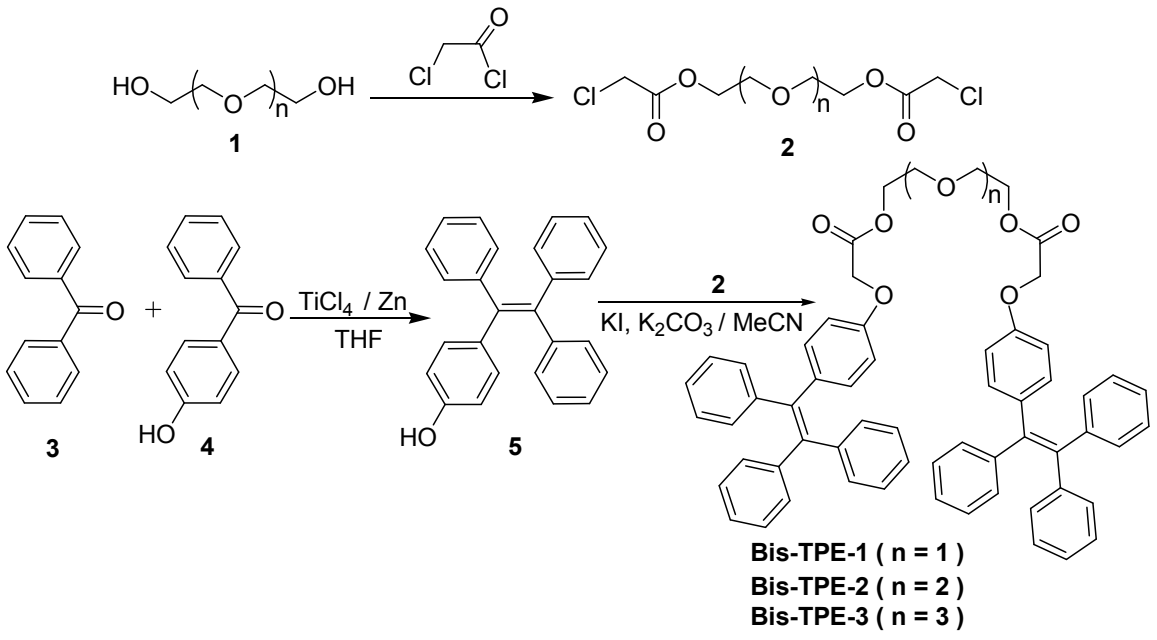
1. General

All chemical reagents were obtained from J&K Chemicals and were used directly. TLC analysis wasdone on pre-coated glass plates. Silica gel (200-300 mesh) was used for the purification of column chromatography. NMR spectra were investigated on a Bruker-ARX 400 instrument at 25°C. MS spectra were measured onBruker mass spectrometer. Compound **2** was prepared by published procedure (European Journal of organic chemistry, 2001, 365-368). Compound **5** was prepared by reacting 2-hydroxybenzophenone and benzophenone in Zn,$TiCl_4$/THF system according to the published literature (J. Mater. Chem., 2012, 22, 3323-3326).

2. The synthetic process and characteristic spectra.



Scheme S1 The synthetic route for target compound **Bis-TPE**

2.1 Synthesis of Bis-TPE-1, Bis-TPE-2 and Bis-TPE-3.

The mixture of compound **5** (0.348 g, 1 mmol), anhydrous potassium carbonate (1.0 g, 7.2 mmol) and compound **2** (0.5 mmol) were stirred and refluxed in 40 mL of dry acetonitrile overnight. TLC detection indicated that the starting materials almost completely disappeared. After reaction, 50 mL of 1 M HCl solution was added dropwise to the reaction mixture, and extracted with $CHCl_3$ (20 mL×3). The organic phase was separated and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: CH_2Cl_2/hexane = 1/2) to afford **Bis-TPE-1**, **Bis-TPE-2** and **Bis-TPE-3** as pale yellow solids in yields of 78%, 80% and 84%, respectively.

Bis-TPE-1: ^{1}H NMR(400 MHz, $CDCl_3$): δppm: 7.06-7.14 (m, 30H, ArH), 6.99(d, *J* = 8.0 Hz, 4H, ArH), 6.68(d, *J* = 8.0 Hz, 8H, ArH), 4.61 (s, 4H, OCH_2), 4.37 (bs, 4H, OCH_2), 3.70 (bs, 4H, OCH_2). ^{13}C NMR (100 MHz, $CDCl_3$), *δ*ppm: 168.93, 156.38, 144.26, 143.99, 143.93, 140.58, 140.36, 137.33, 132.71, 131.43, 128.50, 127.88, 127.77, 127.49, 126.68, 126.57, 126.48, 113.98, 67.83, 65.24, 64.04. MALDI-TOF-MS ($C_{60}H_{50}O_7$) Calcd.for *m*/*z* = 882.356, found: *m*/*z* = 882.346 (M^+). Anal.calcd for $C_{60}H_{50}O_7$: C 81.61, H 5.71; found C 81.66, H 5.66.

Bis-TPE-2: ^{1}H NMR(400 MHz, $CDCl_3$): δppm: 7.01-7.14 (m, 30H, ArH), 6.95(d, *J* = 8.0 Hz, 4H, ArH), 6.65(d, *J* = 8.0 Hz, 4H, ArH), 4.59 (s, 4H, OCH_2), 4.36 (t, *J* = 8.0 Hz, 4H, OCH_2), 3.71 (t, *J* = 8.0 Hz, 4H, OCH_2), 3.62 (s, 4H, OCH_2). ^{13}C NMR (100 MHz, $CDCl_3$), *δ*ppm: 168.92, 156.25, 143.92, 140.52, 140.30, 137.28, 132.71, 128.64, 127.80, 126.48, 126.40, 113.91, 70.60, 69.00, 65.26, 63.98. MALDI-TOF-MS ($C_{62}H_{54}O_8$) Calcd.for *m*/*z* = 926.382, found: *m*/*z* = 926.383 (M^+). Anal.calcd for $C_{62}H_{54}O_8$: C 80.32, H 5.87; found C 80.38, H 5.83.

Bis-TPE-3: ^{1}H NMR(400 MHz, $CDCl_3$): δppm: 7.01-7.13 (m, 30H, ArH), 6.95(d, *J* = 8.0 Hz, 4H, ArH), 6.65(d, *J* = 8.0 Hz, 4H, ArH), 4.59 (s, 4H, OCH_2), 4.36 (bs, 4H, OCH_2), 3.71 (bs, 4H, OCH_2), 3.64 (s, 8H, OCH_2). ^{13}C NMR (100 MHz, $CDCl_3$), *δ*ppm: 168.27, 155.91, 143.92, 140.24, 139.84, 136.99, 132.36, 131.08, 128.27, 127.54, 127.14, 126.70, 126.13, 113.63, 76.01, 68.51, 67.65, 64.78, 63.69. MALDI-TOF-MS ($C_{64}H_{58}O_9$) Calcd.for *m*/*z* = 970.408, found: *m*/*z* = 970.498 (M^+). Anal.calcd for $C_{64}H_{58}O_9$: C 79.15, H6.02; found C 79.19, H 5.97.

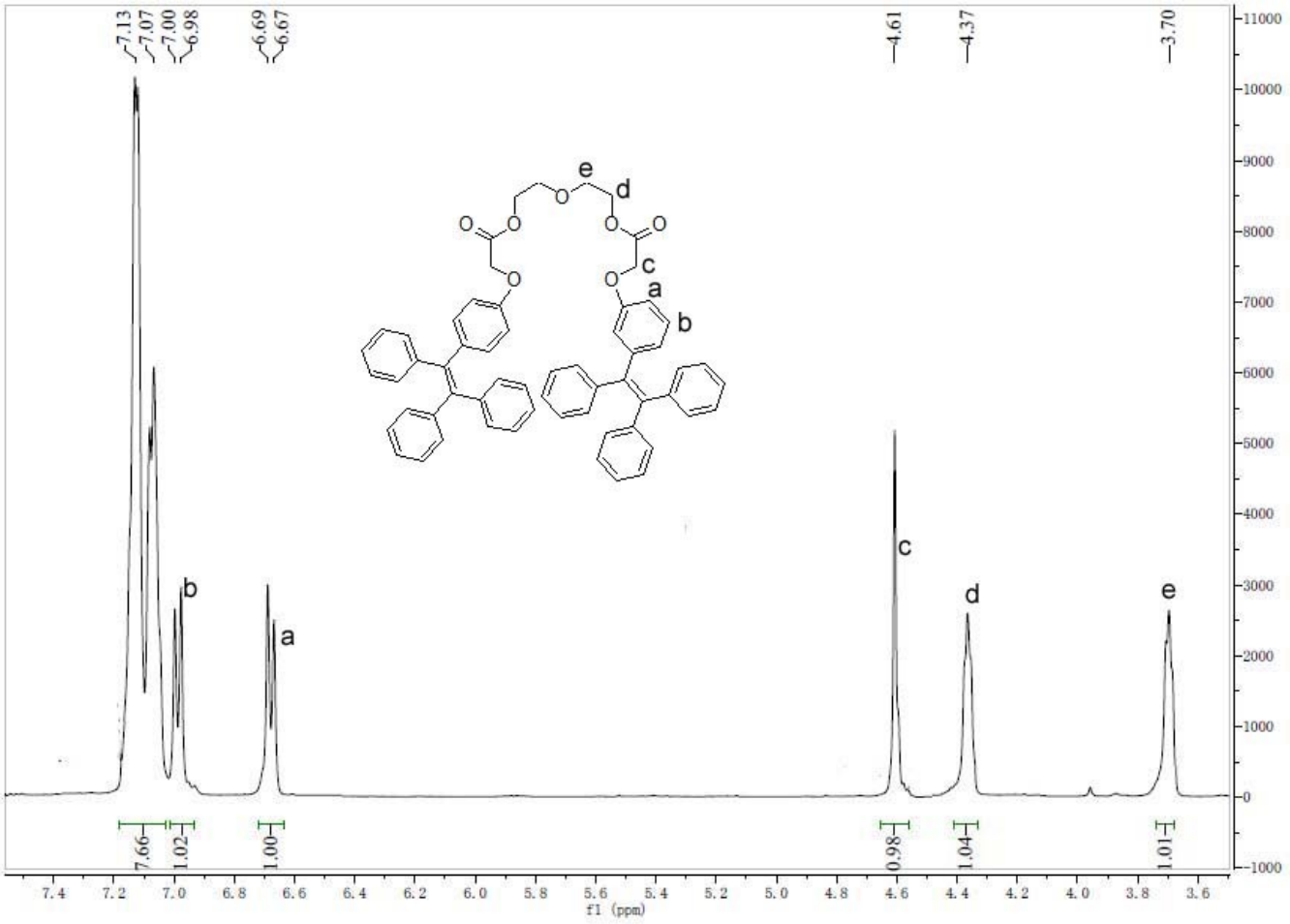


Figure S1. The ^{1}H NMR spectrum of compound **Bis-TPE-1**

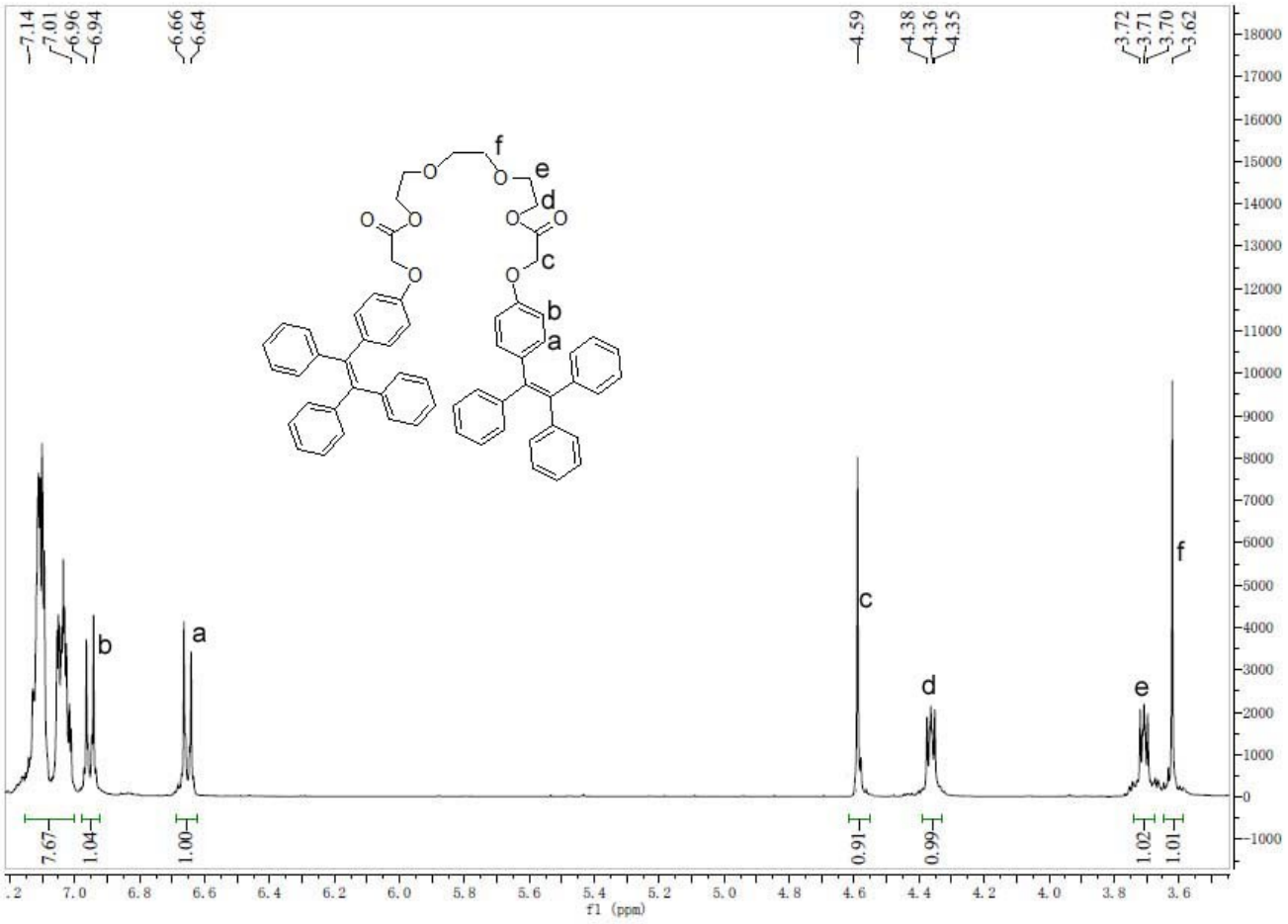


Figure S2. The ^{1}H NMR spectrum of compound **Bis-TPE-2**

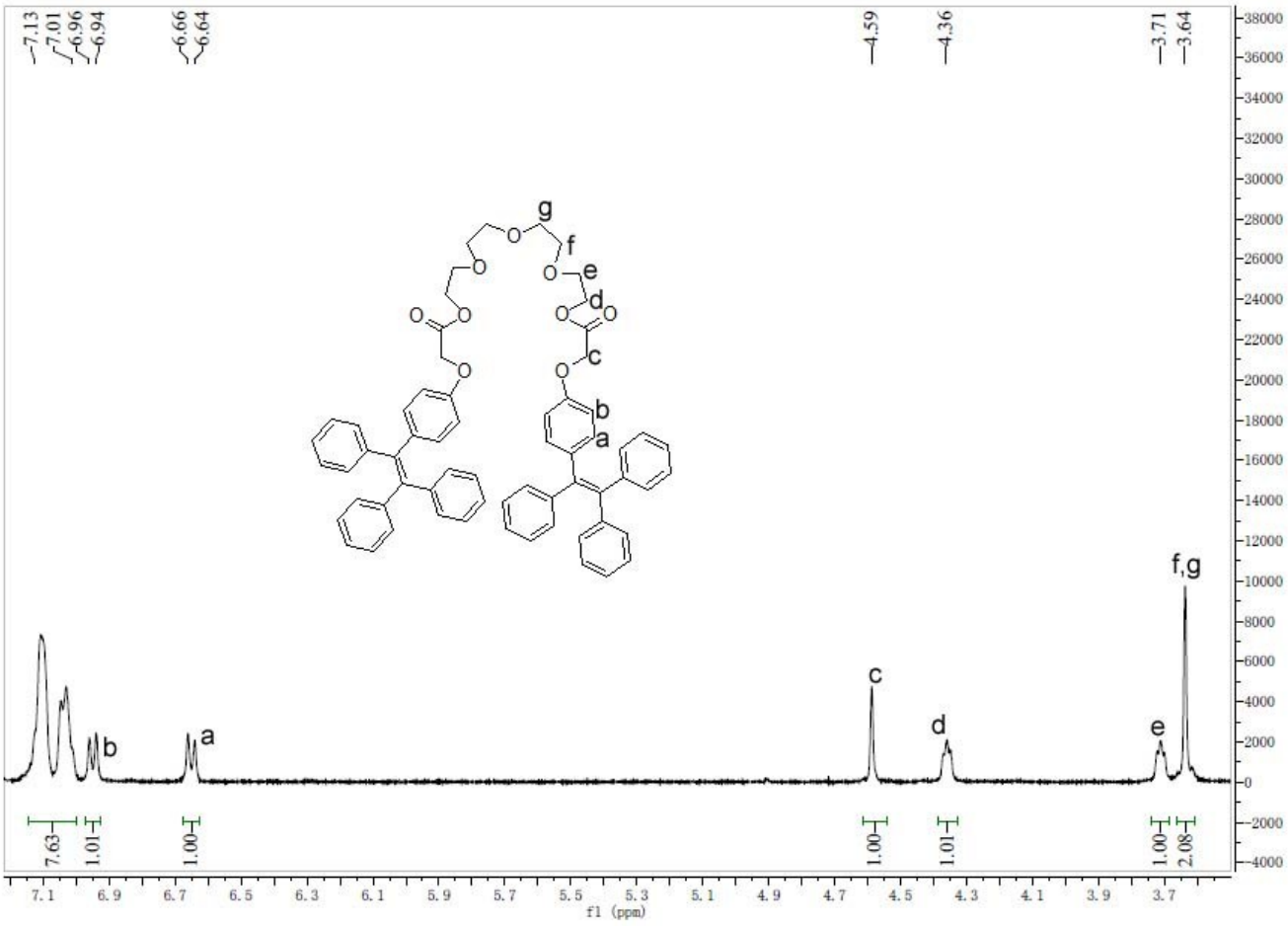


Figure S3. The ^{1}H NMR spectrum of compound **Bis-TPE-3**

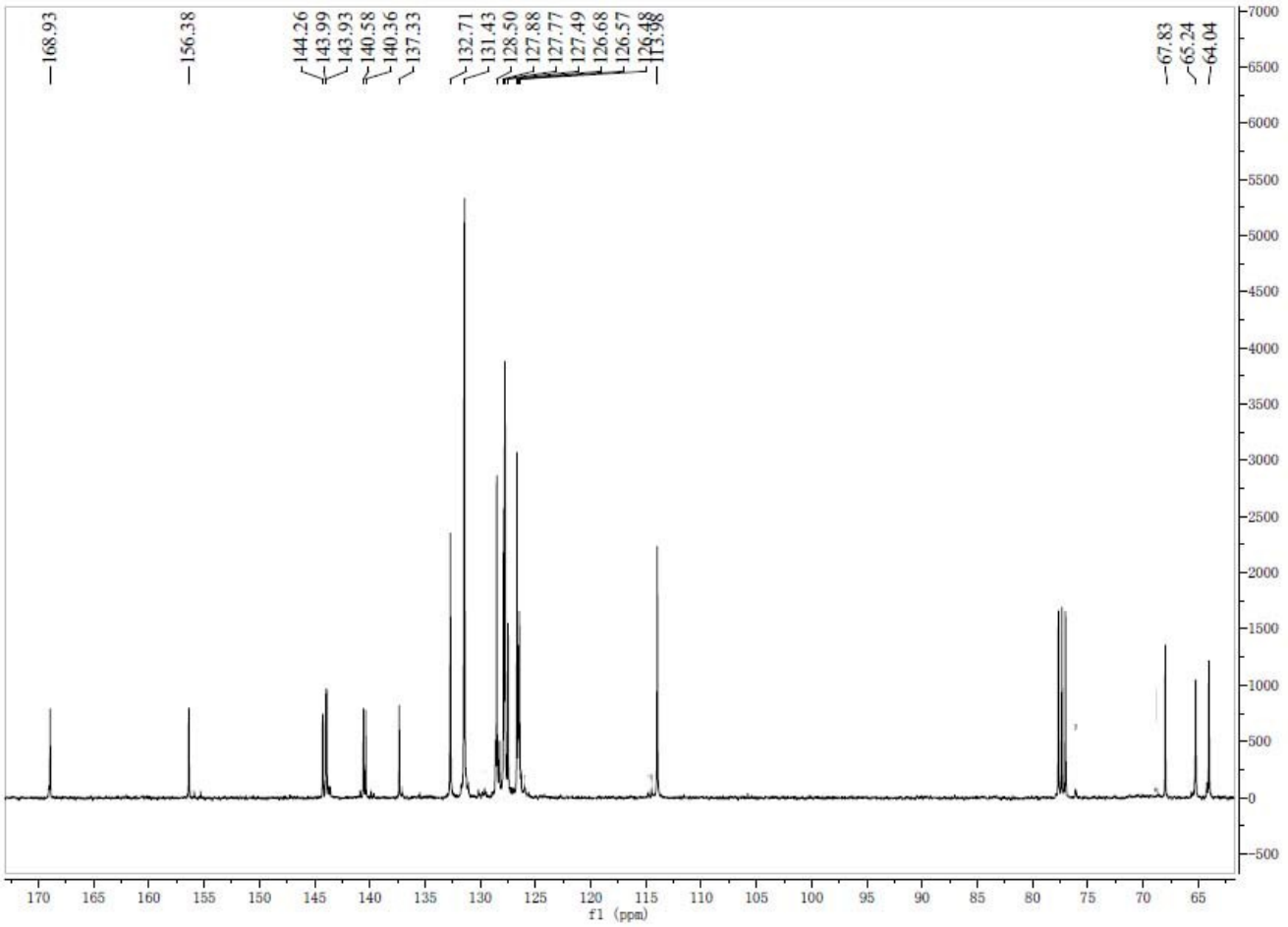


Figure S4. The ^{13}C NMR spectrum of compound **Bis-TPE-1**

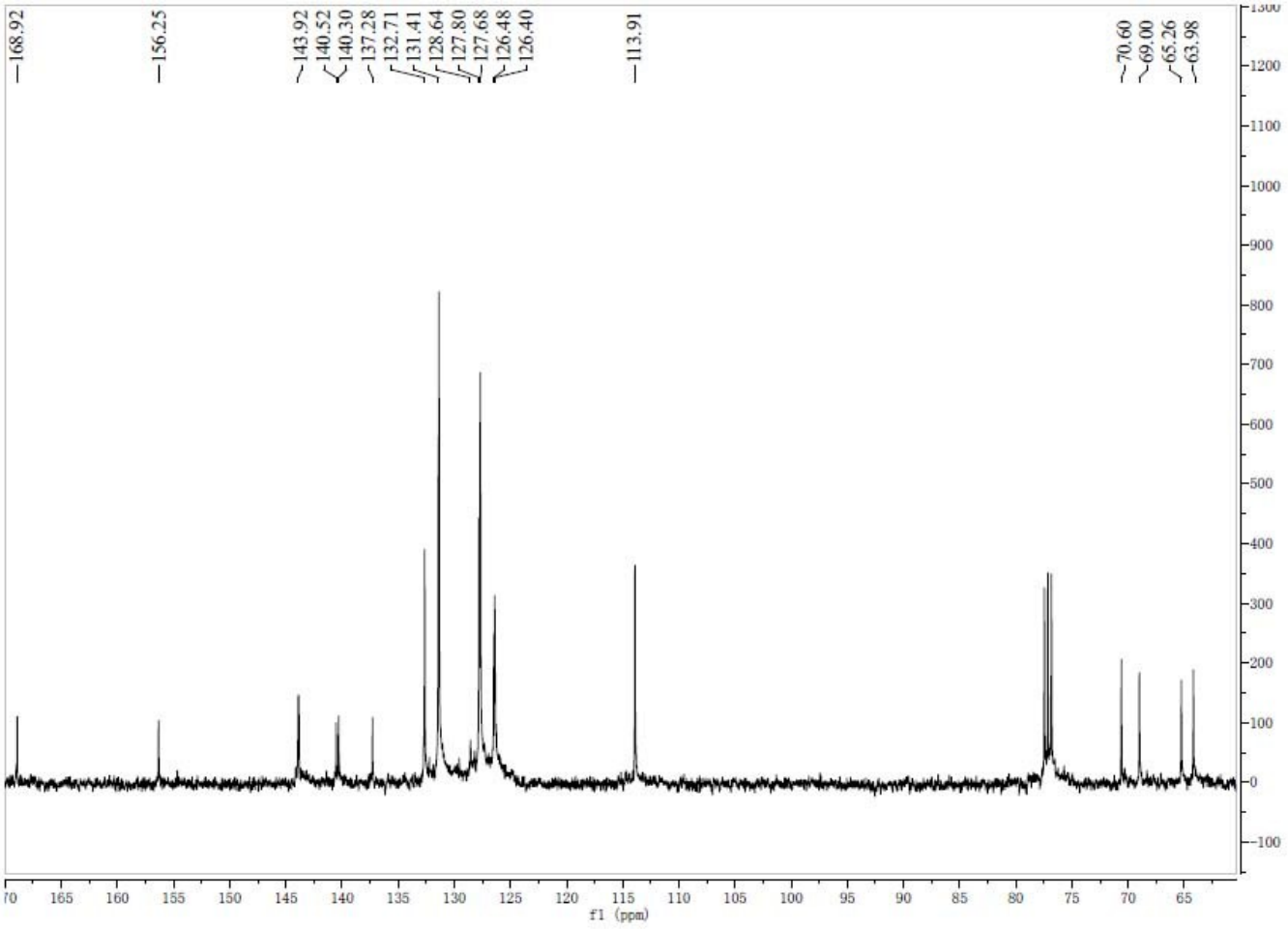


Figure S5. The ^{13}C NMR spectrum of compound **Bis-TPE-2**

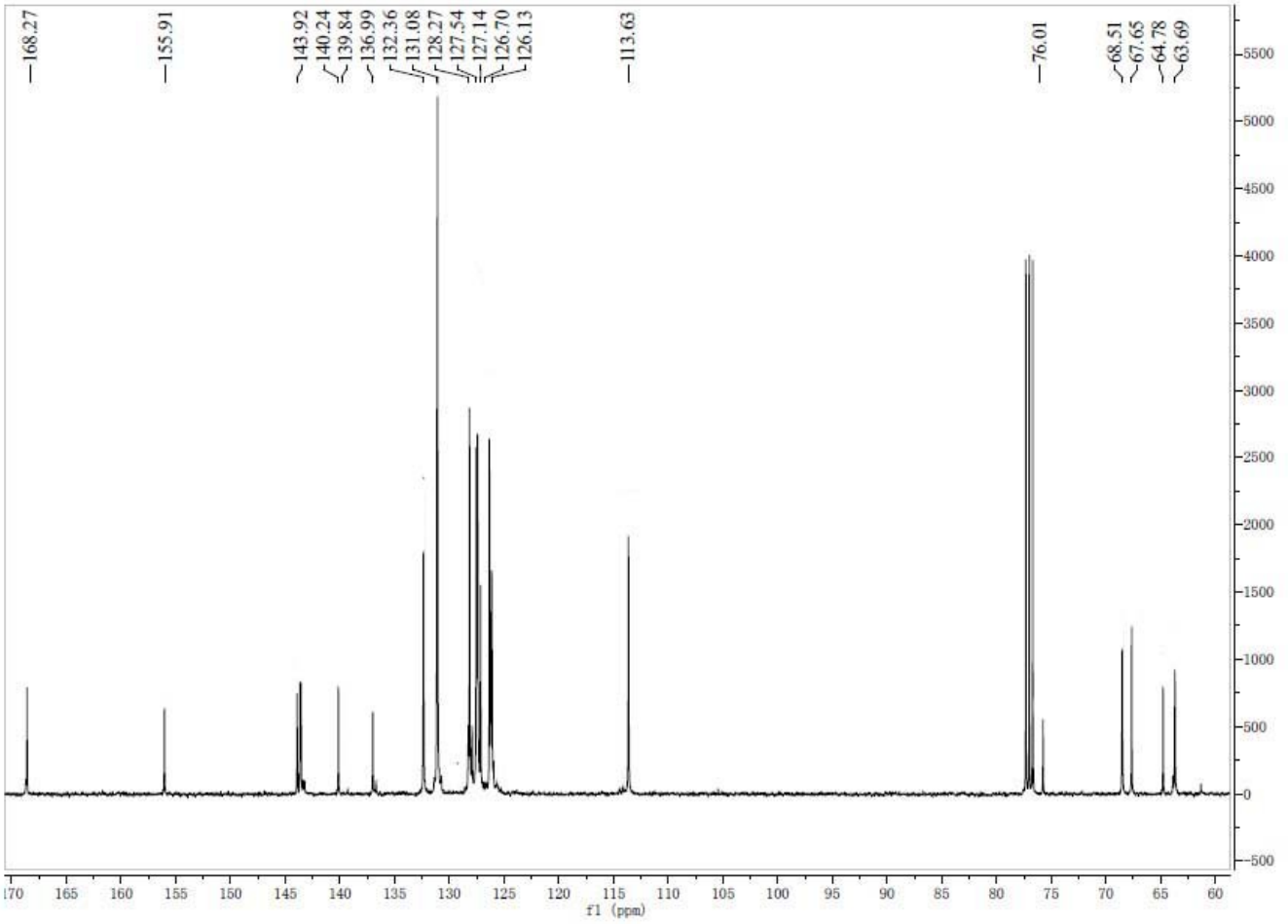


Figure S6. The ^{13}C NMR spectrum of compound **Bis-TPE-3**

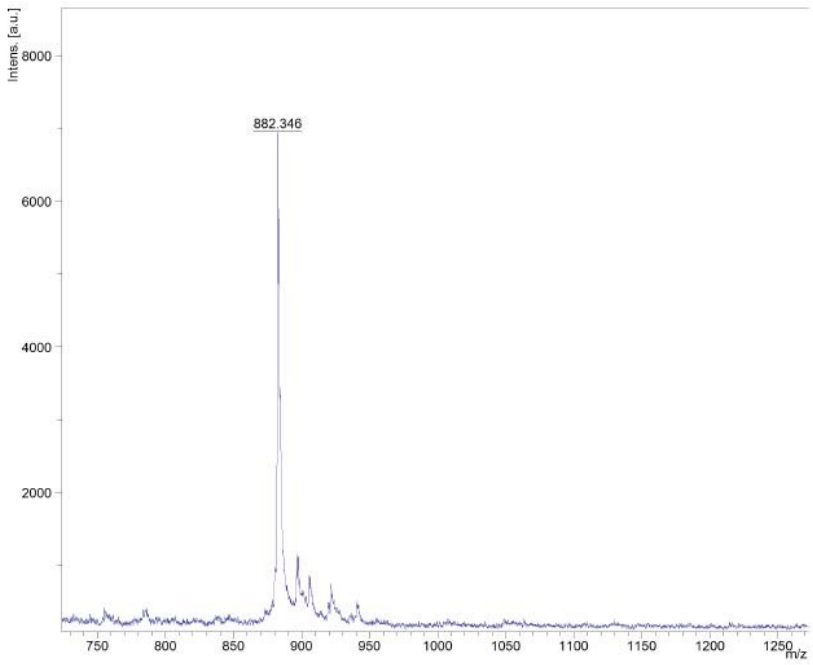


Figure S7. MALDI-TOF-MS spectrum of compound **Bis-TPE-1**

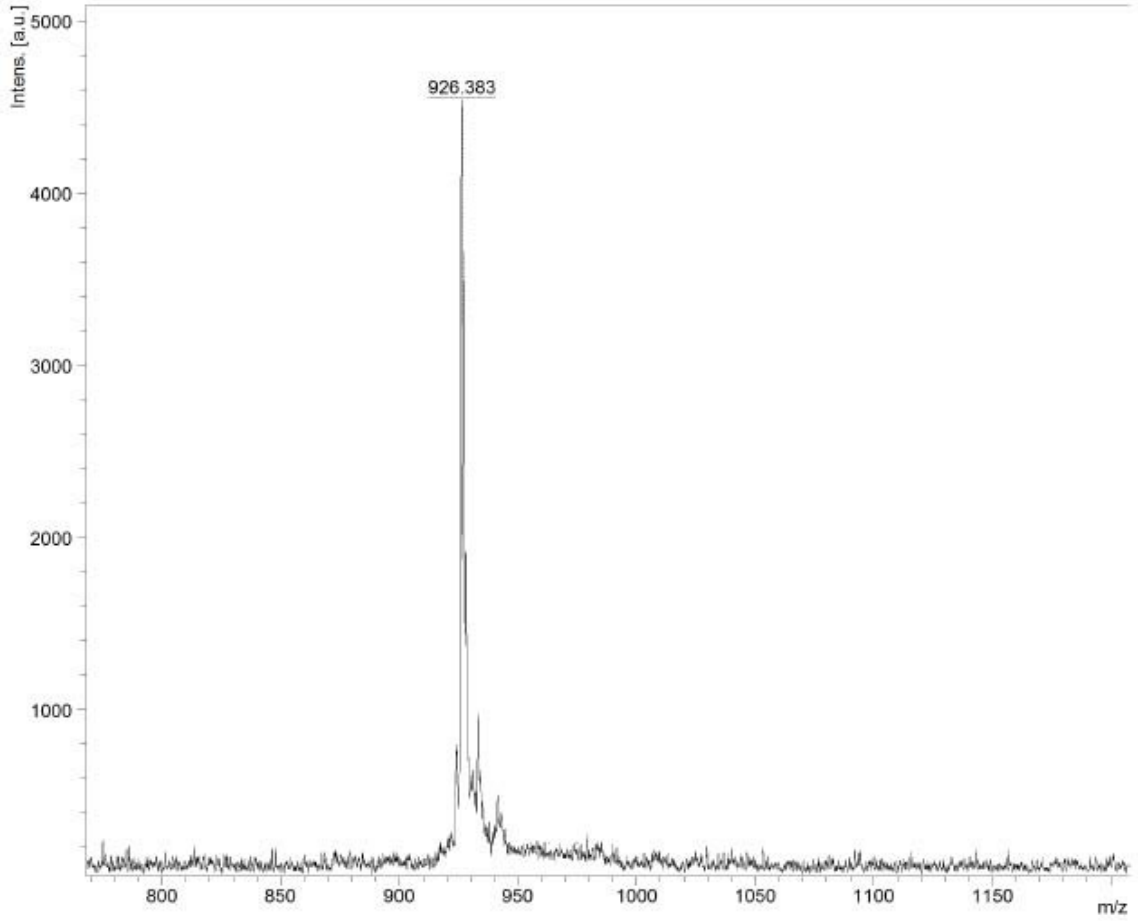


Figure S8. MALDI-TOF-MS spectrum of compound **Bis-TPE-2**

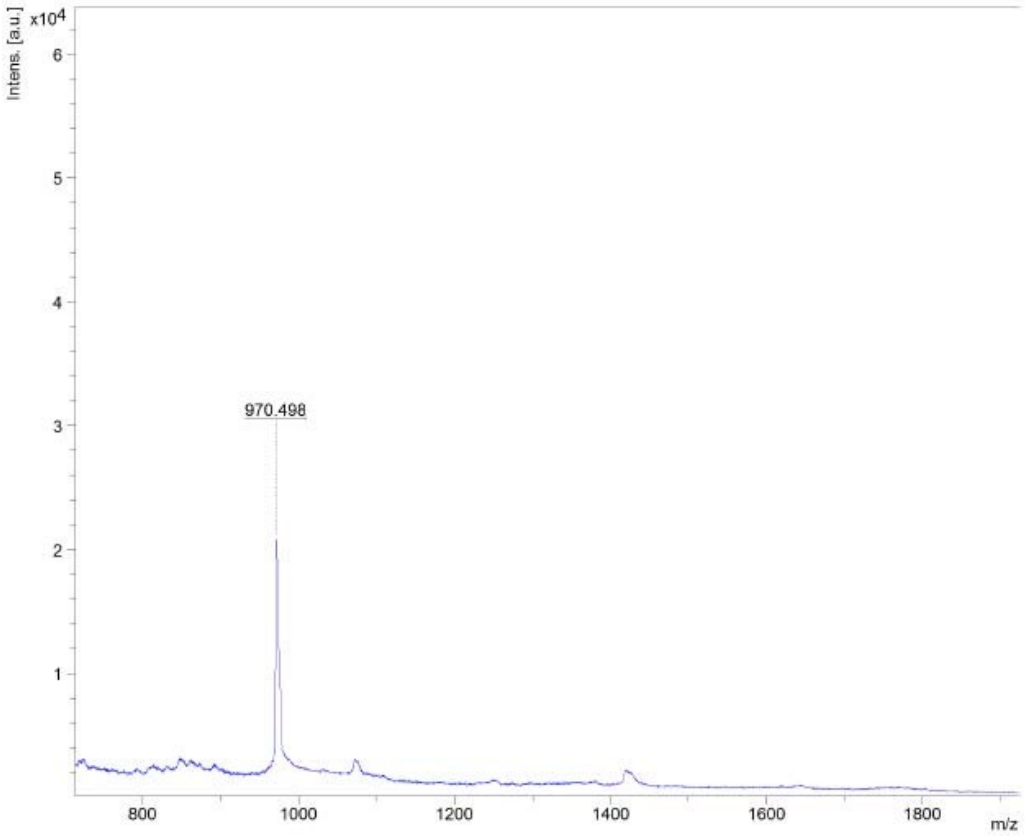


Figure S9. MALDI-TOF-MS spectrum of compound **Bis-TPE-3**

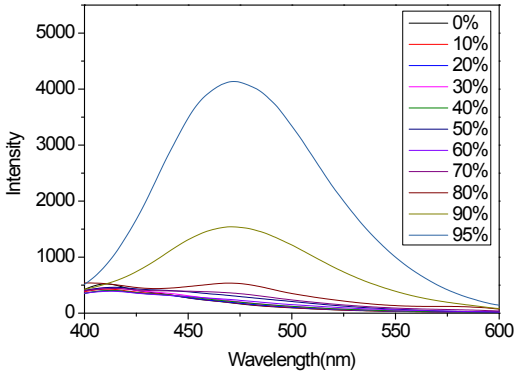


Figure S10 The fluorescence spectra of sample **Bis-TPE-2** in THF/H_2O mixtures with different fractions of H_2O (1×10^{-5} M). excited atλ= 320 nm.

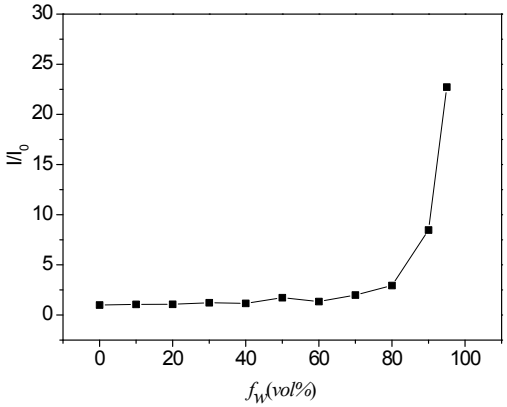


Figure S11 The ratio variation (I/I_0) for fluorescence intensities of sample **Bis-TPE-2** with the changes of fractions of H_2O in THF/H_2O mixtures.

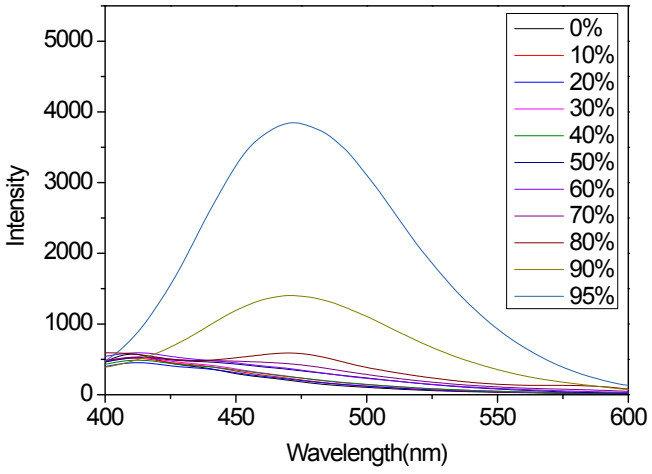


Figure S12 The fluorescence spectra of sample **Bis-TPE-3** in THF/H_2O mixtures with different fractions of H_2O (1×10^{-5} M). excited atλ= 320 nm.

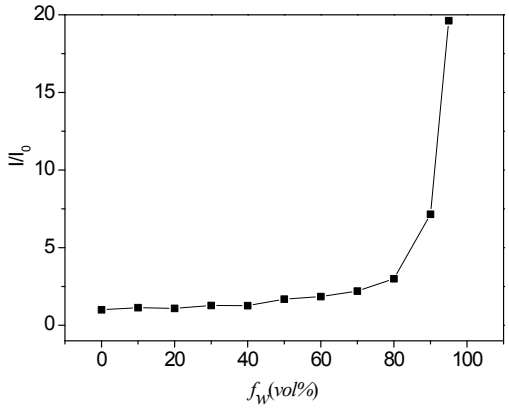


Figure S13 The ratio variation (I/I_0) for fluorescence intensities of sample **Bis-TPE-3** with the changes of fractions of H_2O in THF/H_2O mixtures.

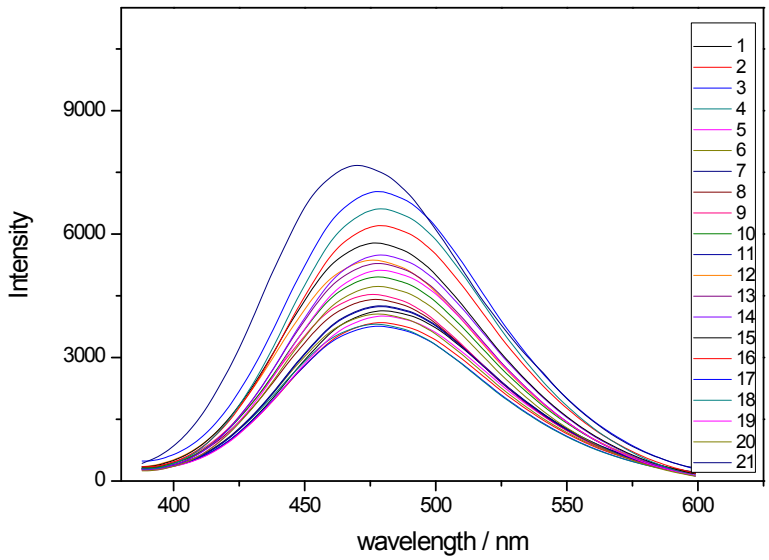


Figure S14 Fluorescence spectra of **Bis-TPE-2** (1×10^{-5} M) with biomolecules 1-21 (2×10^{-5} M) in THF/water (5:95) mixtures λ_{ex}= 360 nm. (1 = None, 2 = leucine, 3 = cysteine, 4 = asprbic acid, 5 = tryptophan, 6 = guanine, 7 = adenine, 8 = cytosine, 9 = thymine, 10 = fructose, 11 = vitamin B1, 12 = starch, 13 = glucose, 14 = sucrose, 15 = vitamin B2, 16 = caffeine, 17 = Na^+, 18 = K^+, 19 = Mg^{2+}, 20 = Ca^{2+}, 21 = FA).

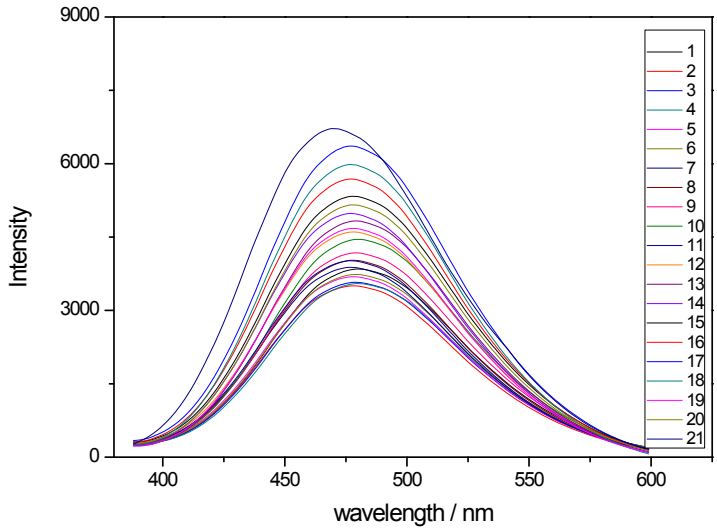


Figure S15 Fluorescence spectra of **Bis-TPE-3** (1×10^{-5} M) with biomolecules 1-21 (2×10^{-5} M) in THF/water (5:95) mixtures λ_{ex}= 360 nm. (1 = None, 2 = leucine, 3 = cysteine, 4 = asprbic acid, 5 = tryptophan, 6 = guanine, 7 = adenine, 8 = cytosine, 9 = thymine, 10 = fructose, 11 = vitamin B1, 12 = starch, 13 = glucose, 14 = sucrose, 15 = vitamin B2, 16 = caffeine, 17 = Na^+, 18 = K^+, 19 = Mg^{2+}, 20 = Ca^{2+}, 21 = FA).

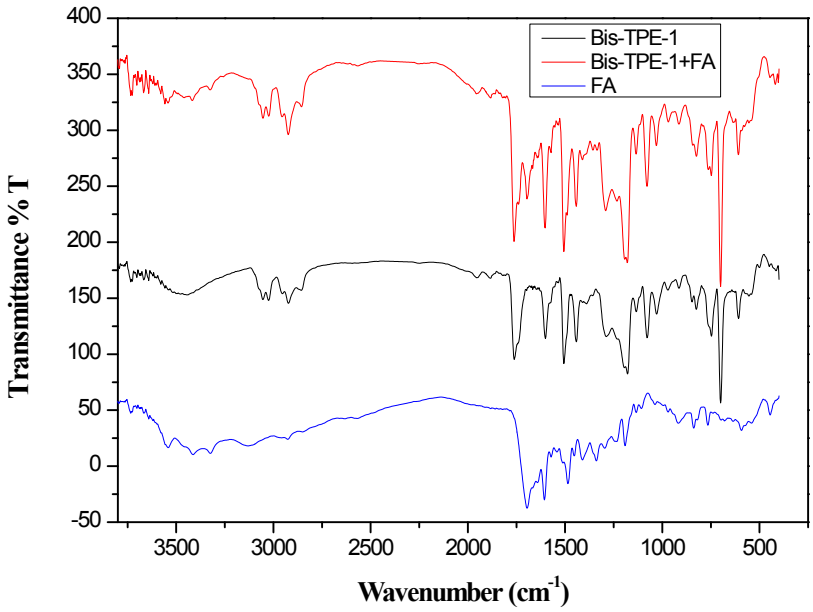


Figure S16 The FT-IR spectra of **Bis-TPE-1**, FA and **Bis-TPE-1** with FA (1:1).

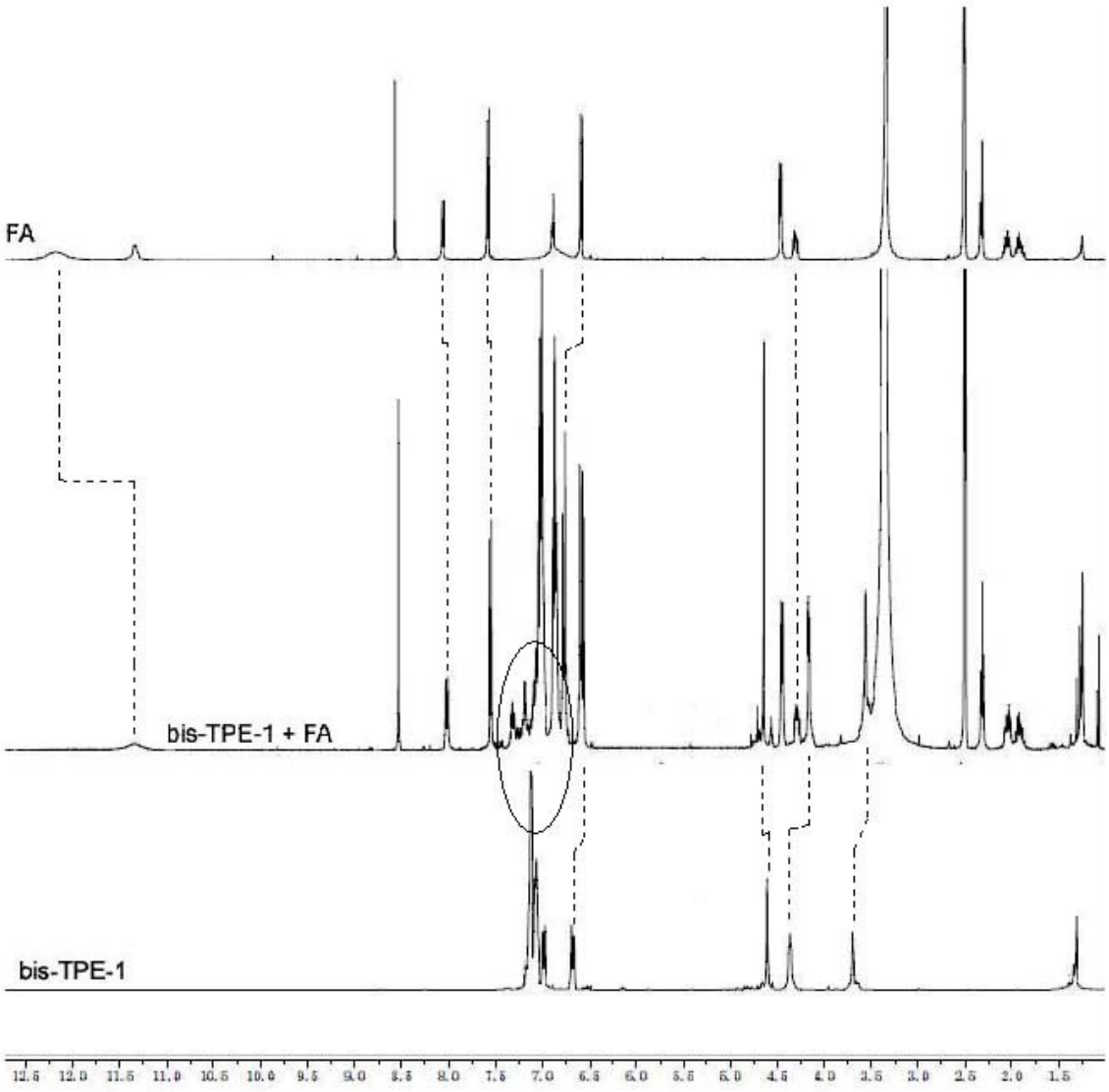


Figure S17 The comparison of ^{1}H NMR of bis-TPE-1, FA and **bis-TPE-1** with FA (1:1).

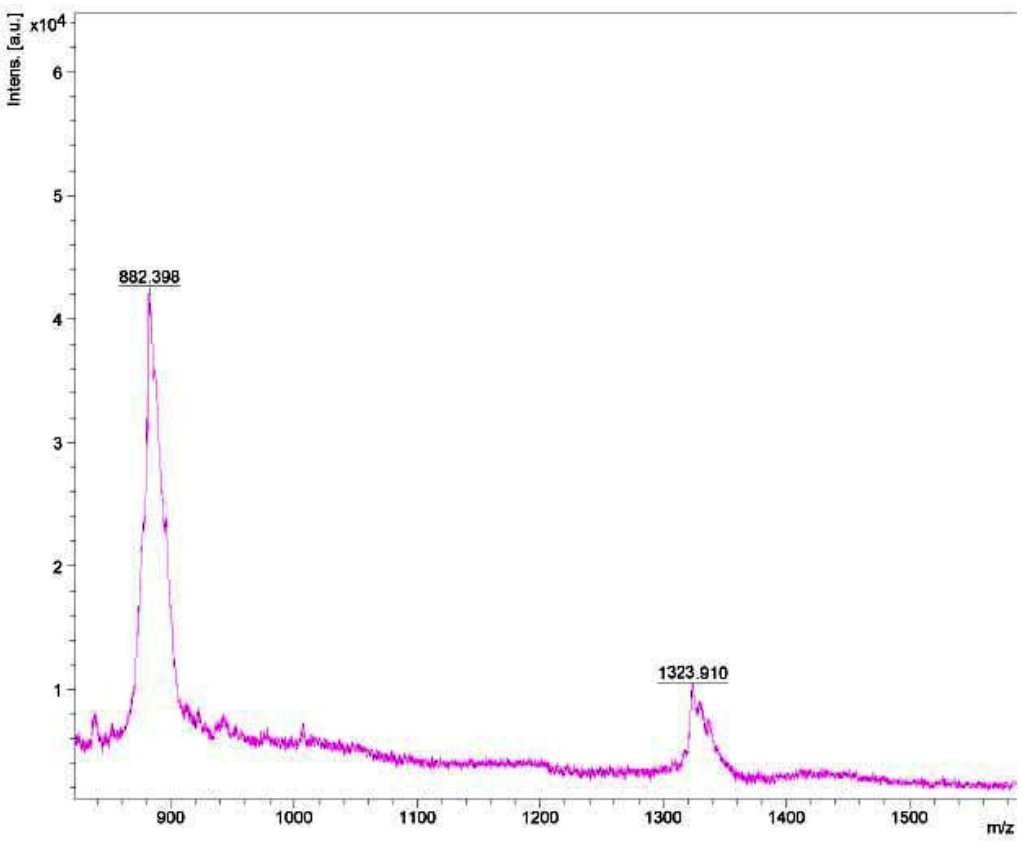


Figure S18 The MALDI-TOF-MS spectrum of compound **Bis-TPE-1** with 5.eq of FA.

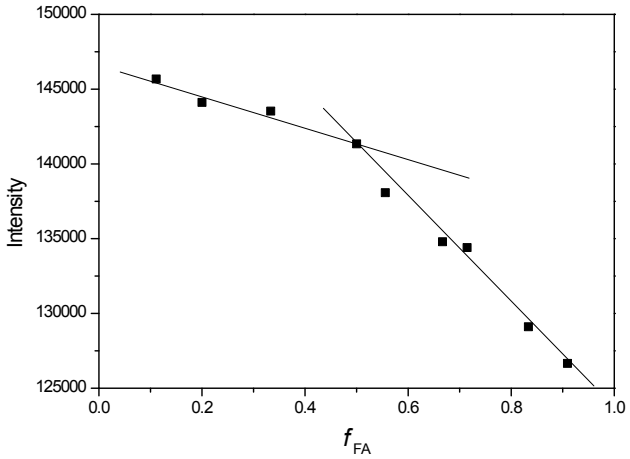


Figure S19. Fluorescence Jobs' plot (λ_{em} = 465 nm, λ_{ex} = 360 nm,) of **Bis-TPE-1** and FA in THF/H_2O (9.5:0.5, V/V) solution with a total concentration of [the sensor] + [folic acid] = 20 μM.

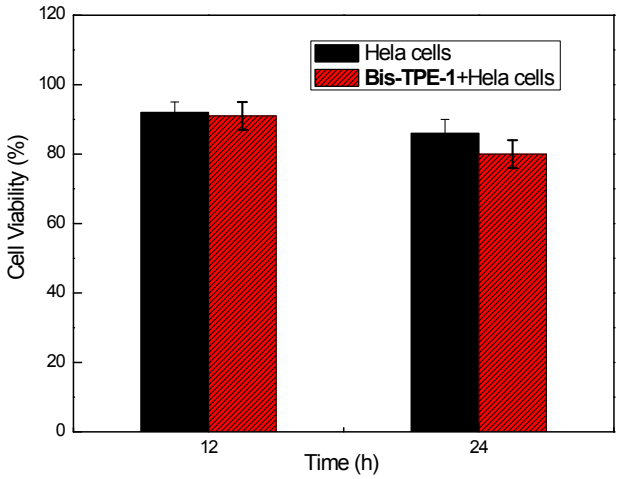


Figure S20 Cell viability of Hela cells before and after incubated with **Bis-TPE-1** (1.0×10^{-5} M) for 12 h and 24 h.