Supporting Information

Highly efficient FRET from aggregation-induced emission to BODIPY emission based on host-guest interaction for mimicking the light-harvesting system

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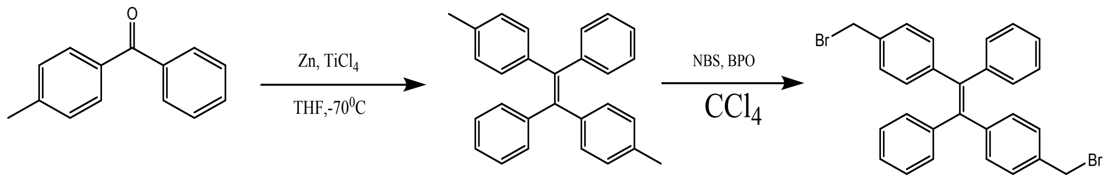
General Information

All chemical reagents were commercially available and of analytical grade without further purification except especially noted.The stock solutions of K+ were prepared form KCl with doubly distilled water. Melting points were measured with a shanghai WRS-1B digital melting point apparatus. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were measured on a Bruker Avance III spectrometer. Electrospray mass spectra (ESI-MS) were recorded on a Thermofisher LCQ. Elemental analyses were obtained using a Perkin-Elmer-240C analyzer. Fluorescence spectra were determined on a Perkin Elmer LS-55. UV-vis spectra were measured on a Shimadzu UV-3600. Transmission electron micrographs were obtained using JEOL 2010 transmission electron microscope (TEM) at an accelerating voltage of 200 KV. Stock solutions for analysis were prepared (1×10^{-5} mol·L^{-1} for compound **M1** or **M2** in THF:H_2O = 1:9, v/v) immediately before the experiments.

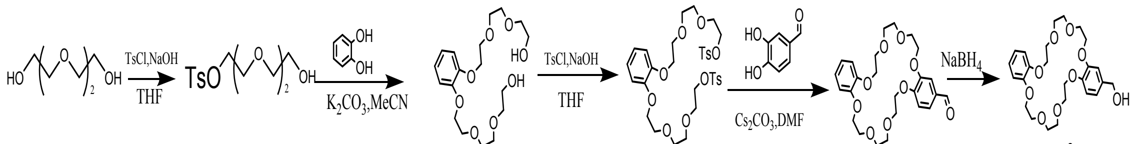
General Procedure for UV-Vis and Fluorescence Studies

Stock solutions of metal ions were prepared (1×10^{-2} mol/L) in deionized water, A stock solution of compound **M2** were prepared (1×10^{-2} mol/L) in THF:H_2O (1:9, v/v) . A stock solution of compounds **M1** or **M2** (1×10^{-5} mol·L^{-1}) was prepared in THF:H_2O (1:9, v/v) immediately before the experiments. In experiments, each time a 3 mL solution of **M1** (10 µM) was filled in a quartz optical cell of 1 cm optical path length, and then the **M2** (10mM) stock solution was added. For fluorescence measurements, fluorescence intensity obtained with the band path 320-600nm upon excitation at 305 nm and band path 460-660 nm upon excitation at 450 nm.

Synthesis and Characterization of Chemodosimeter M1



A_1 A_2 1



B_1 B_2 B_3 B_4 B_5 2

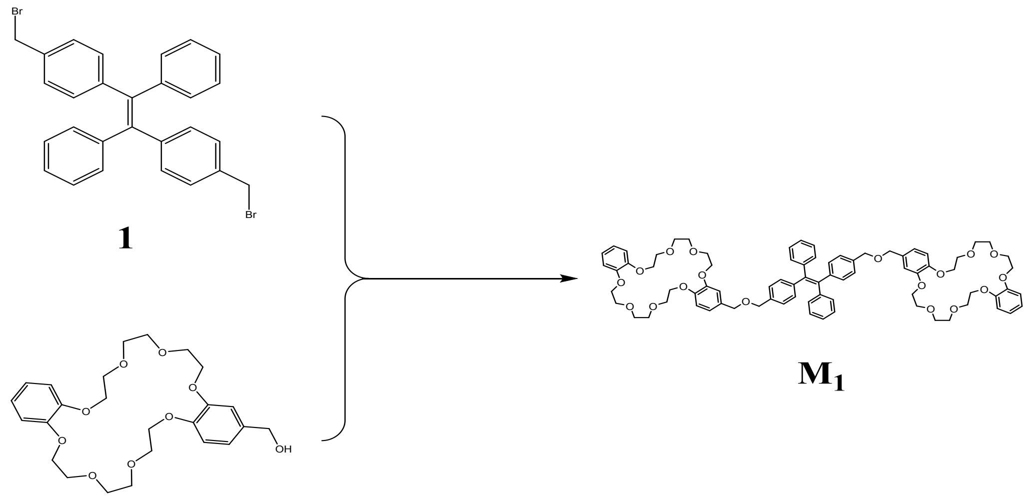


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Fig. S1 Synthetic pathway of compound M1

Compound **1** was synthesized according to known procedure.[S1(a)]

Synthesis of compound 2

(1) A 500ml three-necked round-bottom flask were added **B_1** (80g,0.532mol) with 50ml THF, a solution of NaOH in Deionized water was dropwised into the mixture, then a solution of TsCl in THF was added in ice bath. The mixture was stirred for 5h in room temperature. The solvent was removed at reduced pressure, the residue was dissolved in EA, washed with water several times, The organic layer was dried over Mg SO_4, and concentrated under reduced pressure. The product **B_2** (38g, yield: 89.2%) was obtained.

(2) Into a nitrogen-filled 500ml three-necked round-bottom flask were added **B_2** (15.1g, 49.7 mmol), K_2CO_3 (9.6g, 69 mmol), 1,2-benzenedio(2.5g, 22.7 mmol) and 300ml MeCN. After refluxing overnight, the reaction mixture was cooled to room temperature and concentrated under reduced pressure. The red oil product **B_3** was obtained.

(3) Into a 500ml three-necked round-bottom flask were added **B_3** with 300ml THF,the solution was cooled to 4 ^oC and the solution of NaOH was added dropwise. After stirring a few minutes a solution of TsCl in THF was added dropwise, the reaction mixture was stirred 24 hours at room temperature. The solution was concentrated under reduced pressure, dissolved in DCM, washed several times, dried over $MgSO_4$ and filtered , the filtrate was concentrated under reduced pressure. The crude product was purified in a silica gel column using PE as an eluent to yield **B_4** as Yellow oil (5.1g, yield: 66.1%).

(4) Into a nitrogen-filled 500ml three-necked round-bottom flask were added **B_4** (8.3g, 12.15 mmol), 3,4-dihydroxy-benzaldehyd (1.62g, 11.72 mmol), Cs_2CO_3(8g, 24.8 mmol) and 200ml DMF. After refluxing 4 days, the mixture was filtered and concentrated. The crude product was purified in a silica gel column using PE-EA (v/v=1:3) as an eluent to yield **B_5** as a white solid (2.08g, yield: 37.3%).

(5) Into a 250ml three-necked round-bottom flask were added **B_5** (1.4g, 2.94mmol) with 100ml THF/MeOH (v/v=1:1), the reaction mixture was cooled to 4^oC and then $NaBH_4$ (0.38g,10mmol) was added. After stirring at room temperature overnight, the solution was poured into water and extracted with DCM several times, The organic layer was combined and washed with water and brine, and then dried over $MgSO_4$.After filtration and solvent evaporation, the compound 2 was obtained (1.3g,yield 90%).

Synthesis of compound M1

In a three-necked flask, compound **2** (480mg, 1.0mmol) was dissolved in 50ml of distilled THF. The solution was cooled to 4°C,and then NaH (480mg,20mmol) was added.After stirring a few minutes,the solution of compound **1** (220mg, 0.42mmol) in 20ml of distilled THF was added dropwise into the mixture with continuous stirring for 40 minutes. After refluxing overnight,the solution was concentrated under reduced pressure,dissolved in DCM ,washed several times, dried over $MgSO_4$ and filtered , the filtrate was concentrated under reduced pressure. The crude product was purified in a silica gel column using PE-EA (v/v=1:3) as an eluent to yield **M1** as white solid (188.6mg, yield 34.2%). M.P. 53.0℃-55.5℃. ^{1}H-NMR (500 MHz, $CDCl_3$) δ (TMS, ppm): 7.08 (d, *J* = 6.5, 3.0 Hz, 10H), 7.00 (s, 8H), 6.87 (t, *J* = 2.6 Hz, 10H), 6.82 (s, 4H), 4.41 (d, *J* = 3.0 Hz, 8H), 4.14 (d, *J* = 5.5, 3.0 Hz, 16H), 3.91 (m, *J* = 2.2 Hz, 16H), 3.83 (s, 16H); ^{13}C-NMR (125 MHz, CDCl3) δ (TMS, ppm): 148.97, 148.50, 148.33, 143.68, 143.12, 140.73, 136.29, 134.48, 131.35, 127.67, 127.63, 127.21, 126.44, 121.47, 121.05, 119.89, 114.18, 113.98, 113.82, 113.05, 77.40, 77.14, 76.89, 69.91, 69.90, 69.53, 69.38, 64.96; ESI-MS: m/z = 1335.80 (M+Na$^+$). Element analysis (%) Calca. For $C_{78}H_{88}O_{18}$: C, 71.32; H, 6.75. Found: C, 71.56; H, 6.59.

Synthesis and Characterization of Chemodosimeter M2

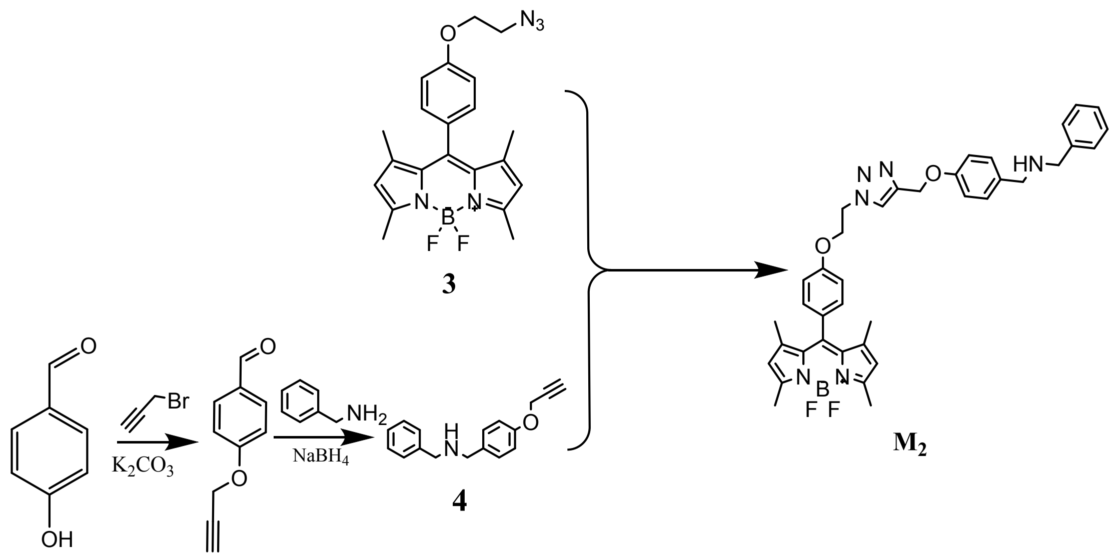


Fig. S2 Synthetic pathway of compound M_2

Compound **3** was synthesized according to known procedure.[S1 (b)]

Synthesis of compound 4

(1) Into a 500ml three-necked round-bottom flask were added 4-Hydroxybenzaldehyde (4.9g, 40 mmol), Propargyl bromide (14.28g,120 mmol) and 300ml acetone with stirring for a few minutes, then Potassium carbonate (11g, 80 mmol) was added. After refluxing for 4 hours, the reaction mixture was cooled to room temperature, the solution was filtered and the filtrate was concentrated under reduced pressure. The residue was dissolved in DCM, washed with water and brine several times, dried over $MgSO_4$ and filtered, the filtrate was concentrated under reduced pressure, recrystallization with PE, the white solid was obtained (5.76g, yield:90%).

(2) Into a 500ml three-necked round-bottom flask were added above white solid (16g, 0.1 mol), benzylamine (22g, 0.2 mol) and 250ml DCM/MeOH (v/v=3:2), the mixture was stirred for

overnight, then the solution was cooled to 4℃, $NaBH_4$ (3.8g,0.1mol) was added with continuous stirring for 40 minutes. After stirring for overnight at room temperature the solution was poured into water and extracted with DCM several times, washed with brine and then dried over $MgSO_4$.After filtration and solvent evaporation, the crude product was purified in a silica gel column using PE-EA (v/v=5:1) as an eluent to give compound **4** as colourless oil (12g, yield: 56%).

Synthesis of compound M2

Into a 50ml three-necked round-bottom flask were added compound **3** (410mg, 1.0 mmol), compound **4** (251mg, 1.0 mmol), $CuSO_4{\cdot}5H_2O$ (400 mg), VCNa (640 mg) and 25ml THF/H_2O (V/V=4:1).The reaction mixture was stirred for 12 hours at room temperature, and then filtered. The filtrate was concentrated under reduced pressure, and the residue was dissolved in DCM, washed with brine several times and dried over $MgSO_4$.After filtration and solvent evaporation, the crude product was purified in a silica gel column using PE-EA (v/v=3:1) as an eluent to give purple solid compound **M2** (370mg,yield 56%). M.P. 124.1℃-126.5℃.^{1}H-NMR (500 MHz, DMSO-$_{d6}$) δ (TMS, ppm): 8.33 (s, 1H), 7.40-7.18 (m, 9H), 7.09 (d, *J* = 8.7 Hz, 2H), 6.99 (d, *J* = 8.6 Hz, 2H), 6.16 (s, 2H), 5.14 (s, 2H), 4.82 (t, *J* = 5.0 Hz, 2H), 4.48 (t, *J* = 5.1 Hz, 2H), 3.65 (d, *J* = 23.6 Hz, 4H), 2.44 (s, 6H), 1.37 (s, 6H); ^{13}C-NMR (125 MHz, DMSO-$_{d6}$) δ (TMS, ppm): 154.01, 142.05, 130.40, 128.57, 128.53, 127.45, 127.36, 125.98, 124.49, 120.61, 114.63, 113.72, 60.36, 51.26, 50.76, 48.41, 38.80, 38.38, 13.56; ESI-MS: m/z = 661.24 [M+H$^+$]. Element analysis (%) Calca. For $C_{38}H_{39}BF_2N_6O_2$: C, 66.09; H, 5.95; N, 12.72. Found: C, 66.18; H, 5.87; N, 12.65.

Emission Spectra of compound M1 in different ratio of THF/H_2O

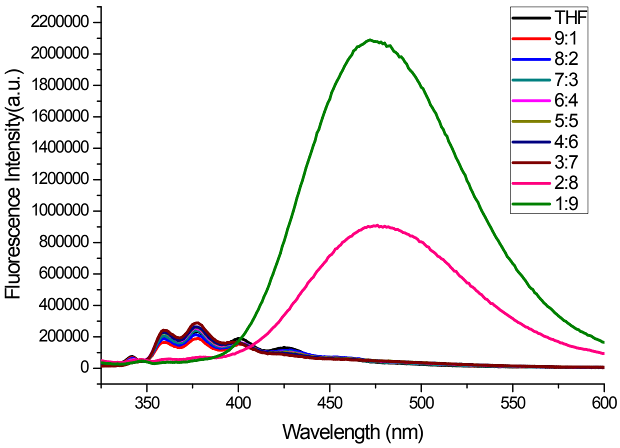
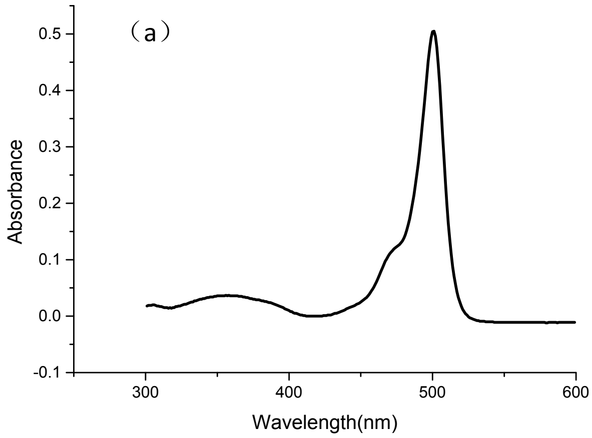
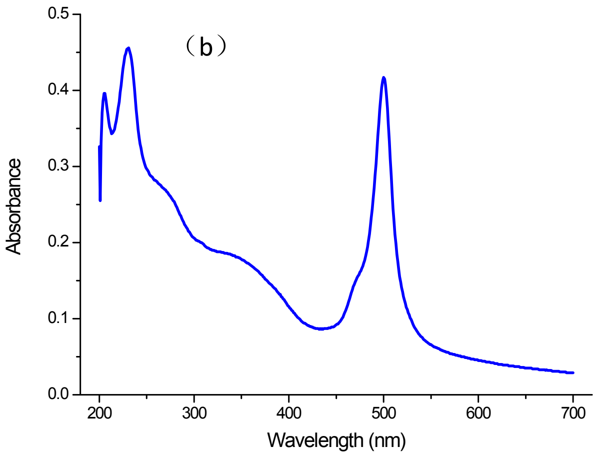
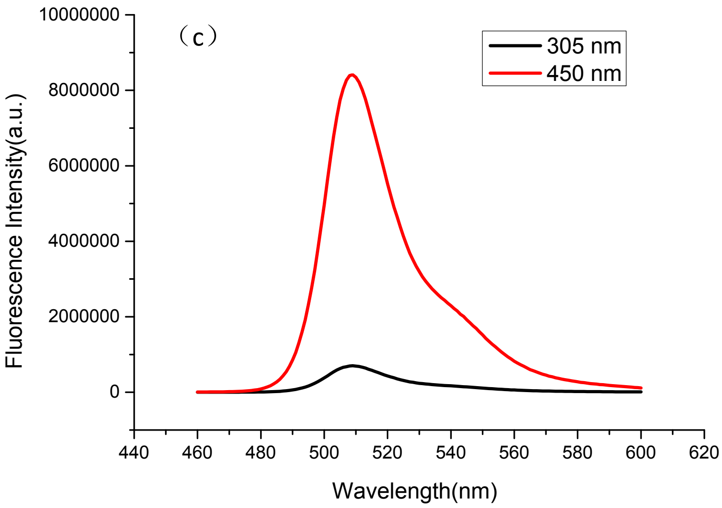


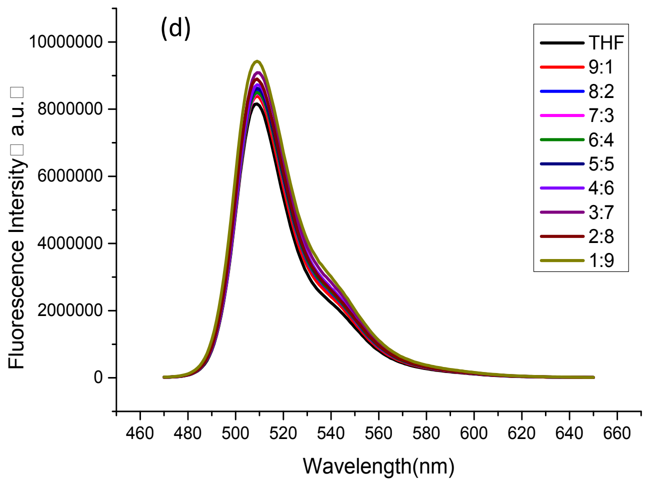
Fig. S3: Fluorescence spectra of compound **M1**(10 μM) in THF/H_2O (v/v) medium (λ_{ex}: 305 nm)

Absorption and Emission Spectra of compound M_2 in THF/H_2O (1:9, v/v)









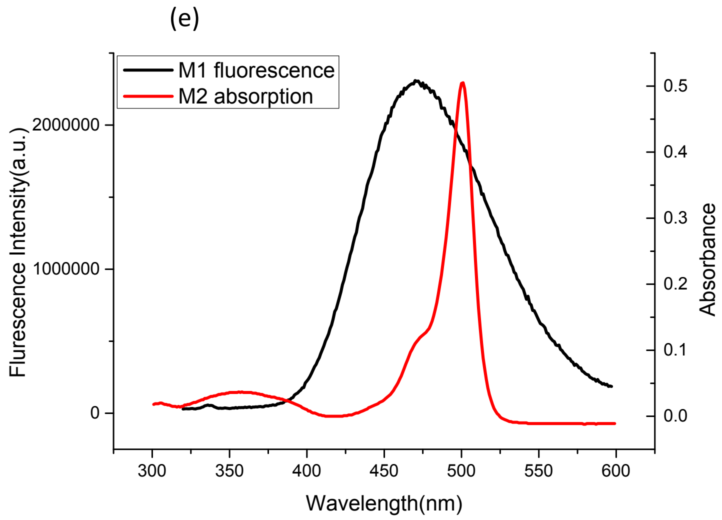
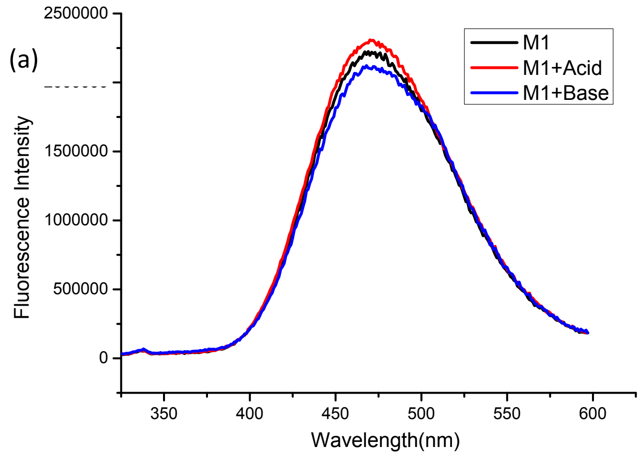


Figure S4:(a) Absorbance of $\mathbf{M_2}$, (b) Absorbance of compound $\mathbf{M_1}$(10μM) with $\mathbf{M_2}$(1.0 equiv) in THF/H_2O (1:9, v/v), (c) fluorescence spectra of compound $\mathbf{M_2}$(10μM) in THF/H_2O (1:9, v/v) medium (λ_{ex}: 305nm& 450nm) , (d) fluorescence spectra of compound $\mathbf{M_2}$(10μM) in different ratio of THF/H_2O (1:9, v/v) medium (λ_{ex}: 450nm), (e)Absorbance of compound $\mathbf{M_2}$(10μM) in THF/H_2O (1:9, v/v) and fluorescence spectra of compound $\mathbf{M_1}$(10μM) in THF/H_2O(1:9, v/v) medium (λ_{ex}: 305nm) .

Emission Spectra of compound M1 or M2 and in the presence of Acid or Base



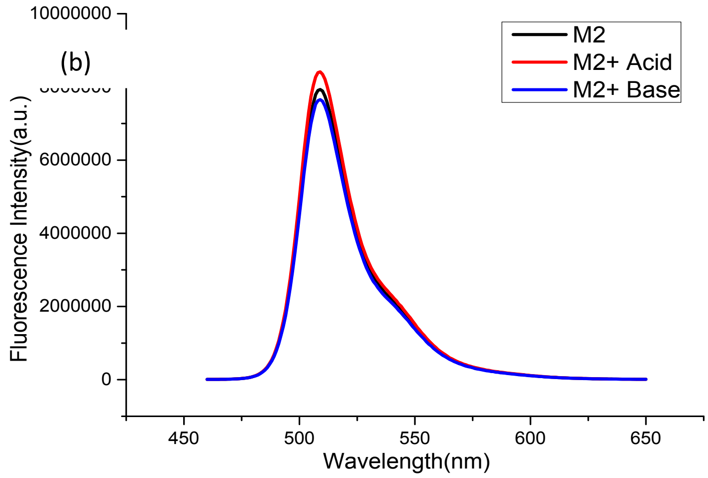


Figure S5: (a) Fluorescence spectra of compound **M1** (10µM) with acid or base (40µM, 4 equiv) in THF/H_2O (1:9, v/v) medium (λ_{ex}: 305nm),(b)Fluorescence spectra of compound **M2** (10µM) with acid or base (40µM, 4 equiv) in THF/H_2O (1:9, v/v) medium (λ_{ex}: 450nm).

Fluorescence Titration Spectra of compound M1 upon addition of M2

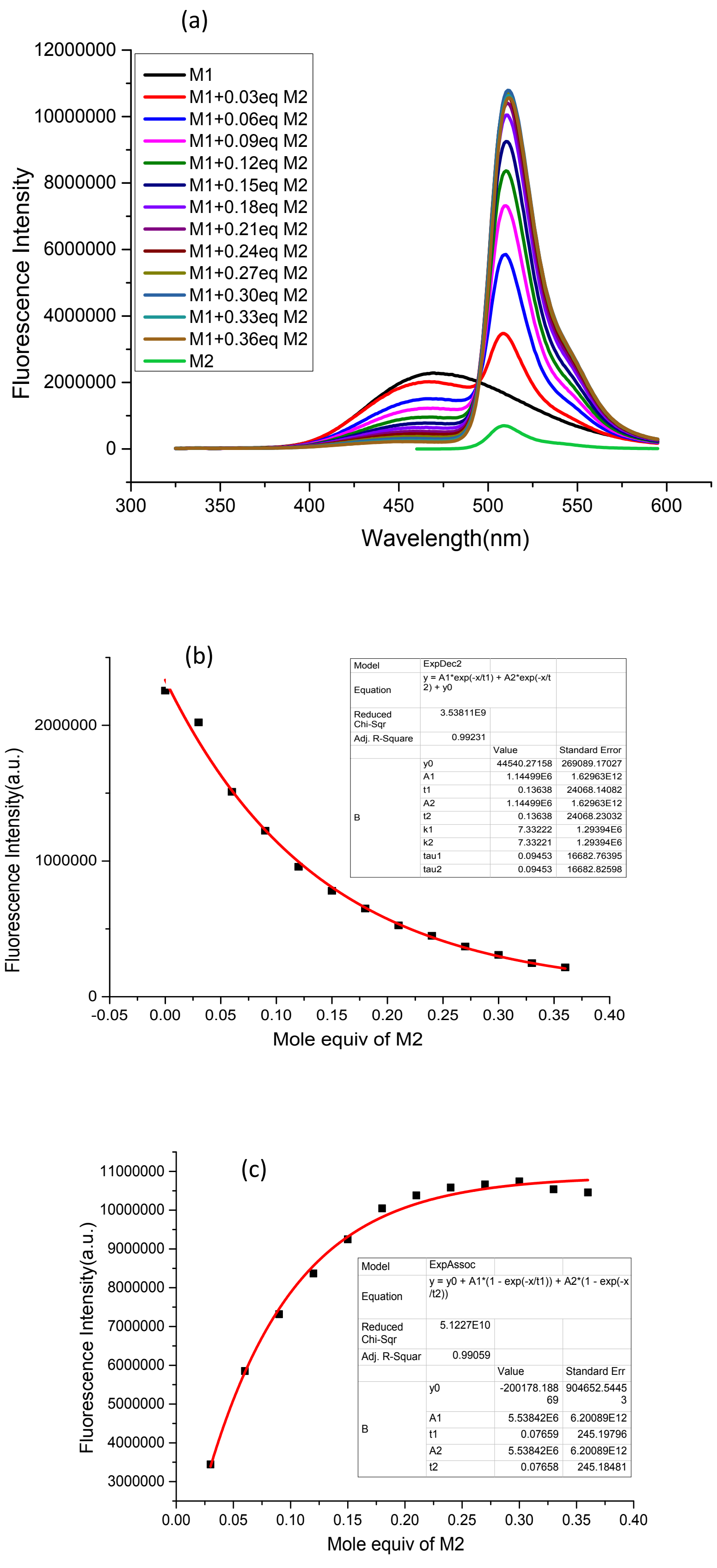
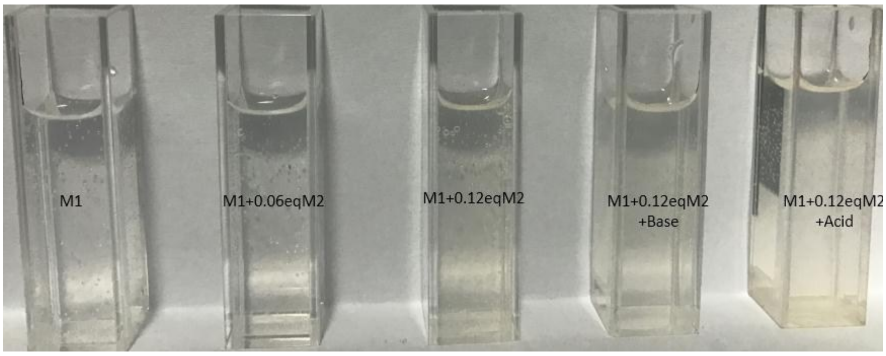


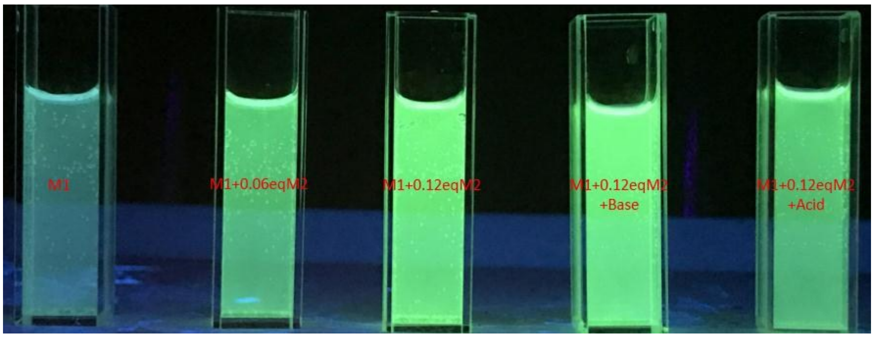
Figure S6: (a)Fluorescence spectra of compound **M1** (10µM) towards **M2** (0, 0.03, 0.06, 0.09, 0.12, 0.15, 0.18, 0.21, 0.24, 0.27, 0.30, 0.33. 0.36 equiv) in THF/H_2O (1:9, v/v) medium (λ_{ex}:

305nm), (b) plot of fluorescence depending on the equiv of **M2** at 465nm,(C)plot of fluorescence depending on the equiv of **M2** at 510nm.

The observed visual color change to the reaction



(a) Visible light



(b) UV light (365 nm lamp)

Figure S7: Observed visual color and fluorescence change of compound **M1** (10µM) upon addition of 0.12equiv of compound **M2** in THF/H_2O (1:9, v/v) medium for 3 hours.

Diameter of M_1

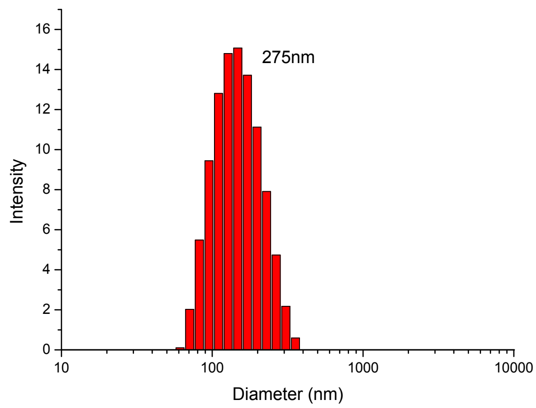
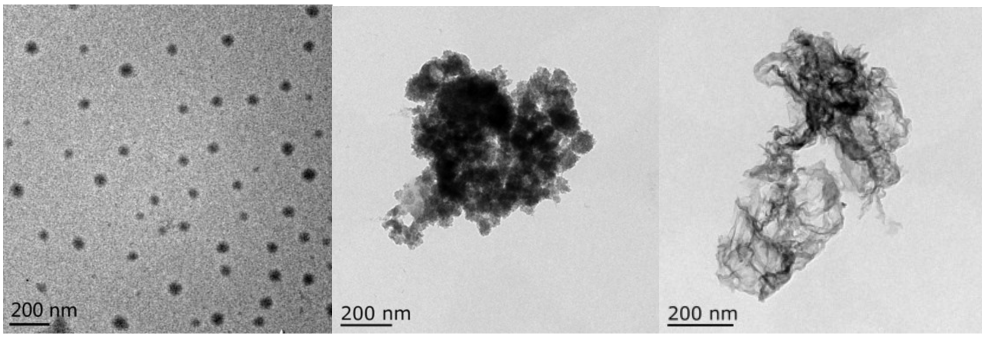


Figure S8. DLS data of the M_1 aggregated practicle

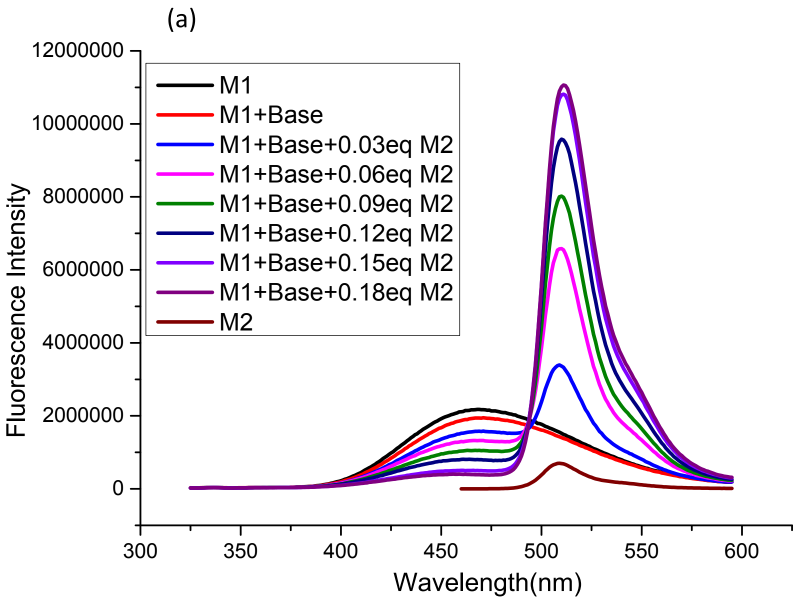
Imaging of M_1&M_2 in TEM



（a） （b） (c)

Figure S9. (a) Imagine of **M1** (10μM) in TEM at 1000nm, (b) Imagine of **M1** (10μM) upon addition of **M2**(0.3equiv) in TEM at 200nm, (c)Imagine of $\mathbf{M_1}$ (10μM) with $\mathbf{M_2}$(1.0equiv) in TEM at 200nm.

The Fluorescence Titration Spectra of M1 under Acid and Base conditiosn



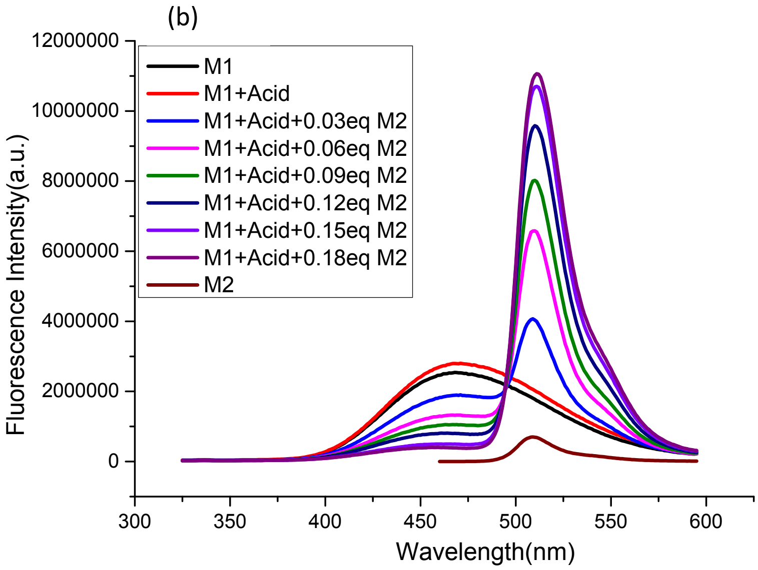
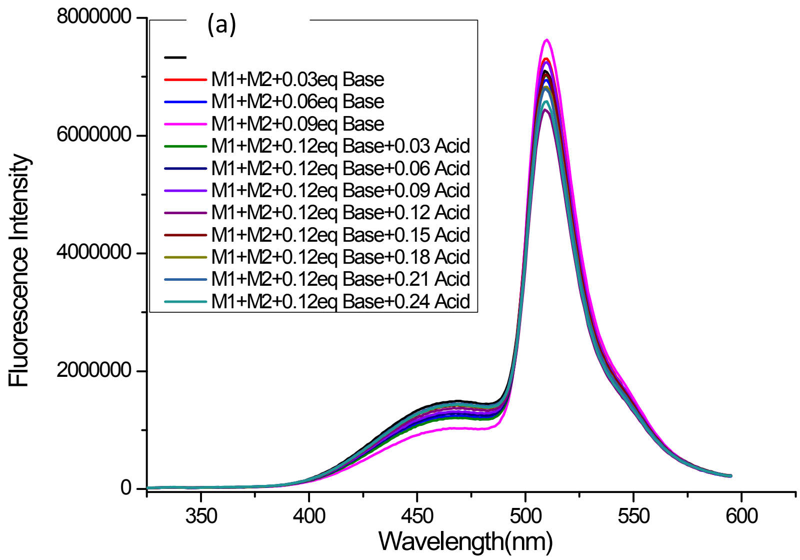


Figure S10: (a) Fluorescence spectra of compound $\mathbf{M_1}$ (10μM) with Base towards $\mathbf{M_2}$ (0, 0.03, 0.06, 0.09, 0.12, 0.15, 0.18 equiv) in THF/H_2O (1:9, v/v) medium (λ_{ex}: 305nm),(b) fluorescence spectra of compound $\mathbf{M_1}$ (10μM) with Acid towards $\mathbf{M_2}$ (0, 0.03, 0.06, 0.09, 0.12, 0.15, 0.18 equiv) in THF/H2O (1:9, v/v) medium (λ_{ex}: 305nm).

The Fluorescence Titration Spectra of M1 and M2 under Acid and Base conditiosn



Figure

Figure S11: Fluorescence spectra of compound **M_1** (10µM) with **M_2** (0.12equiv) towards Base (0, 0.03, 0.06, 0.09equiv) and Acid(0, 0.03, 0.06, 0.09, 0.12, 0.15, 0.18, 0.21, 0.24equiv) in THF/H_2O (1:9, v/v) medium (λ_{ex}: 305nm).

Fluorescence Titration Spectra of compound M_1&M_2 upon addition of K^+

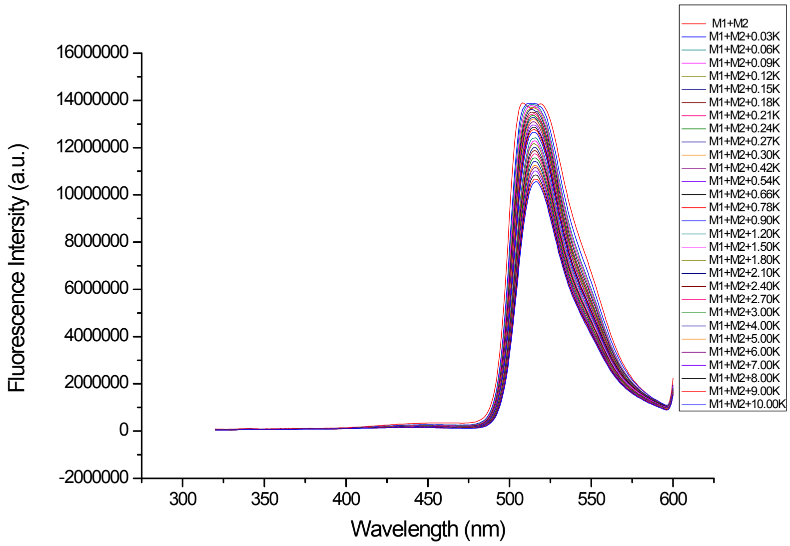


Figure S12: Fluorescence spectra of compound **M1** (10µM) with **M2** (0.50equiv) towards K^+ (0, 0.03, 0.06, 0.09, 0.12, 0.15, 0.18, 0.21, 0.24, 0.27, 0.30, 0.42, 0.54, 0.66, 0.78, 0.90, 1.20, 1.50, 1.80, 2.10, 2.40, 2.70, 3.00, 4.00, 5.00, 6.00, 7.00, 8.00, 9.00, 10.00equiv) in THF/H2O (1:9, v/v) medium (λ_{ex}: 305nm),

References:

S1: (a) Liang, Jing et al . *J. Mater. Chem. B*, 2014, 2,4363

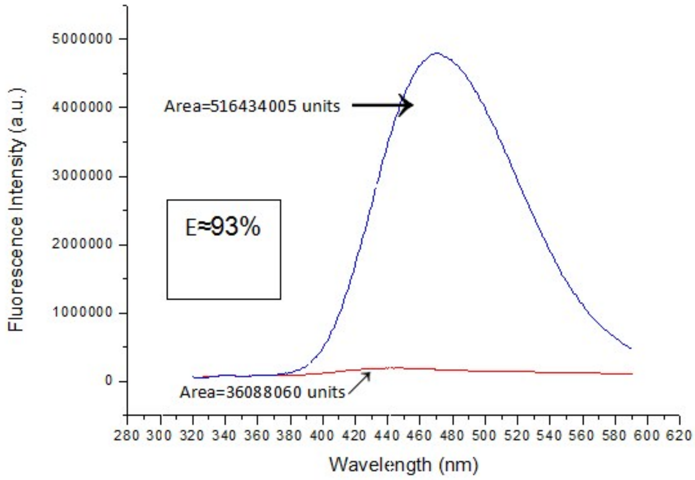
(b) J. Ye, W. Ye, C. Xiao, Y. Chen, G. Wang, and W. Zhang, *Chin. J. Org. Chem.*, 2012, 32, 1503.

Calculation of FRET Efficiency:

$$E=1-F_{DA}/F_D$$

Where F_{DA} is the integrated fluorescence intensity of donor in presence of acceptor and F_D is in absence of acceptors.

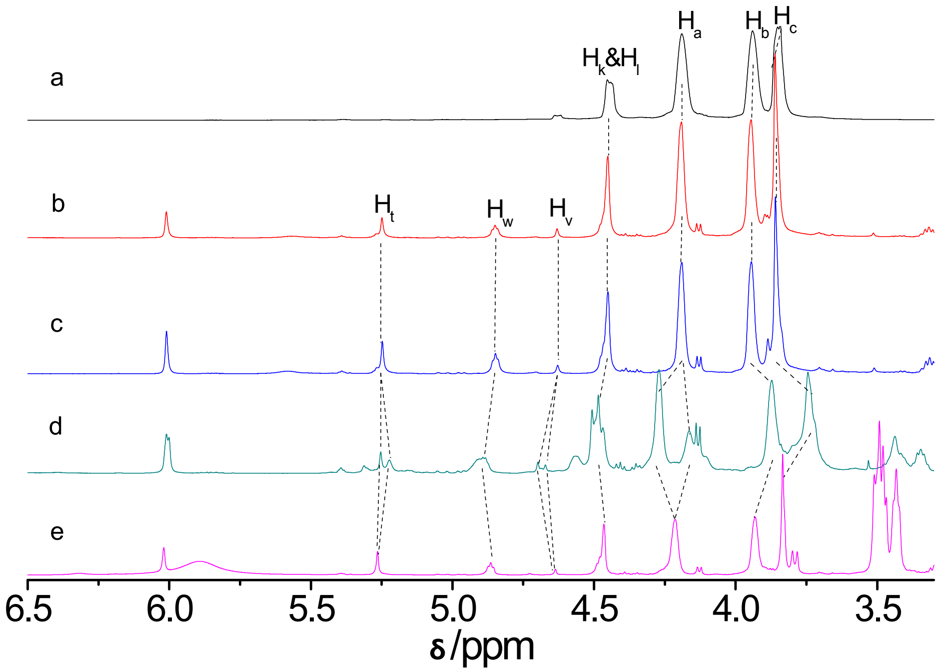
Efficiency in each case has been calculated based on the integrated donor emission intensities in absence and presence of acceptors.



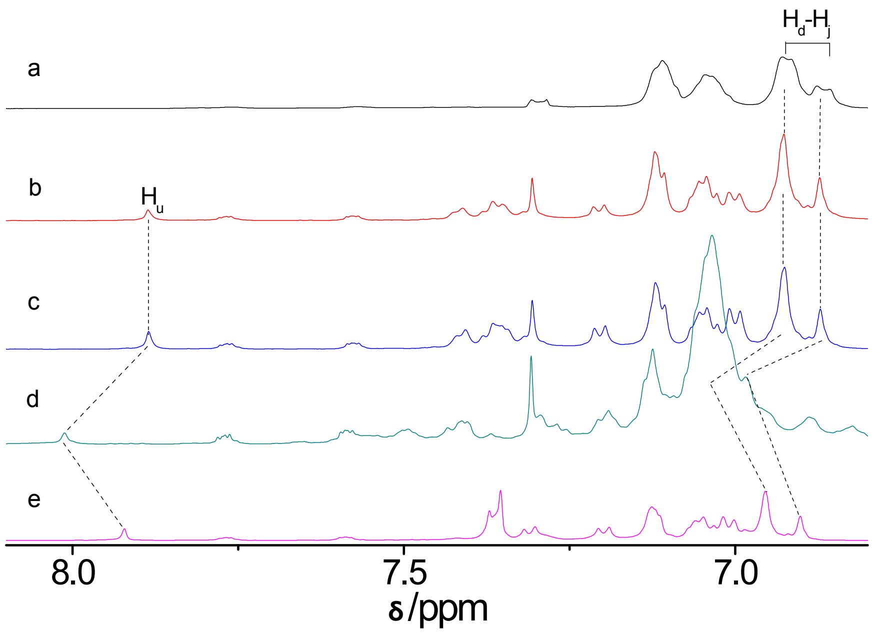
Efficiency = $1 - F_{DA}/F_{D}$ = [1-(36088060/516434005)] x100= 93%

Figure S13. Emission spectra of donor **M1** in absence of acceptor **M2**. The integrated area for the M_1 contribution after titration has been marked in red line.

The change of the ^{1}H NMR spectra after the addition of acid and base



(A)



(B)

Figure S14. Partial ^{1}H NMR spectra (500 MHz, CDCl3): (a) ^{1}H NMR spectrum of host **M1** (1.0 mM), (b) ^{1}H NMR spectrum of host **M1** (1.0 mM) upon addition of 0.5 equiv. of guest **M2**, (c) ^{1}H NMR spectrum of host **M1** (1.0 mM) upon addition of 1.0 equiv. of guest **M2** in $CDCl_3$, (d) ^{1}H NMR spectrum of host-guest system in (b) upon addition of 2.0 equiv. of CF_3COOH, (e) ^{1}H NMR spectrum of host-guest system in (c) upon addition of 4.0 equiv. of DBU。

(A): δ (TMS,ppm): （a）H_a: 4.190，H_b: 3.941，H_c: 3.842，H_k&H_l:4.452 （b）H_a: 4.192，H_b: 3.946，H_c: 3.861，H_k&H_l:4.453，H_t: 5.249，H_v: 4.631，H_w: 4.850，（c）

H_a：4.192，H_b：3.945，H_c：3.860，H_k&H_l:4.453，H_t：5.248，H_v：4.629，H_w：4.848，（d）H_a：4.271&4.165，H_b：3.873，H_c：3.745，H_k&H_l:4.485，H_t：5.245&5.223，H_v：4.686 (4.699,4.672)，H_w：4.893,（e）H_a：4.214，H_b：3.931，H_c：3.834，H_k&H_l:4.466，H_t：5.265，H_v：4.637，H_w：4.865

(B): δ (TMS,ppm)：（a）H_d-Hj：6.929~6.877，（b）H_d-Hj：6.927～6.873，H_u：7.886，（c）H_d-Hj：6.926～6.872，H_u：7.885，（d）H_d-Hj：7.035～6.985，H_u：8.012，（e）H_d-Hj：6.955～6.902，H_u：7.922

^{1}H NMR、^{13}C NMR and MS spectrum

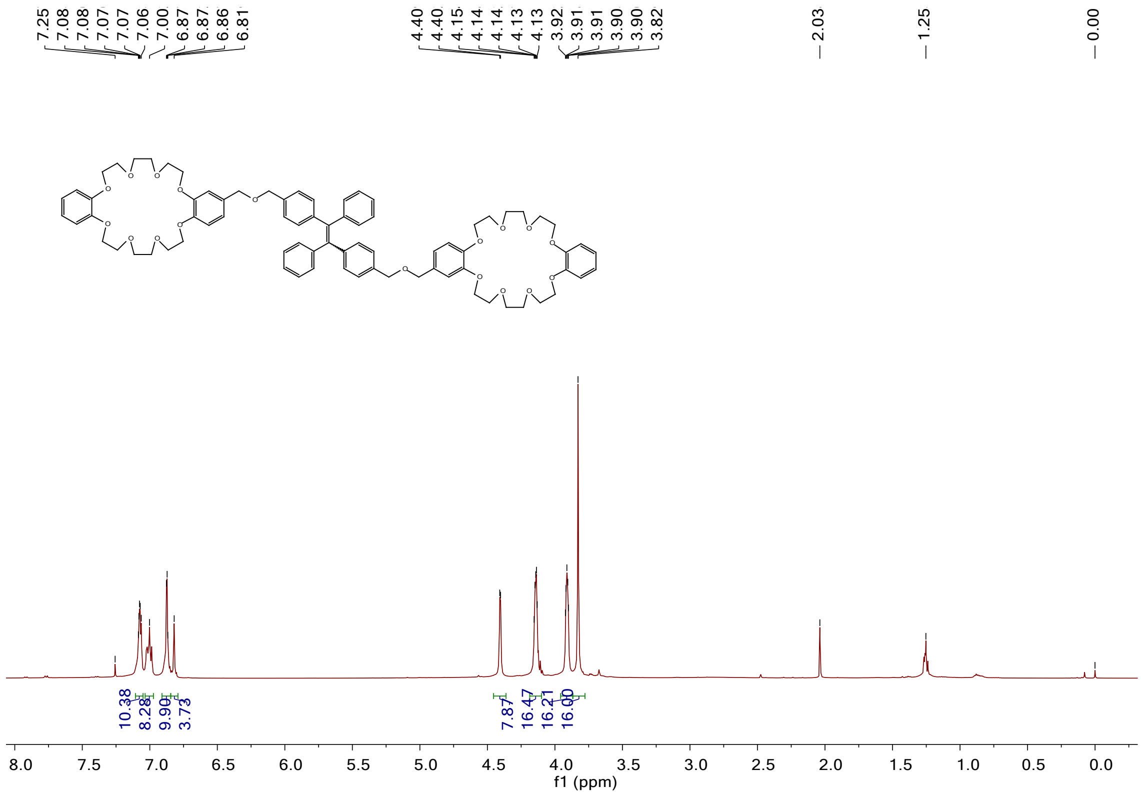


Figure S15: ^{1}H NMR spectrum of compound **M_1** in $CDCl_3$

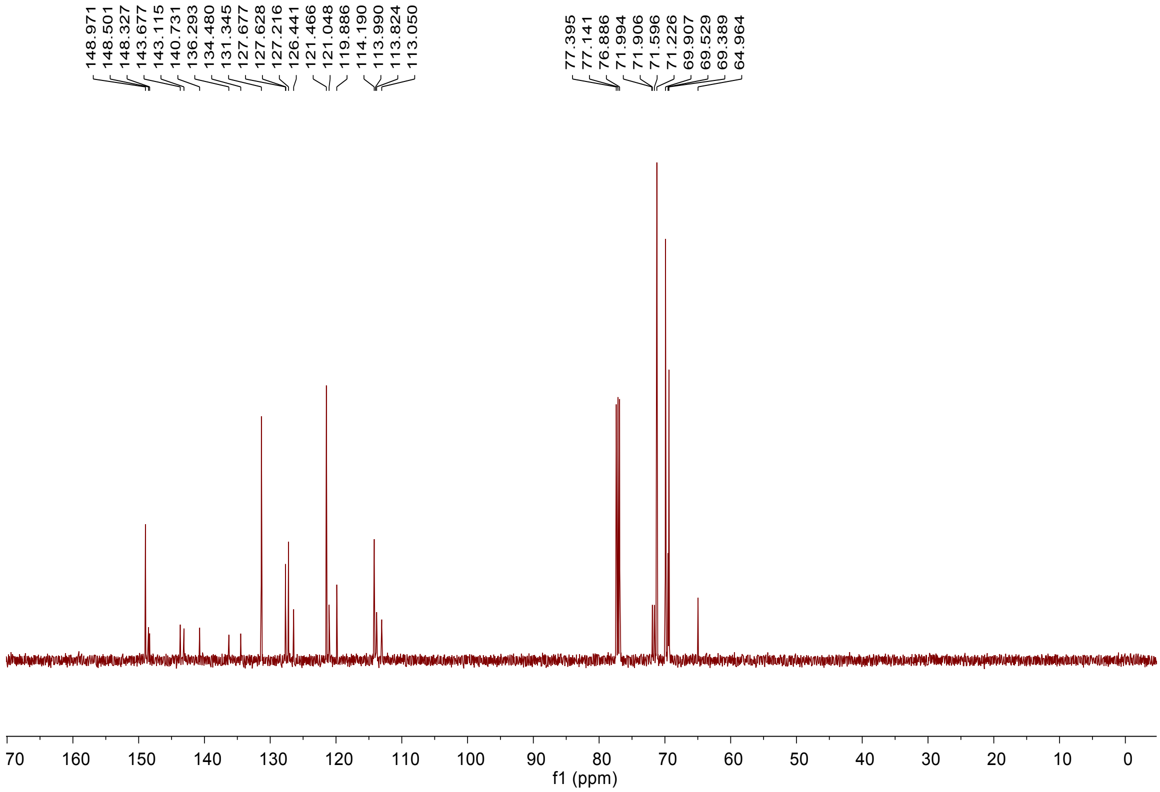


Figure S16: ^{13}C NMR spectrum of compound $\mathbf{M_1}$ in $CDCl_3$

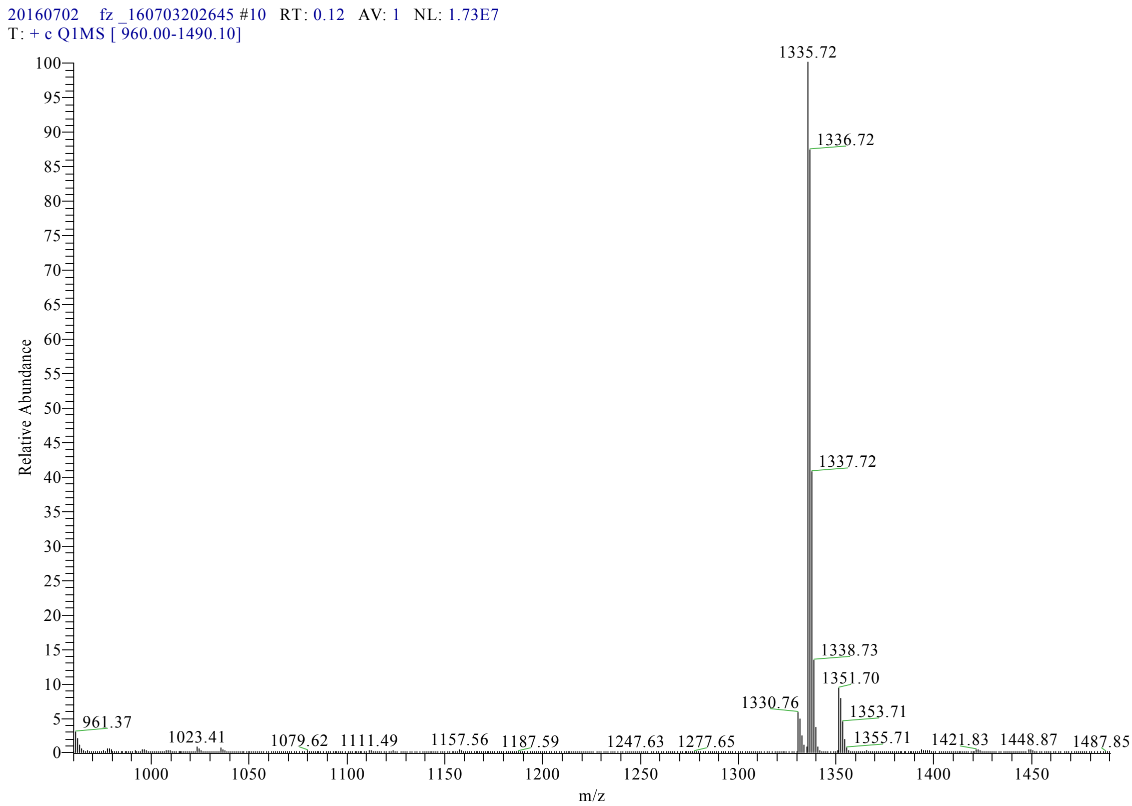


Figure S17: MS spectrum of compound $\mathbf{M_1}$

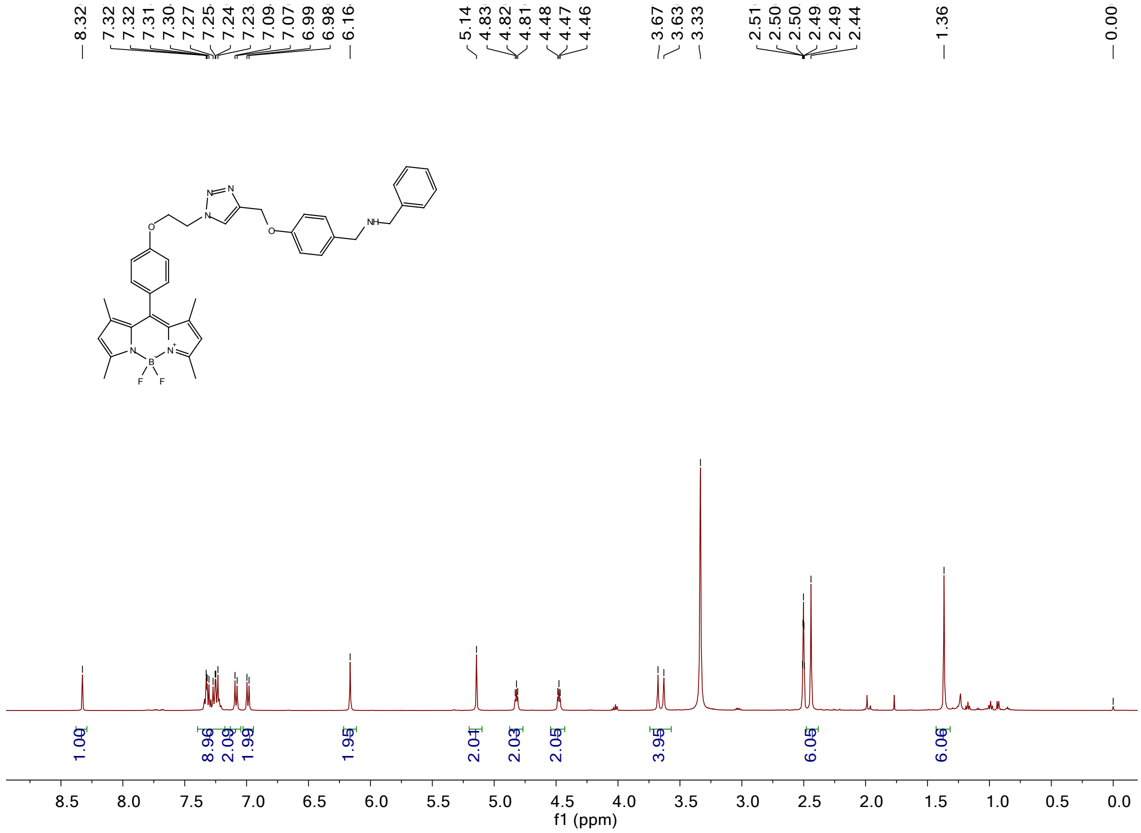


Figure S18: ^{1}H NMR spectrum of compound $\mathbf{M_2}$ in d6-DMSO

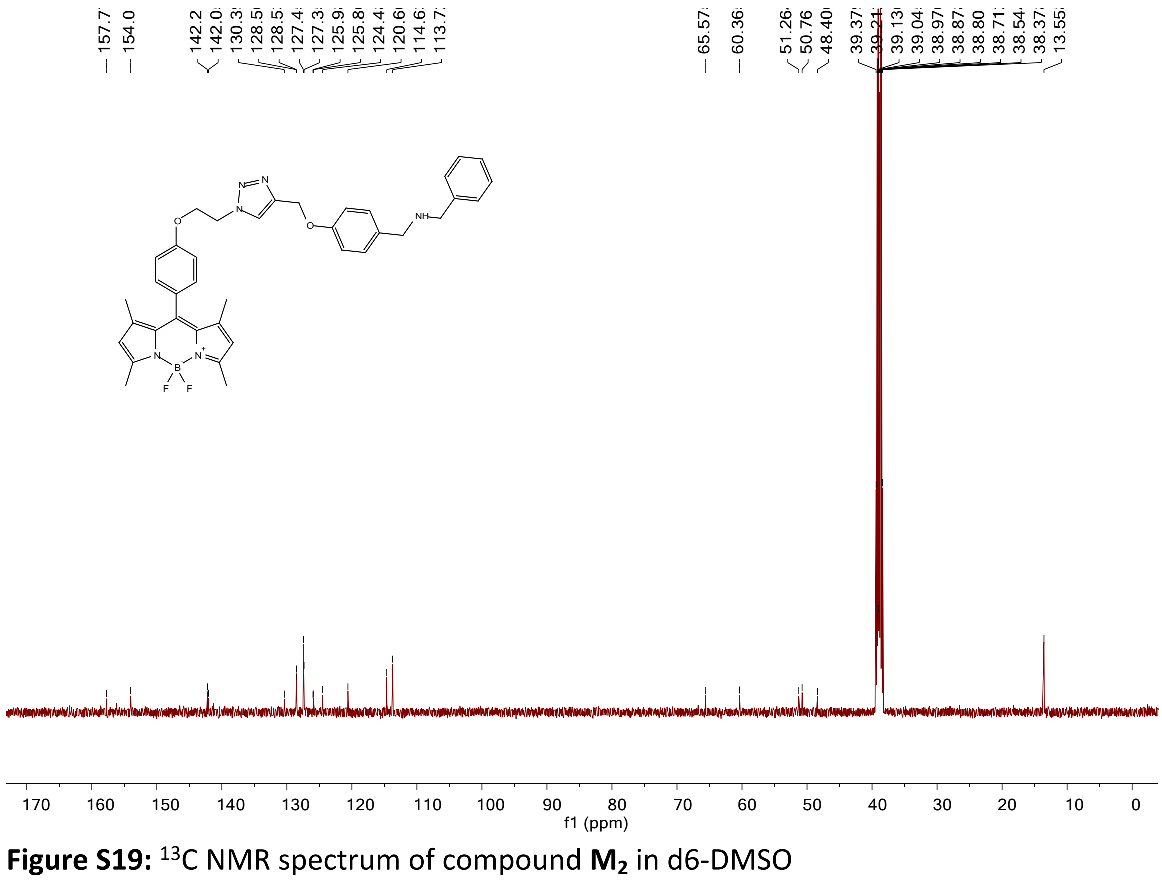


Figure S19: ^{13}C NMR spectrum of compound $\mathbf{M_2}$ in d6-DMSO

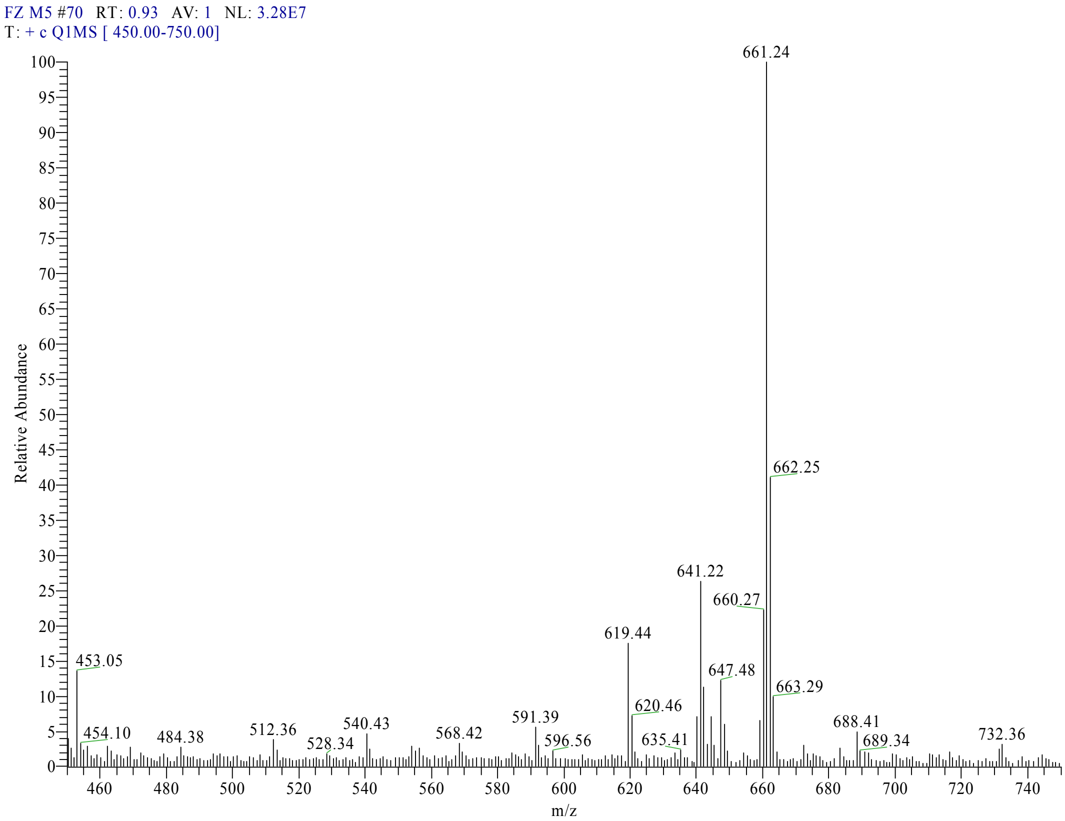


Figure S20: MS spectrum of compound $\mathbf{M_2}$