

Electronic Supplementary Information

pH-Tunable phosphorescence and light harvesting in cucurbit[8]uril host-guest assemblies

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SUPPORTING INFORMATION

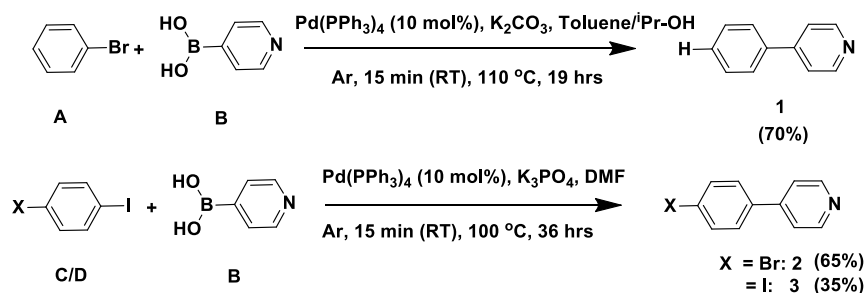
| Table of Contents | Page No. |
|---|-----------------|
| Experimental Procedure | S3 |
| 1. Materials and Method | S3 |
| 2. Synthetic Schemes and Characterization Data | S3 |
| 3. Preparation of Solutions | S5 |
| 4. Energy Transfer Efficiency Calculation | S5 |
| 5. Antenna Effect Calculation | S5 |
| Results and Discussion | S6 |
| 1. Photophysical Properties of 1, 2, and | S6 |
| 2. pH-responsive Room Temperature Phosphorescence from Host-Guest Assembly | S8 |
| 3. RTP Energy Transfer from CB[8]-based Host-guest Assembly of 2 | S16 |
| 4. NMR Spectra of the Compounds | S21 |
| 5. Mass Spectra of the Compounds | S26 |
| 6. FTIR Spectra of the Compounds | S27 |
| References | S27 |

Experimental Procedures

1. Materials and Method:

All starting materials were purchased from commercially available sources and used without further purification. Pyridine-4-boronic acid, bromobenzene, 4-bromoiodobenzene, 1,4-diiodobenzene, and tetrakis(triphenylphosphine)palladium(0) were purchased from Sigma-Aldrich. All solvents, potassium carbonate, and potassium phosphate were purchased from Merck. UV-Vis spectroscopic measurements were carried out in Agilent Technologies Cary 8454 spectrophotometer. Emission spectroscopic measurements were carried out in Horiba Fluoromax 4 spectrofluorometer. Fluorescence images were taken under 365 nm UV lamp. DLS measurements were carried out using Malvern Zetasizer NanoZS. A Horiba Jobin Yvon Fluorocube instrument fitted with a 340 nm diode laser excitation source (with a temporal resolution of 70 ps) was used for the time-resolved fluorescence experiments applying the time-correlated single photon counting (TCSPC) method. RTP quantum yields were measured in Edinburgh FLS1000 spectrofluorometer. ^1H and ^{13}C NMR were performed on Jeol 400 MHz and Bruker 500 MHz spectrometers. Mass spectra were recorded in a Bruker mass spectrometer. FESEM images were recorded in a ZEISS instrument. Spectral overlap integral values were calculated using FluorTools software.

2. Synthetic Schemes and Characterization Data:



Scheme S1 Synthetic routes for the preparation of **1**, **2** and **3**

A. Synthesis of 1: Bromobenzene (**A**) (0.17 mL, 1.62 mmol), pyridine-4-boronic acid (**B**) (100 mg, 0.81 mmol), and 2M aq. K_2CO_3 solution (0.9 mL) were taken in a reaction tube. Toluene (2.5 mL) and isopropanol (2.5 mL) were added into it and the mixture was purged with Ar for 15 min at room temperature. Then, $\text{Pd(PPh}_3)_4$ (100 mg, 0.086 mmol) was added to it and the reaction mixture was stirred for 19 hours at 110°C . The reaction mixture was cooled to room temperature and ethyl acetate (50 mL) was added to it and finally washed 3 times with water (20 mL \times 3). The

organic layer was collected and the solvent was evaporated under a vacuum. Finally, the product was separated by column chromatography using silica as a stationary phase and 10% ethyl acetate/DCM as the eluent.

B. Synthesis of 2 and 3: 4-bromiodobenzene (**C**) or 1,4-diiodobenzene (**D**) (0.98 mmol), pyridine-4-boronic acid (**B**) (0.81 mmol), and K_3PO_4 (2.44 mmol) were taken in a reaction tube. DMF (5 mL) was then added to it and the mixture was purged with Ar for 15 min at room temperature. Then, $Pd(PPh_3)_4$ (0.09 mmol) was added to it (added in portions: first 0.06 mmol and after 24 hrs 0.03 mmol) and the reaction mixture was stirred for 36 hours at 100 °C. The reaction mixture was cooled to room temperature and added into water (30 mL). The organic parts were extracted with ethyl acetate (50 mL \times 3) was added to it and finally washed 3 times with water (20 mL \times 3). The organic layer was collected and the solvent was evaporated under a vacuum. Finally, the product was separated by column chromatography using silica as a stationary phase and 20% ethyl acetate/DCM as the eluent.

C. Characterization of the compounds

1: From 100 mg of **B**, 89 mg of **1** was obtained. Yield = 70%

1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.67 (d, J = 6 Hz, 2H), 7.64 (d, J = 8 Hz, 2H), 7.51 (t, J = 6.8 Hz, 1H), 7.43-7.48 (m, 4H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ (ppm) = 150.35, 148.48, 138.26, 129.22, 129.17, 127.11, 121.76. **HRMS (ESI):** m/z calculated for $C_{11}H_{10}N^+$ [(M-H) $^+$]: 156.0808; found: 156.0817. **Melting Point:** 79 °C.

2: From mg of 100 mg of **B**, 124 mg of **2** was obtained. Yield = 65%

1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.66 (d, J = 6 Hz, 2H), 7.62 (d, J = 8 Hz, 2H), 7.50 (d, J = 8 Hz, 2H), 7.47 (d, J = 6 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ (ppm) = 150.50, 147.28, 137.17, 132.43, 128.66, 123.68, 121.48. **HRMS (ESI):** m/z for $C_{11}H_9BrN^+$ [(M-H) $^+$]: calculated: 233.9913; found: 233.9939; [(M-H) $^+$]+2: calculated: 235.9993; found: 235.9912. **Melting Point:** 132 °C.

3: From 100 mg of **B**, 79 mg of **3** was obtained. Yield = 35%

1H NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.66 (d, J = 6 Hz, 2H), 7.82 (d, J = 6 Hz, 2H), 7.46 (d, J = 6 Hz, 2H), 7.37 (d, J = 8 Hz, 2H). **^{13}C NMR (125 MHz, $CDCl_3$):** δ (ppm) = 150.58, 147.39,

138.41, 137.82, 128.82, 121.42, 95.42. **HRMS (ESI):** m/z for C₁₁H₉IN⁺ [(M-H)⁺]: calculated: 281.9774; found: 281.9770. **Melting Point:** 205 °C.

3. Preparation of Solutions

Initially, the stock solutions of **1**, **2**, and **3** were prepared in HPLC-grade methanol. Then their aqueous solutions were prepared by diluting the stock solutions into the buffer made in Milli-Q water. The aqueous solutions/suspensions were equilibrated for 10 mins and then their spectral properties were recorded. **CB[7]** and **CB[8]** stock solutions were prepared in buffer. **RhB**, **Rh6G**, and **EY** (Chart S1) stock solutions were prepared in methanol.

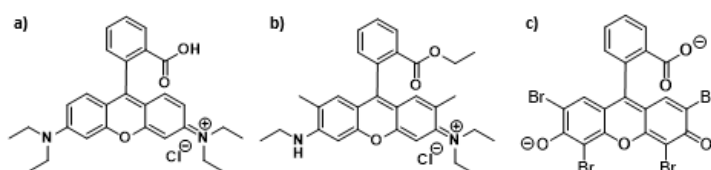


Chart S1. Chemical structures of (a) rhodamine B (**RhB**), (b) rhodamine 6G (**Rh6G**), and (c) eosin Y (**EY**).

4. Energy Transfer Efficiency Calculation

Energy transfer (ET) efficiency is the percentage of the absorbed energy that is transferred to the acceptor and is expressed by the following equation

$$ET = (1 - I/I_0) \times 100\%$$

where, I and I₀ are the fluorescence intensities without and in the presence of acceptor in aqueous buffer.

5. Antenna Effect Calculation

The antenna effect (AE) value under certain concentrations of donor and acceptor is the ratio of the emission intensities at emission maximum of the acceptor in presence of the donor upon excitation of the donor and is expressed as follows^{S1}-

$$AE = \frac{I_{D+A}(\lambda_{ex} = 365 \text{ nm}) - I_D(\lambda_{ex} = 365 \text{ nm})}{I_A(\lambda_{ex} = \text{abs maxima of A})}$$

where,

- $I_{D+A}(\lambda_{ex} = 365 \text{ nm})$ = Emission intensity of acceptor in the presence of donor upon the excitation of donor
- $I_D(\lambda_{ex} = 365 \text{ nm})$ = Emission intensity of donor in the absence of acceptor upon the excitation of the donor
- $I_A(\lambda_{ex} = \text{abs maxima of A})$ = Emission intensity of acceptor in the presence of donor upon the excitation of the acceptor

Results and Discussion

1. Photophysical Properties of 1, 2, and 3

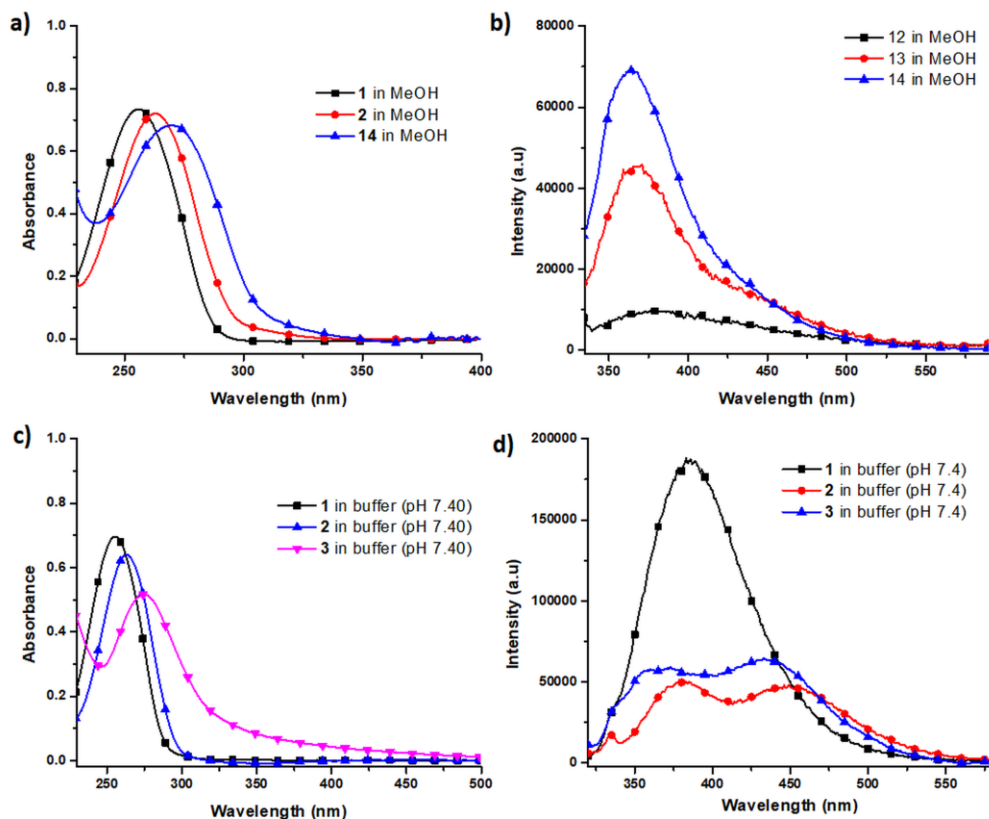


Fig. S1 (a) Absorption and (b) emission spectra of **1**, **2**, and **3** in methanol (25 μM of each). (c) Absorption and (d) emission spectra of **1**, **2**, and **3** in aqueous buffer (pH 7.40, 25 μM of each).

Table S1 TCSPC data of **1**, **2**, and **3** in methanol.

| Derivative | λ_{em} | Lifetime parameters | Average Lifetime | χ^2 |
|------------------------------|----------------|--|------------------|----------|
| 1 (25 μM) | 382 nm | $\tau_1 = 0.61$ ns (51%), $\tau_2 = 1.02$ ns (49%) | 0.81 ns | 1.04 |
| 2 (25 μM) | 370 nm | $\tau_1 = 0.41$ ns (44%), $\tau_2 = 0.95$ ns (56%) | 0.71 ns | 1.01 |
| 3 (25 μM) | 365 nm | $\tau_1 = 0.76$ ns (92%), $\tau_2 = 2.2$ ns (8%) | 0.88 ns | 1.15 |

Table S2 Hydrodynamic diameters for **1**, **2**, and **3** in buffer (pH 7.40) obtained from DLS measurement.

| 1 (100 μM) | 2 (25 μM) | 3 (10 μM) |
|-------------------------------|------------------------------|------------------------------|
| 572 nm (KCPS = 154) | 252 nm (KCPS = 217) | 170 nm (KCPS = 160) |

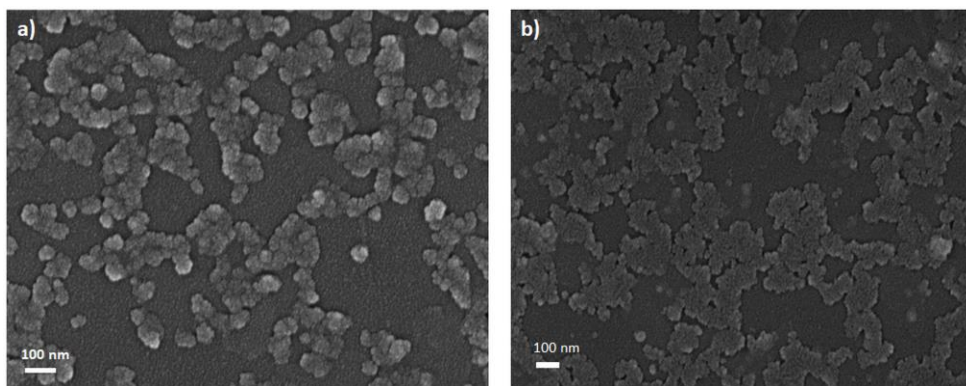


Fig. S2 FESEM images of (a) **2** and (b) **3** obtained from their aqueous solutions after drying.

Table S3 TCSPC data of **1**, **2**, and **3** in buffer (pH 7.40).

| Derivative | λ_{em} | Lifetime parameters | Average Lifetime | χ^2 |
|-----------------------|----------------|--|------------------|----------|
| 1 (25 μ M) | 384 nm | $\tau_1 = 0.34$ ns (27%), $\tau_2 = 1.04$ ns (73%) | 0.85 ns | 1.21 |
| 2 (25 μ M) | 366 nm | $\tau_1 = 0.97$ ns (77%), $\tau_2 = 2.52$ ns (23%) | 1.32 ns | 1.09 |
| | 450 nm | $\tau_1 = 2.46$ ns (100%) | 2.46 ns | 1.04 |
| 3 (25 μ M) | 368 nm | $\tau_1 = 0.15$ ns (42%), $\tau_2 = 1.13$ ns (58%) | 0.72 ns | 1.11 |
| | 440 nm | $\tau_1 = 0.19$ ns (8%), $\tau_2 = 2.51$ ns (92%) | 2.32 ns | 1.03 |

Table S4 RTP lifetime (delay time = 50 μ s) data of **2**, and **3** in buffer (pH 7.40) at different concentrations.

| Derivative | λ_{em} | Lifetime parameters | Average Lifetime |
|-----------------------|----------------|--|------------------|
| 3 (25 μ M) | 509 nm | $\tau_1 = 0.15$ ms (44%), $\tau_2 = 0.88$ ms (56%) | 0.56 ms |

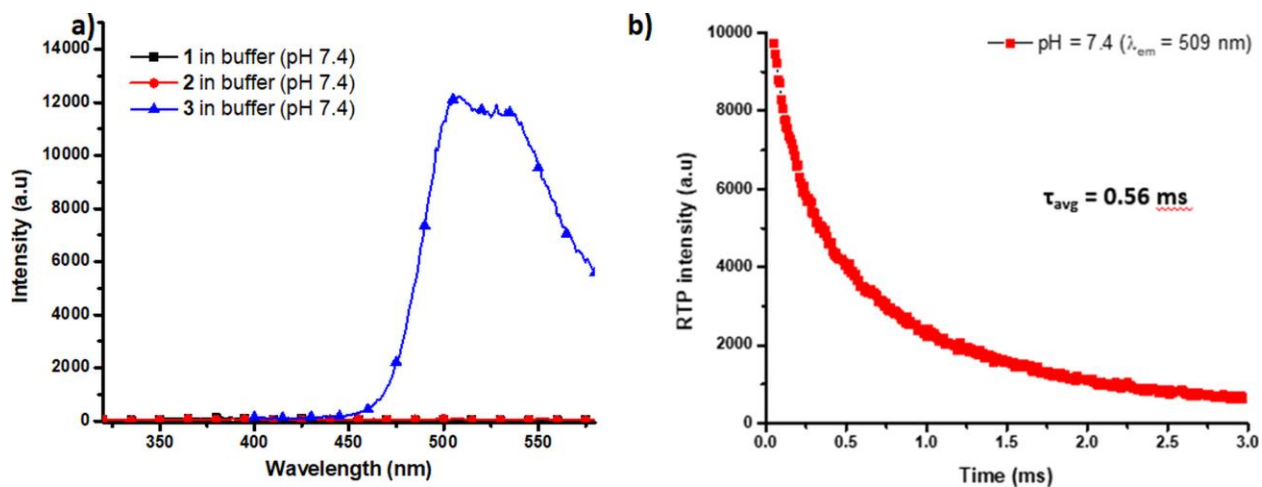


Fig. S3 (a) Gated emission spectra (delay time = 50 μ s) of **1**, **2**, and **3** in aqueous buffer (pH 7.40, 25 μ M of each). (b) RTP lifetime of **3** at 25 μ M concentrations in aqueous buffer (pH 7.40).

2. pH-responsive Room Temperature Phosphorescence from Host-Guest Assembly

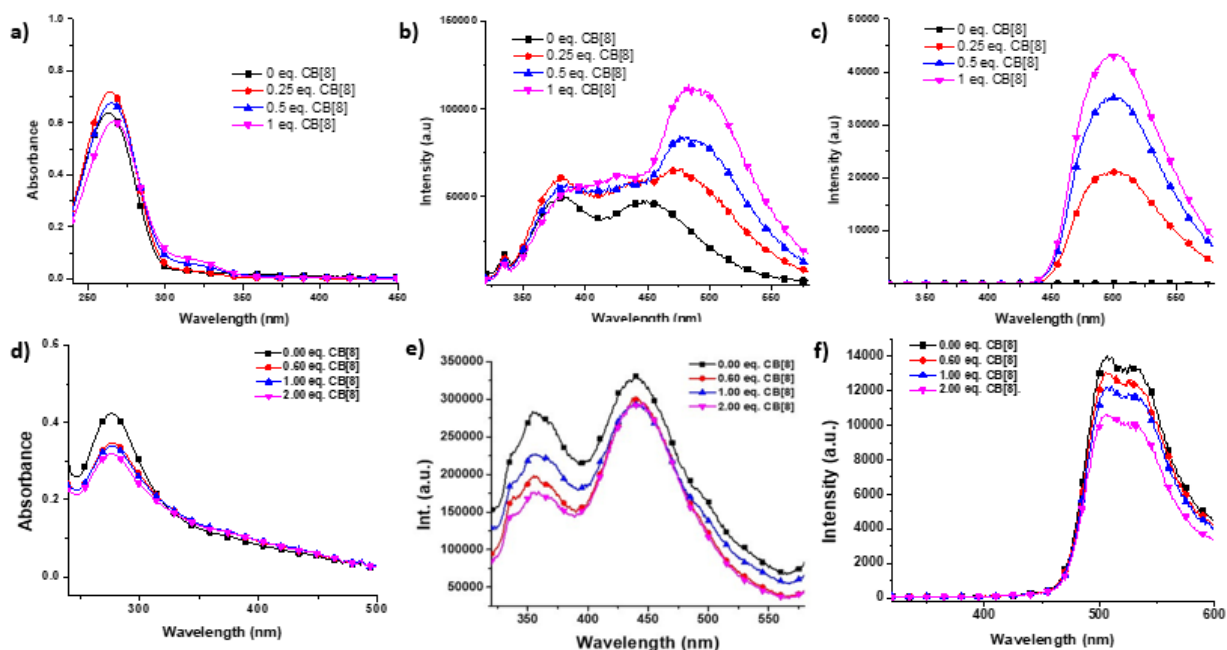


Fig. S4 (a) Absorption, (b) steady-state emission, and (c) gated emission (delay time = 50 μs) spectra of **2** (25 μM) in the presence of **CB[8]** in buffer (pH 7.40). (d) Absorption, (e) steady-state emission, and (f) gated emission (delay time = 50 μs) spectra of **3** (25 μM) in the presence of **CB[8]** in buffer (pH 7.40).

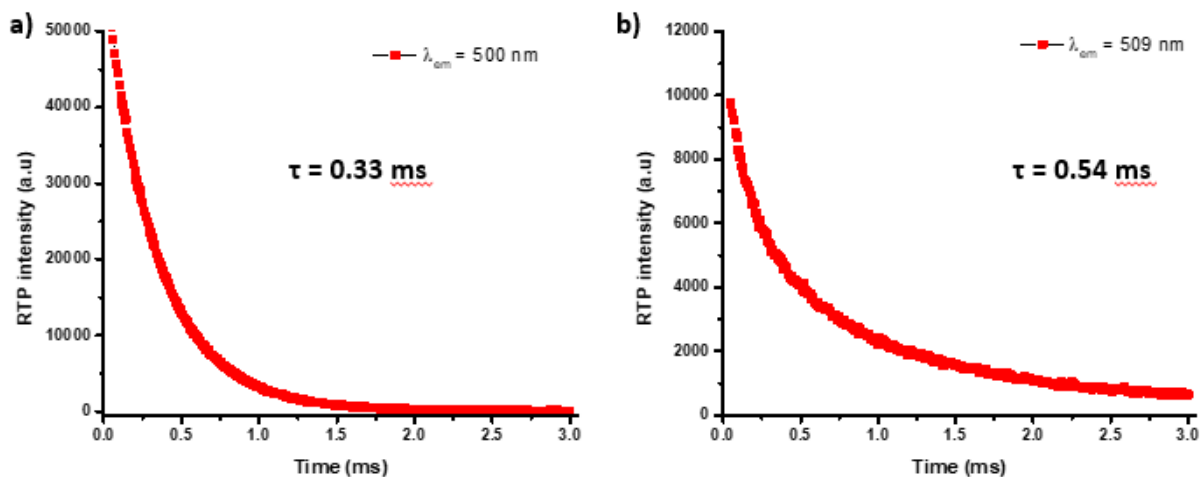


Fig. S5 RTP lifetimes of (a) **2** and (b) **3** at 25 μM concentrations in the presence of **CB[8]** in aqueous buffer (pH 7.40).

Table S5 RTP lifetime (delay time = 50 μ s) data of **2** and **3** in the presence of **CB[8]**.

| Sample | λ_{em} | Lifetime parameters | Average Lifetime |
|--|----------------|---------------------------|------------------|
| 2 (25 μ M)- CB[8] (15 μ M) at pH 7.40 | 500 nm | $\tau_1 = 0.33$ ms (100%) | 0.33 ms |
| 3 (25 μ M)- CB[8] (15 μ M) at pH 7.40 | 509 nm | $\tau_1 = 0.54$ ms (100%) | 0.54 ms |
| 2 (25 μ M)- CB[8] (15 μ M) at pH 2.50 | 500 nm | $\tau_1 = 0.43$ ms (100%) | 0.43 ms |
| 3 (25 μ M)- CB[8] (15 μ M) at pH 2.50 | 535 nm | $\tau_1 = 0.30$ ms (100%) | 0.30 ms |

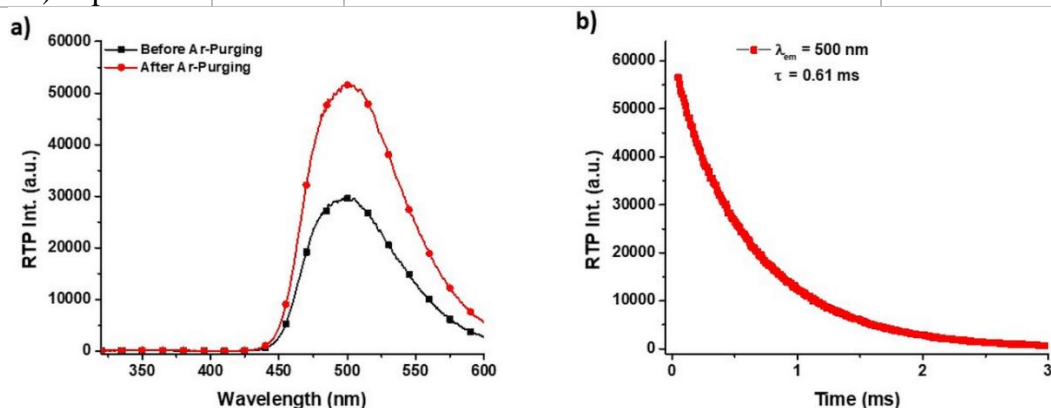


Fig. S6 (a) Gated emission (delay time = 50 μ s) spectra of **2** (25 μ M) in the presence of **CB[8]** (15 μ M) before and after Ar-purging in buffer (pH 7.40). (b) RTP lifetimes of **2** (25 μ M) in the presence of **CB[8]** (15 μ M) after Ar-purging in buffer (pH 7.40).

Table S6 Hydrodynamic diameters for **2** (25 μ M) and **3** (25 μ M) in the presence of **CB[8]** (15 μ M) in buffer at different pH (pH 7.40 and pH 2.50) obtained from DLS measurement.

| 2-CB[8] at pH 7.40 | 2-CB[8] at pH 2.50 | 3-CB[8] at pH 7.40 | 3-CB[8] at pH 2.50 |
|---------------------------|---------------------------|---------------------------|---------------------------|
| 256 nm (KCPS = 223) | 289 nm (KCPS = 217) | 230 nm (KCPS = 408) | 365 nm (KCPS = 184) |

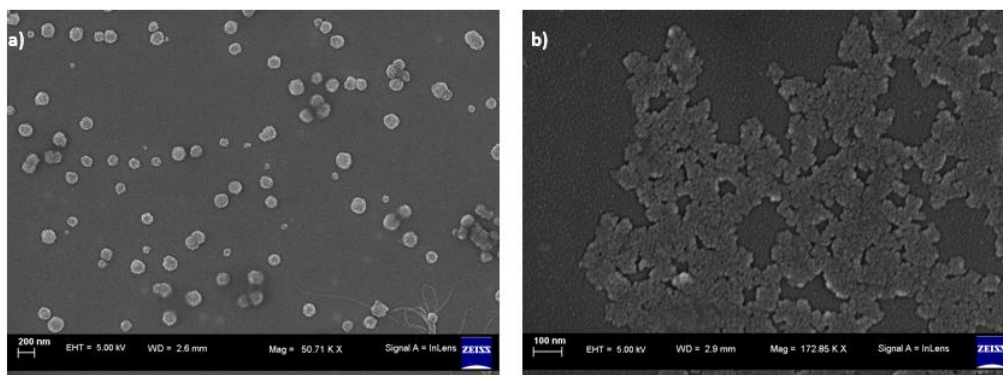


Fig. S7 FESEM images of (a) **2** (25 μ M)-**CB[8]** (15 μ M) and (b) **3** (25 μ M)-**CB[8]** (15 μ M) obtained from their dried aqueous solutions.

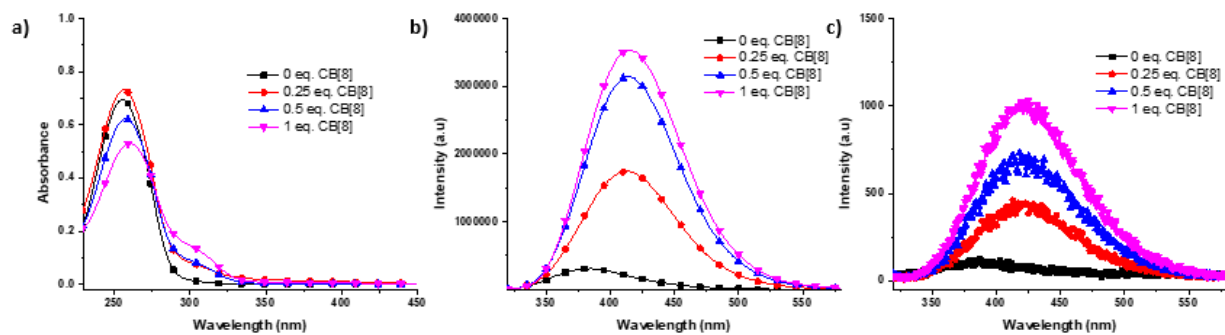


Fig. S8 (a) Absorption, (b) steady-state emission, and (c) gated emission (delay time = 50 μ s) spectra of **1** (25 μ M) in the presence of different amounts of **CB[8]** in buffer (pH 7.40).

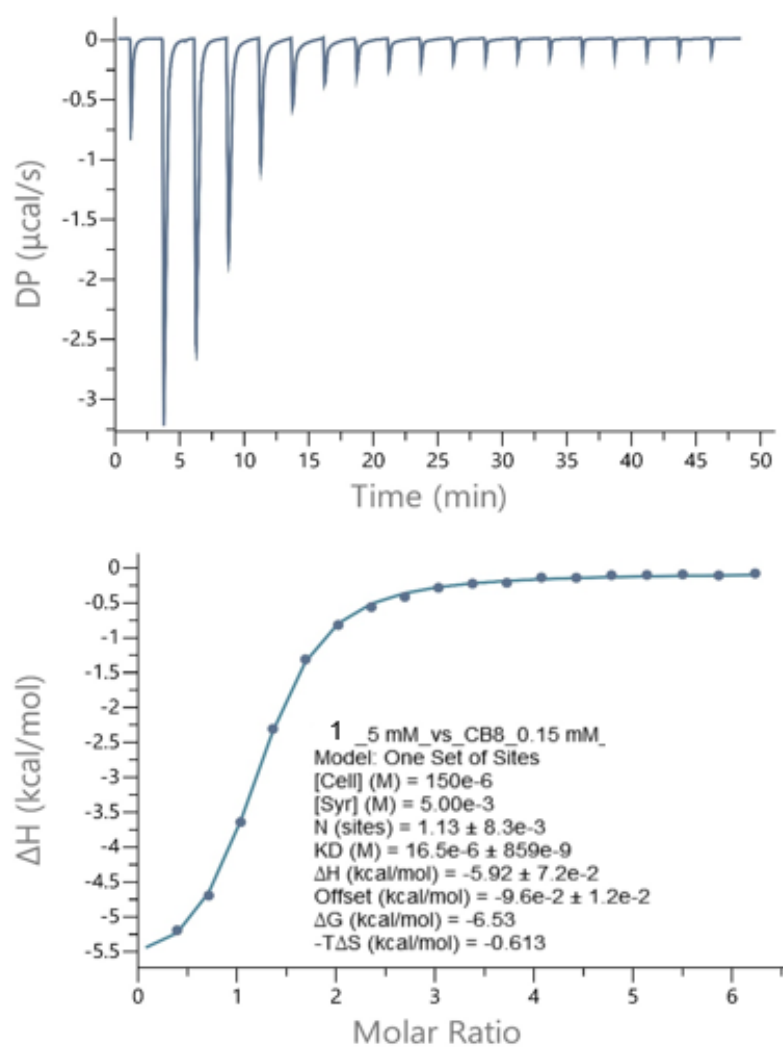


Fig. S9 ITC thermogram of **1** vs **CB[8]** in water (**1** in the syringe: 5 mM; **CB[8]** in the cell: 0.15 mM).

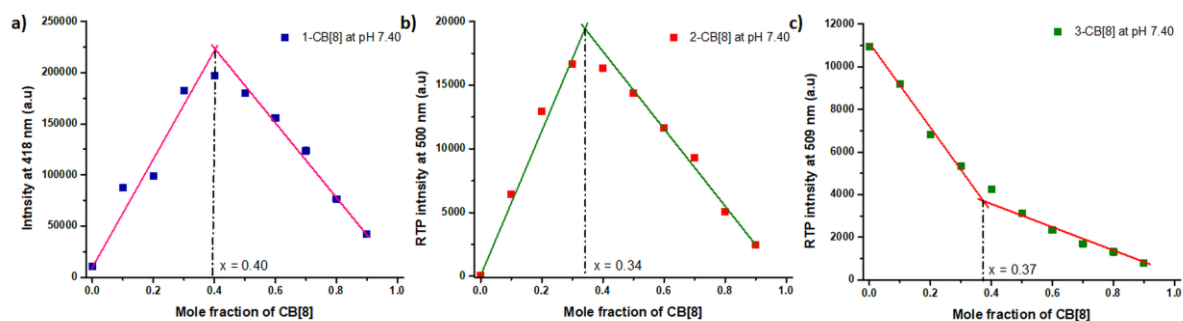


Fig. S10. Job's plots for (a) **1-CB[8]**, (b) **2-CB[8]**, and (c) **3-CB[8]** at pH 7.40. For **1-CB[8]**, emission intensity at 418 nm was monitored. For **2-CB[8]** and **3-CB[8]**, gated emission intensities (delay = 0.05 ms) at 500 nm and 509 nm were monitored respectively.

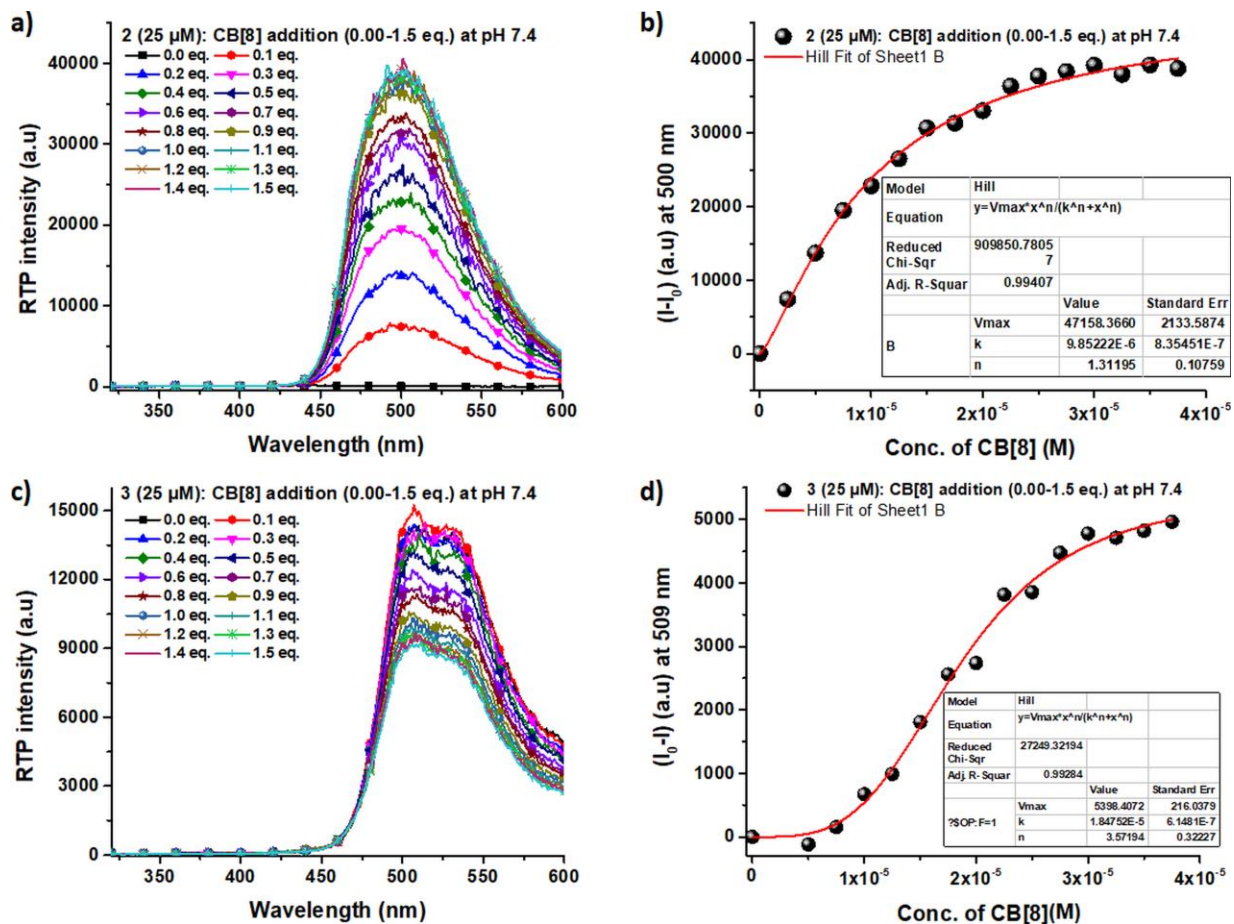


Fig. S11 Gated emission spectra (delay = 0.05 ms) of (a) **2** (25 μM) and (c) **3** (25 μM) upon the addition of different amounts of **CB[8]**. Hill plots for (b) $(I-I_0)$ vs conc. of **CB[8]** for **2** and (d) $(I-I_0)$ vs conc. of **CB[8]** for **3** in aqueous buffer (pH 7.40).

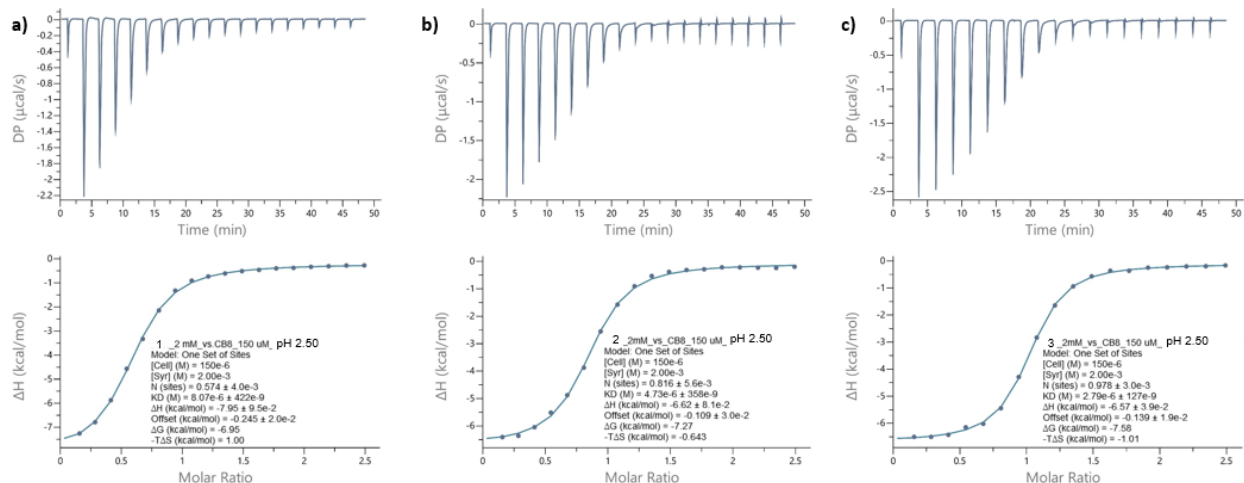


Fig. S12 ITC thermograms of (a) **1** vs **CB[8]**, (b) **2** vs **CB[8]**, and (c) **3** vs **CB[8]** at pH 2.50 (**1**, **2**, or **3** in the syringe: 2 mM; **CB[8]** in the cell: 0.15 mM).

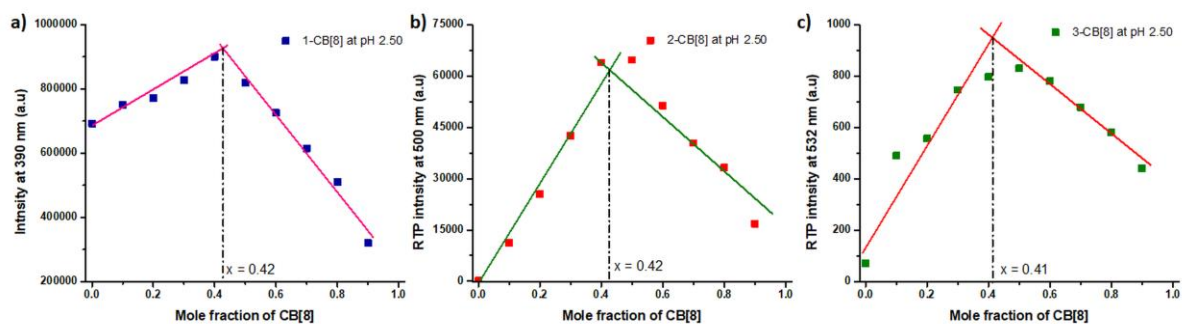


Fig. S13. Job's plots for (a) **1-CB[8]**, (b) **2-CB[8]**, and (c) **3-CB[8]** at pH 2.50. For **1-CB[8]**, emission intensity at 390 nm was monitored. For **2-CB[8]** and **3-CB[8]**, gated emission intensities (delay = 0.05 ms) at 500 nm and 532 nm were monitored respectively.

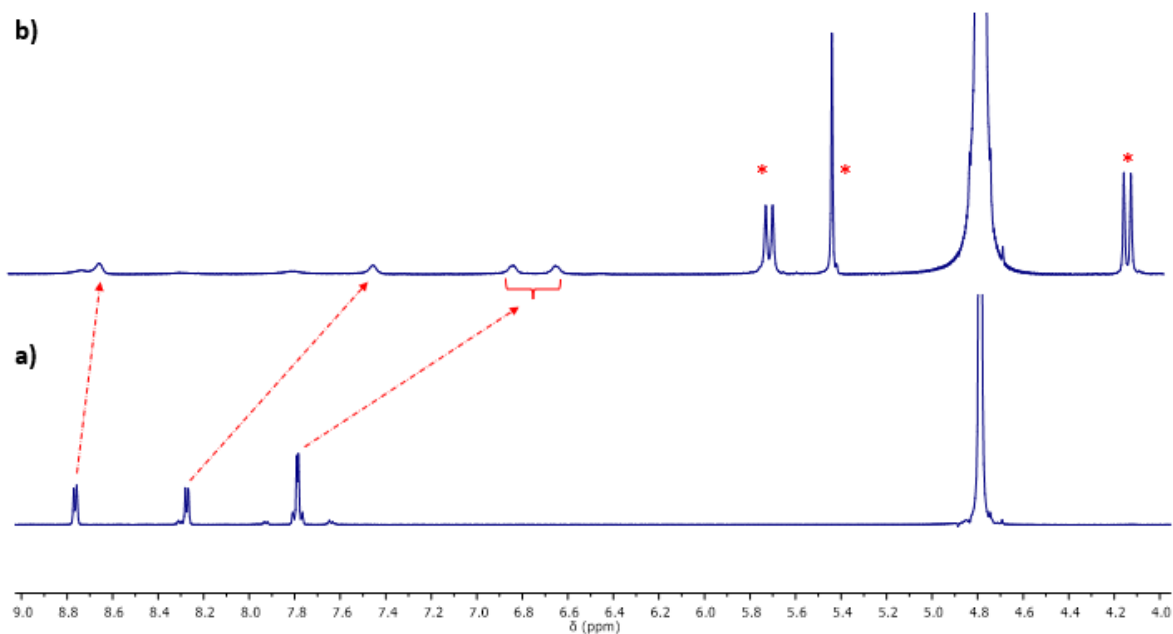


Fig. S14 ^1H NMR spectra of 2H^+ (0.5 mM) (a) in the absence and (b) in the presence of **CB[8]** (0.6 eq.) in 1% DCl- D_2O . ‘*’-marked peaks are from **CB[8]**.

Table S7 Phosphorescence quantum yields of **2** (25 μM)-**CB[8]** (15 μM) (pH = 7.4) and **2** (25 μM)-**CB[8]** (15 μM) (pH = 2.5). Samples were excited at 300 nm.

| Sample | Phosphorescence Quantum Yield |
|---|-------------------------------|
| 2 (25 μM)- CB[8] (15 μM) (pH = 7.4) | 7.1% |
| 2 (25 μM)- CB[8] (15 μM) (pH = 2.5) | 10.2% |

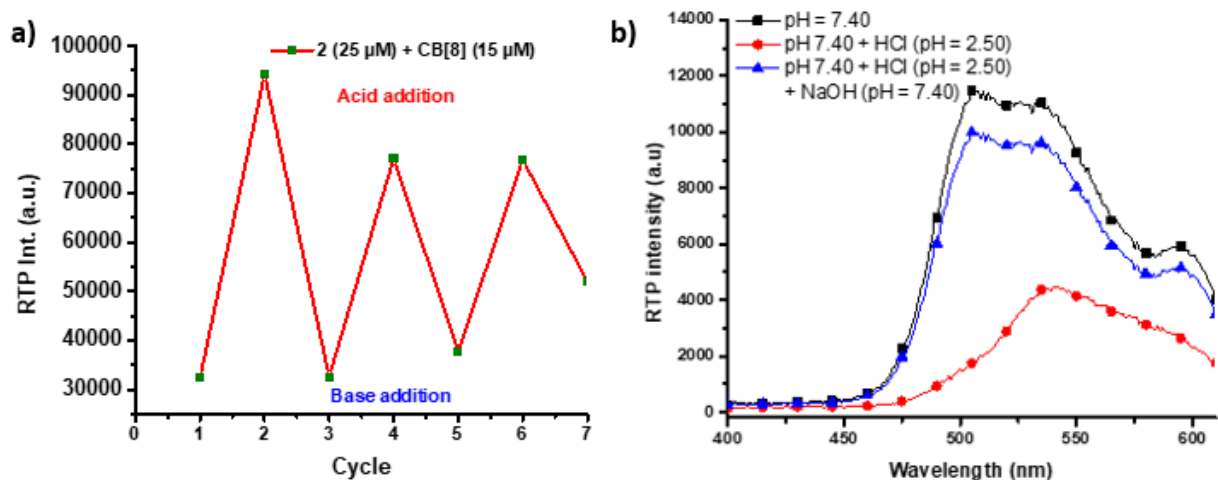


Fig. S15 (a) Reversibility cycle of RTP from 2-CB[8] (2: 25 μM; CB[8]: 15 μM) after consecutive additions of HCl and NaOH. (b) Gated emission spectra (delay time = 50 μs) of 3-CB[8] (3: 25 μM; CB[8]: 15 μM) after consecutive additions of HCl and NaOH ($\lambda_{\text{ex}} = 300$ nm).

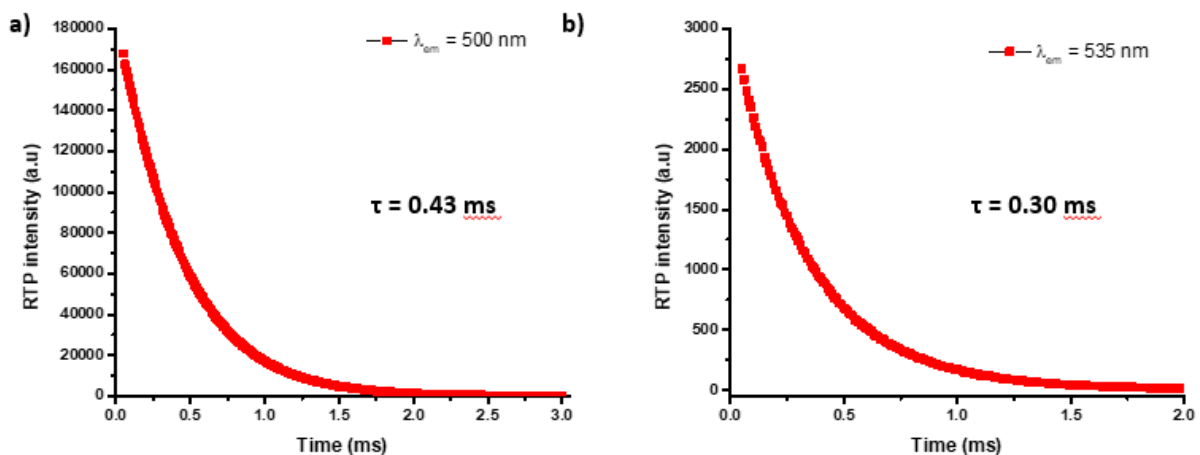


Fig. S16 RTP lifetimes of 2 and 3 at 25 μM concentrations in the presence of CB[8] in aqueous buffer (pH 2.50).

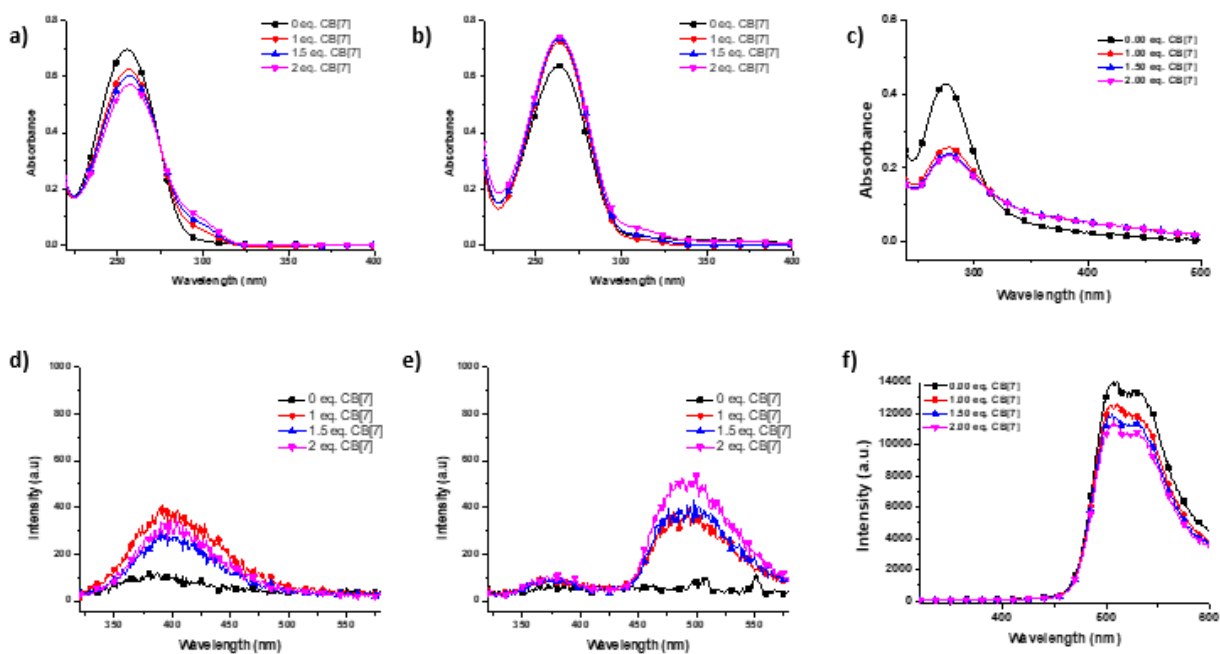


Fig. S17 (a)-(c) Absorption and (d)-(f) gated emission (delay = 0.05 ms) spectra of **1** (25 μM), **2** (25 μM), and **3** (25 μM) respectively in the presence of CB[7] at pH 7.40.

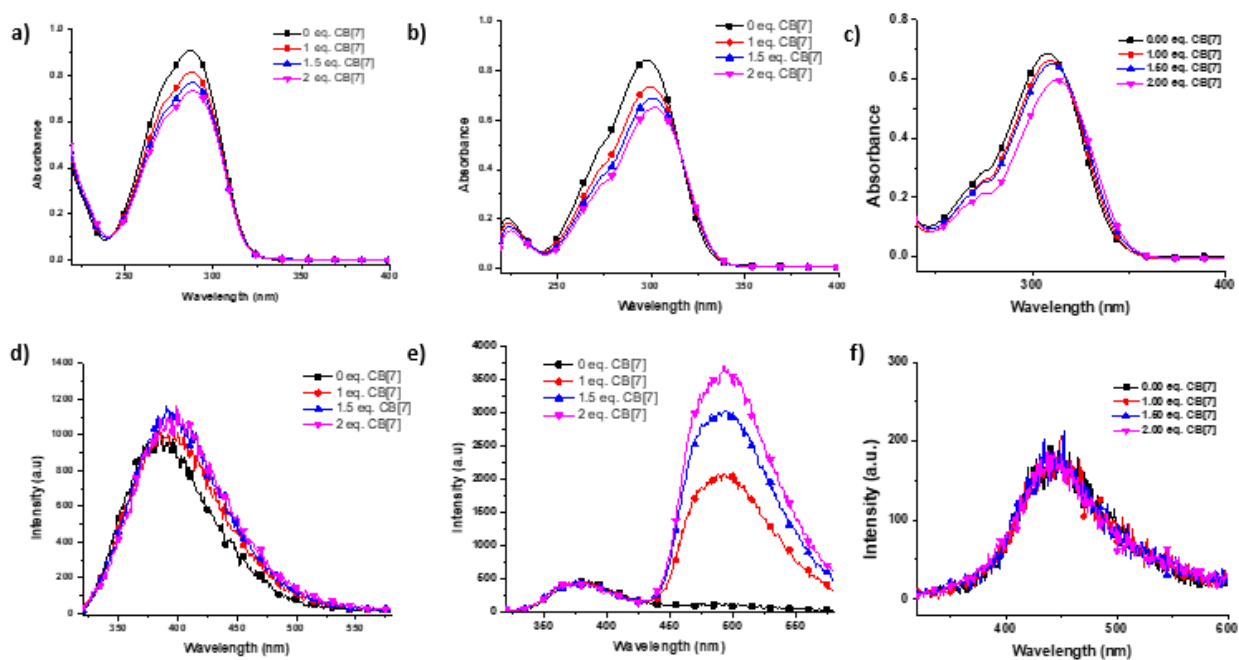


Fig. S18 (a)-(c) Absorption and (d)-(f) gated emission (delay = 0.05 ms) spectra of **1** (25 μM), **2** (25 μM), and **3** (25 μM) respectively in the presence of CB[7] at pH 2.50.

3. RTP Energy Transfer from CB[8]-based Host-guest Assembly of **2**

Table S8 Spectral overlap between RTP emission spectra of **2**-CB[8] and the acceptors.

| Spectral overlap using Rh6G | Spectral overlap using RhB | Spectral overlap using EY |
|---|---|---|
| $2.88 \times 10^{15} \text{ nm}^4\text{M}^{-1}\text{cm}^{-1}$ | $5.15 \times 10^{15} \text{ nm}^4\text{M}^{-1}\text{cm}^{-1}$ | $4.35 \times 10^{14} \text{ nm}^4\text{M}^{-1}\text{cm}^{-1}$ |

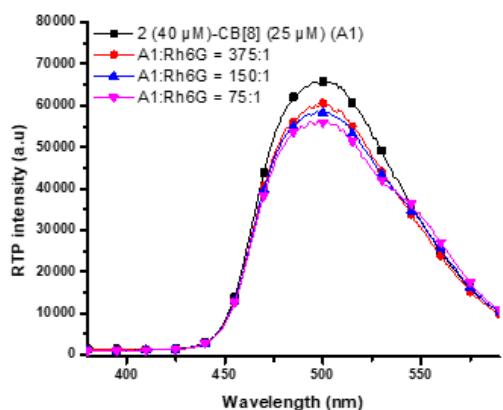


Fig. S19 Gated emission spectra (delay time = 50 μs) of **2** (40 μM)-CB[8] (25 μM) in the presence of **Rh6G** at different D/A ratios (pH = 7.40).

Table S9 Energy transfer (ET) efficiencies for **2** (40 μM)-CB[8] (25 μM)-**Rh6G** system at different donor/acceptor ratios.

| D/A ratio | ET efficiency |
|-----------|---------------|
| 375:1 | 7% |
| 150:1 | 11% |
| 75:1 | 15% |

Table S10 Energy transfer (ET) efficiencies and antenna effect (AE) values for **2** (300 μM)-CB[8] (180 μM)-**Rh6G** system at different donor/acceptor ratios.

| D/A ratio | ET efficiency | AE value |
|-----------|---------------|----------|
| 750:1 | 13% | 2.90 |
| 375:1 | 26% | 3.60 |
| 150:1 | 41% | 4.30 |
| 75:1 | 57% | 4.80 |
| 37.5:1 | 76% | 4.75 |

Table S11 Energy transfer (ET) efficiencies and antenna effect (AE) values for **2** (300 μM)-**CB[8]** (180 μM)-**RhB** system at different donor/acceptor ratios.

| D/A ratio | ET efficiency | AE value |
|-----------|---------------|----------|
| 750:1 | 16% | 4.44 |
| 375:1 | 27% | 4.30 |
| 150:1 | 47% | 3.93 |
| 75:1 | 64% | 3.83 |
| 37.5:1 | 80% | 3.15 |

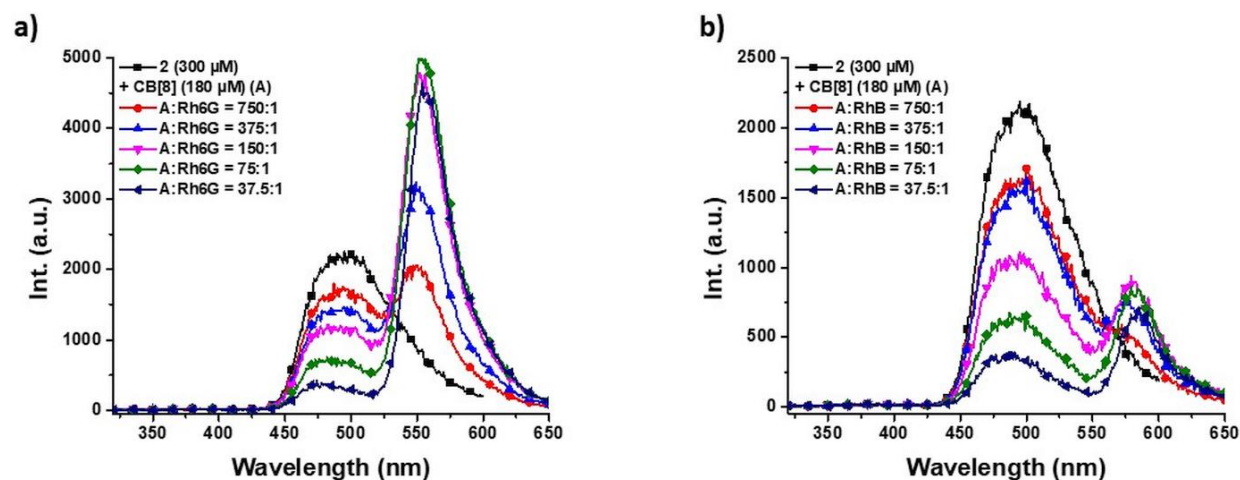


Fig. 20 Gated emission spectra (delay time = 50 μs) of **2** (300 μM)-**CB[8]** (180 μM) in the presence of a) **Rh6G** and b) **RhB** at different D/A ratios (pH = 2.50).

Table S12 Energy transfer (ET) efficiencies and antenna effect (AE) values for **2** (300 μM)-**CB[8]** (180 μM)-**Rh6G** system at pH = 2.5 for different donor/acceptor ratios.

| D/A ratio | ET efficiency | AE value |
|-----------|---------------|----------|
| 750:1 | 26% | 0.53 |
| 375:1 | 37% | 0.61 |
| 150:1 | 48% | 0.69 |
| 75:1 | 69% | 0.67 |
| 37.5:1 | 87% | 0.62 |

Table S13 Energy transfer (ET) efficiencies and antenna effect (AE) values for **2** (300 μ M)-**CB[8]** (180 μ M)-**RhB** system at pH = 2.5 for different donor/acceptor ratios.

| D/A ratio | ET efficiency | AE value |
|-----------|---------------|----------|
| 750:1 | 19 | 0.40 |
| 375:1 | 23 | 0.43 |
| 150:1 | 50 | 0.41 |
| 75:1 | 69 | 0.29 |
| 37.5:1 | 84 | 0.24 |

Table S14 Lifetime of **2** (300 μ M)-**CB[8]**, **Rh6G** and **RhB** in the **2** (300 μ M)-**CB[8]** (180 μ M)-**Rh6G** and **2** (300 μ M)-**CB[8]** (180 μ M)-**RhB** triads.

| Sample | RTP lifetime of 2 (300 μ M)- CB[8] | Lifetime of acceptor |
|--|--|----------------------|
| 2 (300 μ M)- CB[8] (180 μ M) | 0.36 ms | - |
| 2 (300 μ M)- CB[8] (180 μ M)- Rh6G (D/A = 37.5:1) | 0.13 ms | 0.147 ms |
| 2 (300 μ M)- CB[8] (180 μ M)- RhB (D/A = 37.5:1) | 0.094 ms | 0.098 ms |

Table S15 Lifetime of **2** (300 μ M)-**CB[8]**, **Rh6G** and **RhB** in the **2** (300 μ M)-**CB[8]** (180 μ M)-**Rh6G** and **2** (300 μ M)-**CB[8]** (180 μ M)-**RhB** triads at pH = 2.5

| Sample | RTP lifetime of 2 (300 μ M)- CB[8] | Lifetime of acceptor |
|---|--|----------------------|
| 2 (300 μ M)- CB[8] (180 μ M) | 0.214 ms | - |
| 2 (300 μ M)- CB[8] (180 μ M)- Rh6G (D/A = 150:1) | 0.145 ms | 0.153 ms |
| 2 (300 μ M)- CB[8] (180 μ M)- RhB (D/A = 150:1) | 0.127 ms | 0.135 ms |

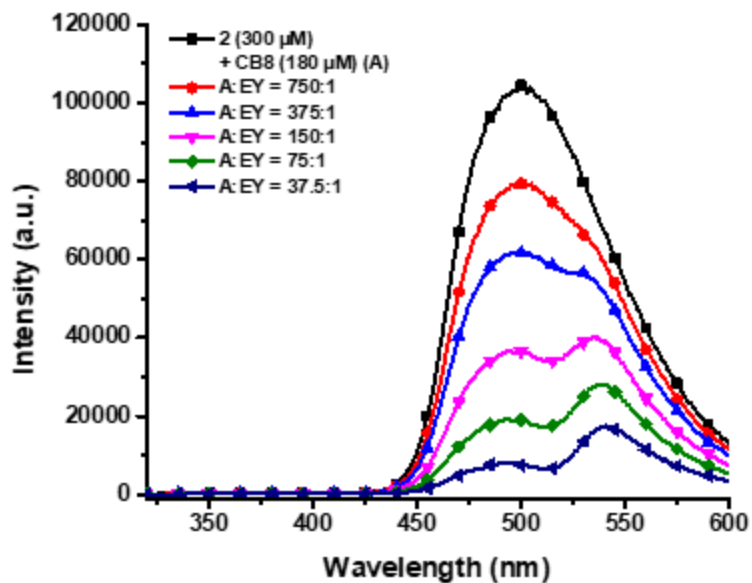


Fig. S21 Gated emission spectra (delay time = 50 μ s) of **2** (300 μ M)-**CB[8]** (180 μ M) in the presence of **EY** at different D/A ratios (pH = 7.40).

Table S16 Energy transfer (ET) efficiencies and antenna effect (AE) values for **2** (300 μ M)-**CB[8]** (180 μ M)-**EY** system at pH = 7.40 for different donor/acceptor ratios.

| D/A ratio | ET efficiency | AE value |
|-----------|---------------|----------|
| 750:1 | 25% | 6.5 |
| 375:1 | 41% | 9.0 |
| 150:1 | 65% | 6.76 |
| 75:1 | 82% | 4.80 |
| 37.5:1 | 93% | 3.0 |

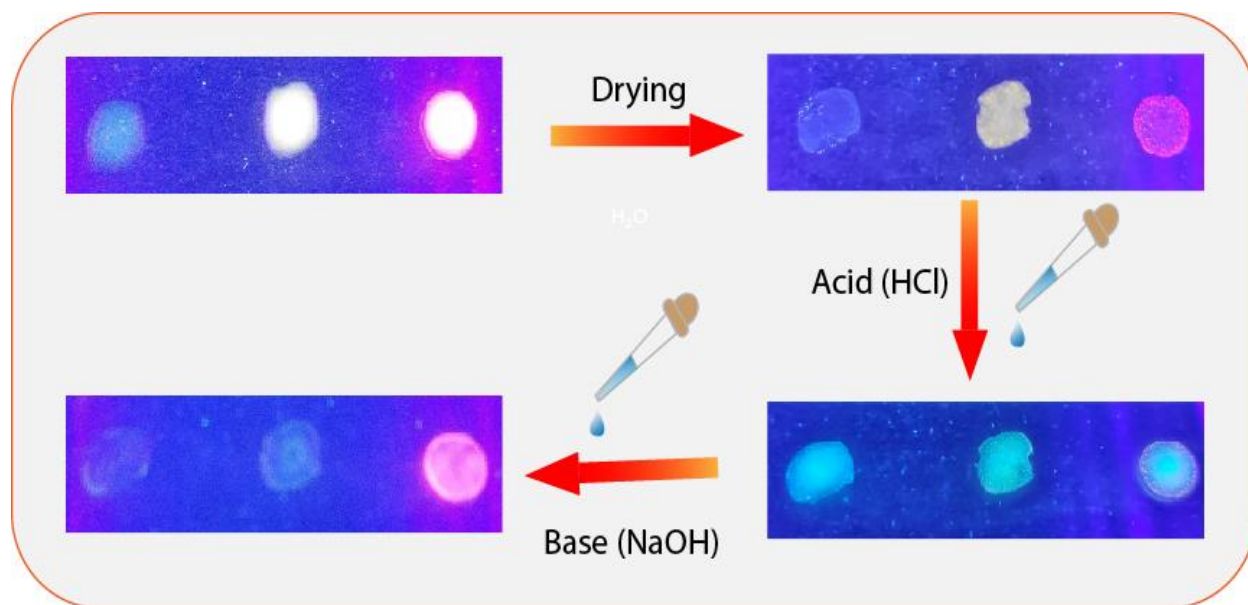
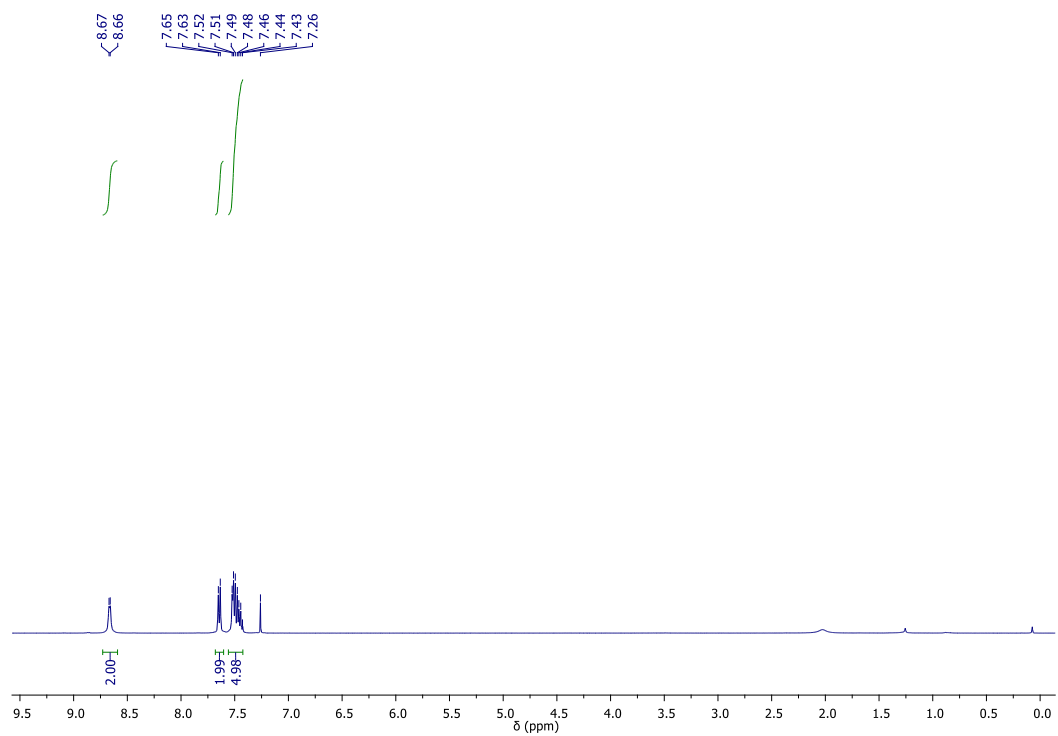


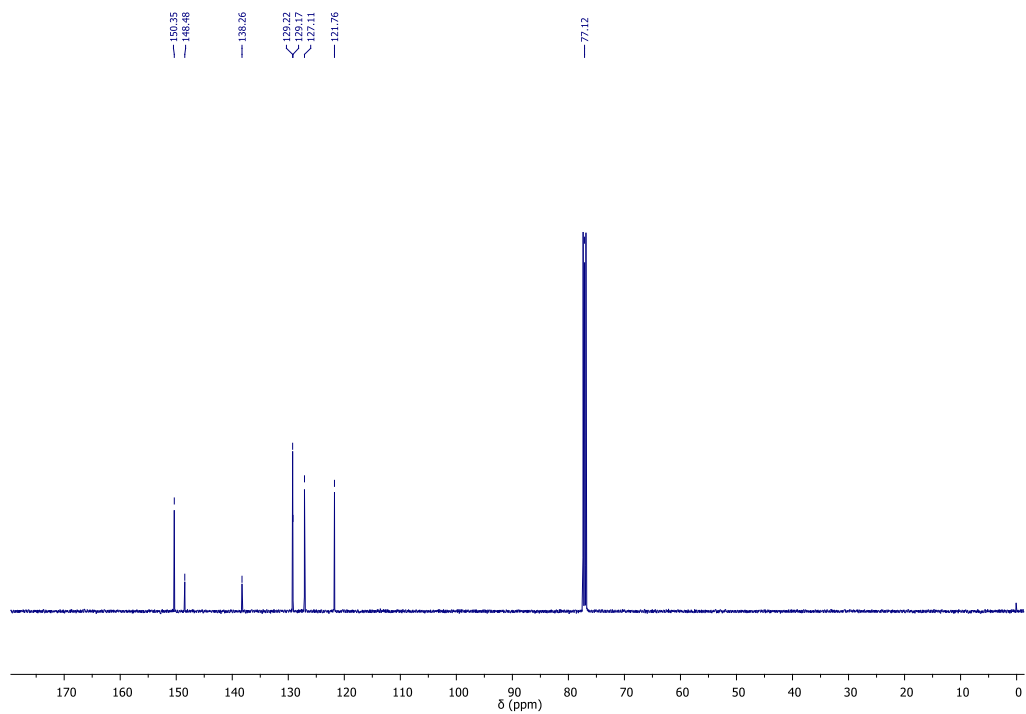
Fig. S22 Schematic illustration of data encryption-decryption using **2** (300 μM)-**CB[8]** (180 μM) assemblies in the absence and in the presence of acceptor dyes (**Rh6G** and **RhB**).

4. NMR Spectra of the Compounds

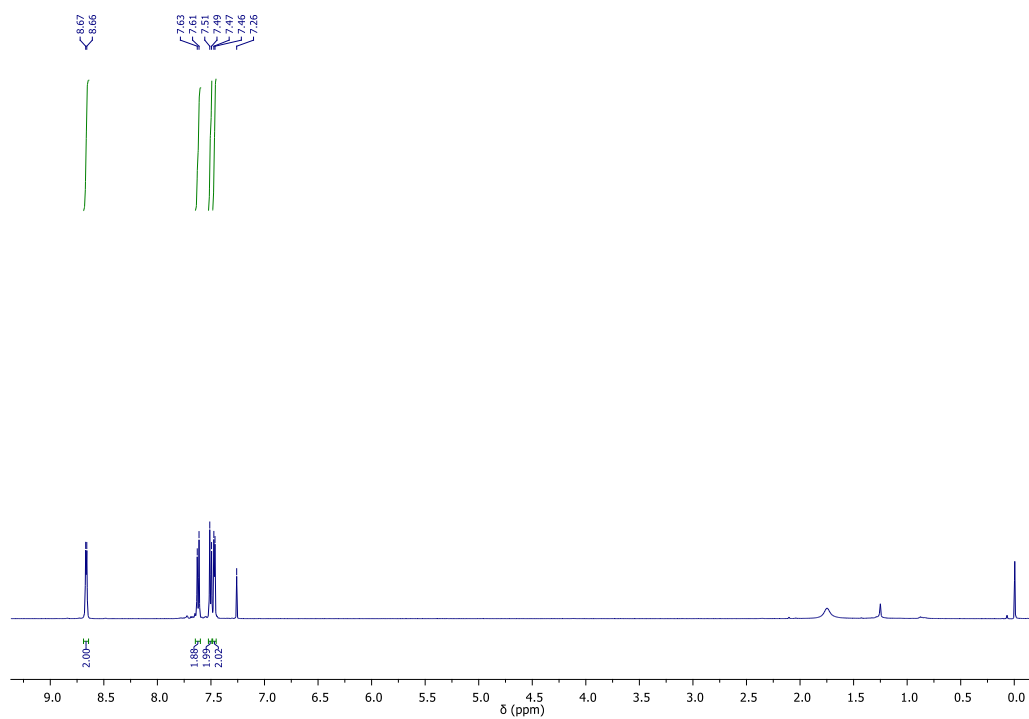
A. ^1H NMR spectra of 1 (CDCl_3 , 400 MHz)



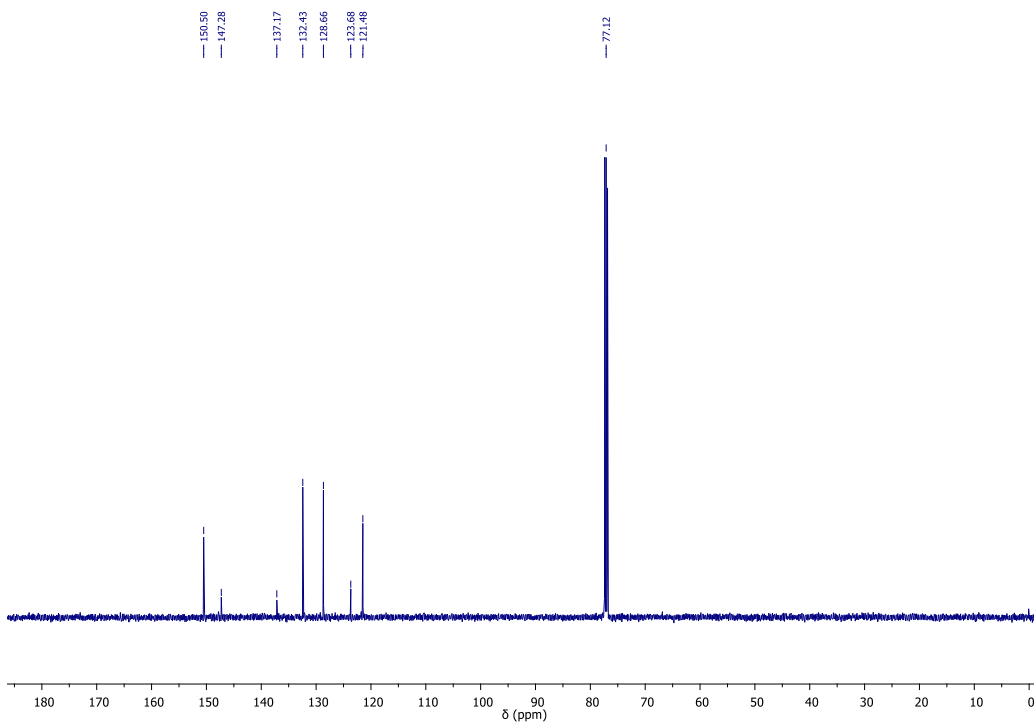
B. ^{13}C NMR spectra of 1 (CDCl_3 , 100 MHz)



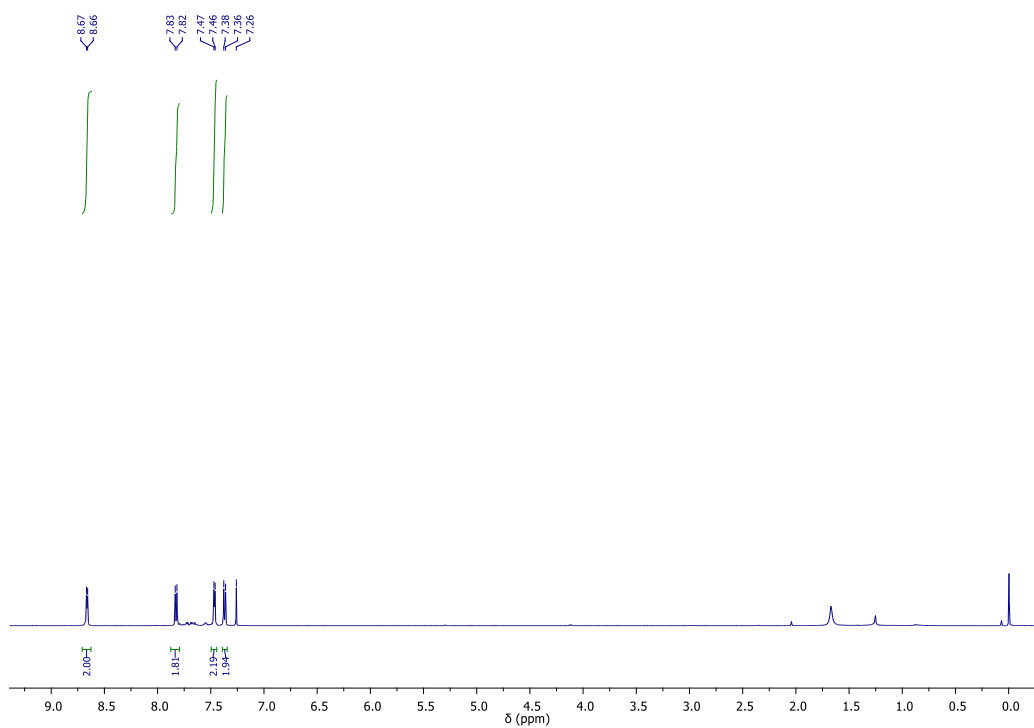
C. ^1H NMR spectra of **2** (CDCl_3 , 400 MHz)



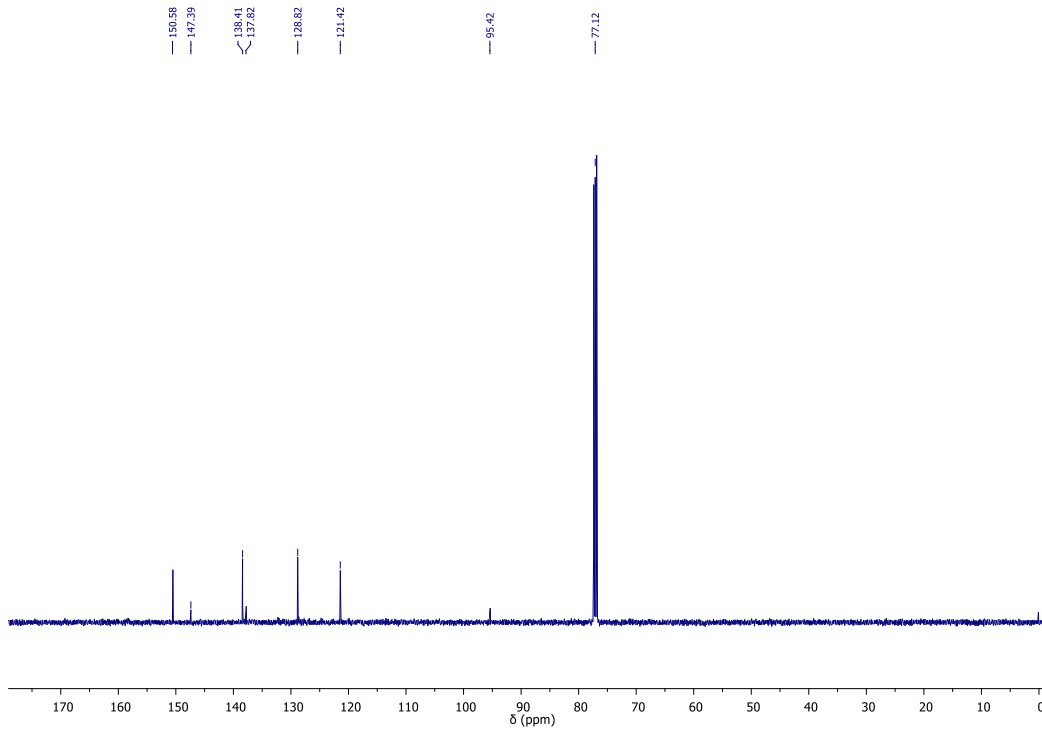
D. ^{13}C NMR spectra of **2** (CDCl_3 , 100 MHz)



E. ^1H NMR spectra of 3 (CDCl_3 , 400 MHz)

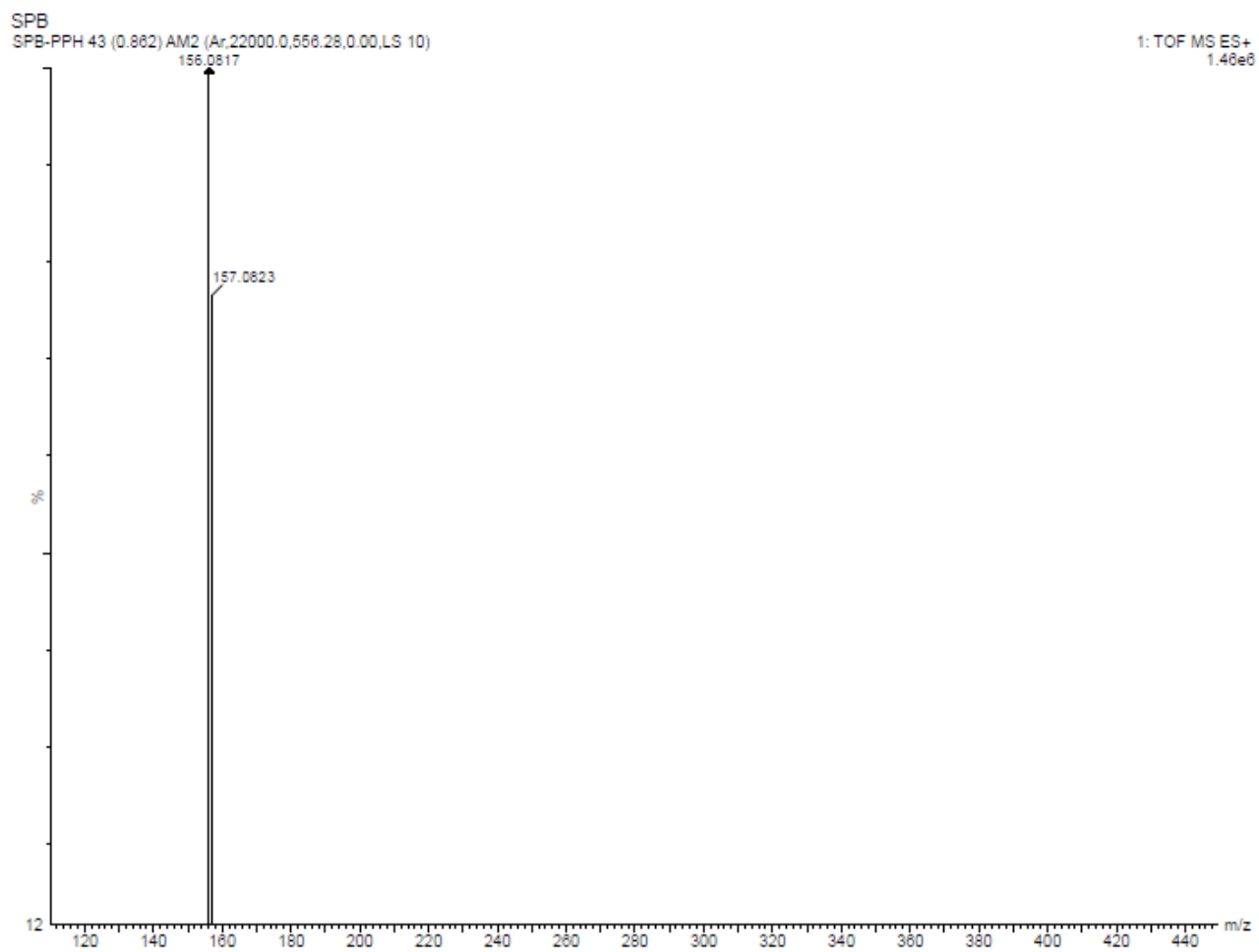


F. ^{13}C NMR spectra of 3 (CDCl_3 , 100 MHz)

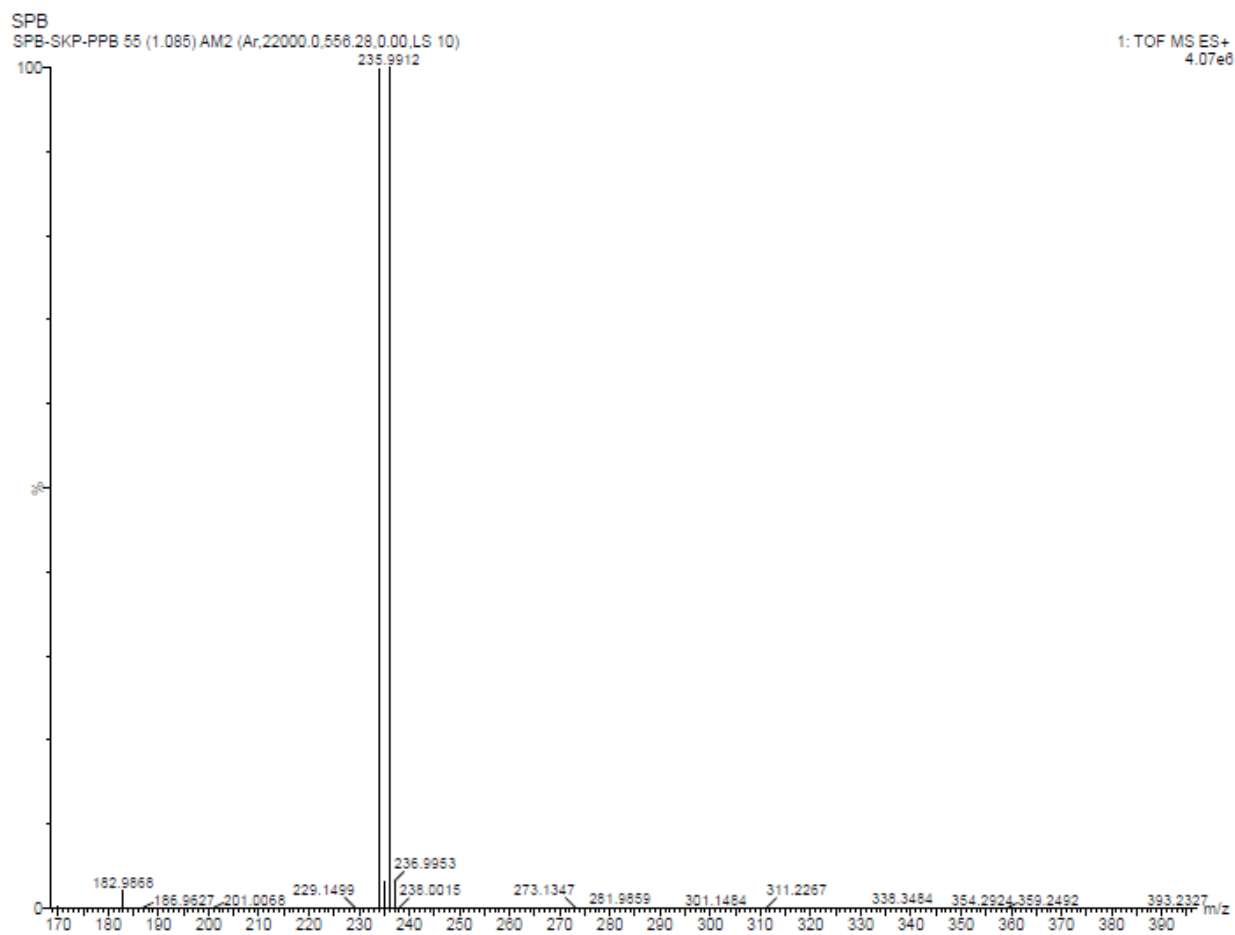


4. Mass Spectra of the Compounds

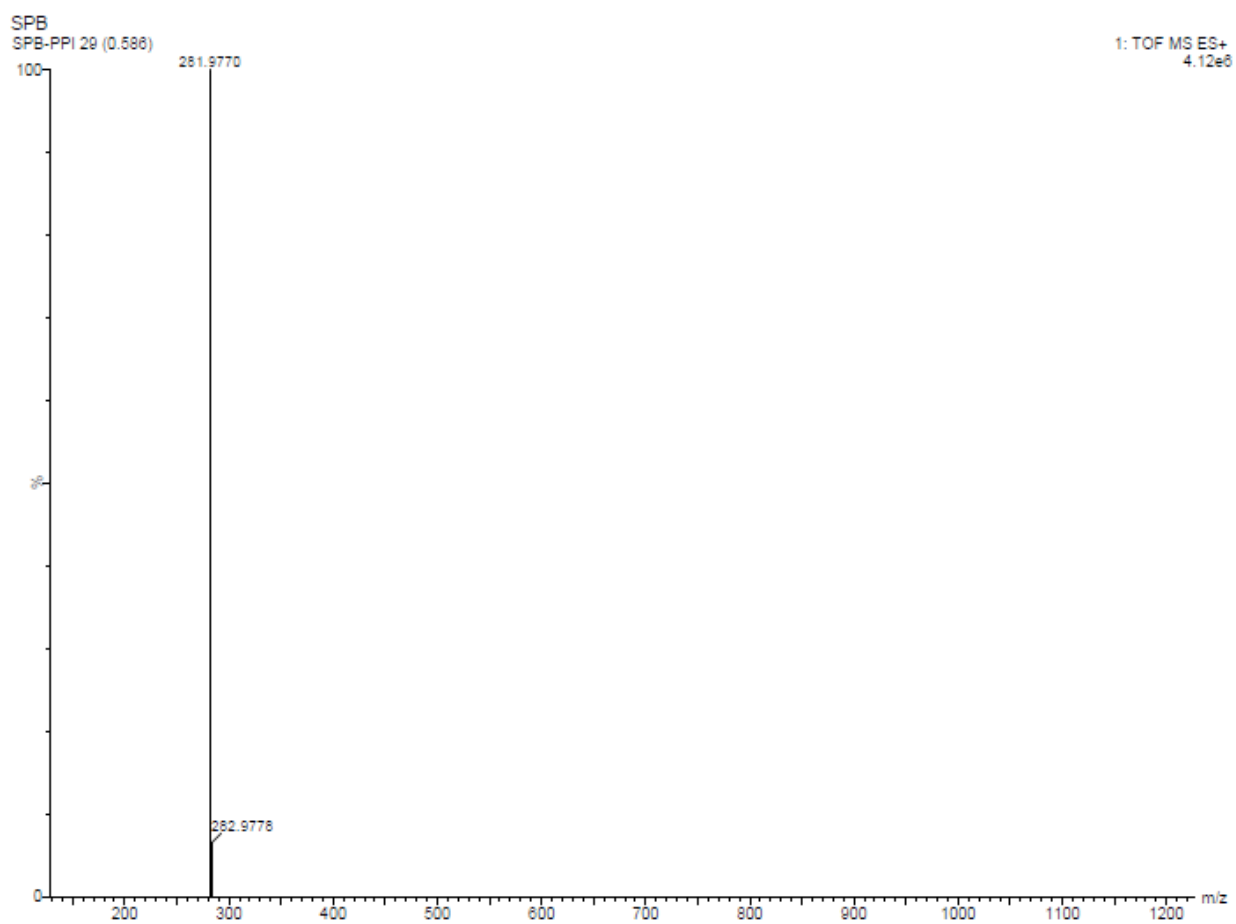
A. HRMS of 1



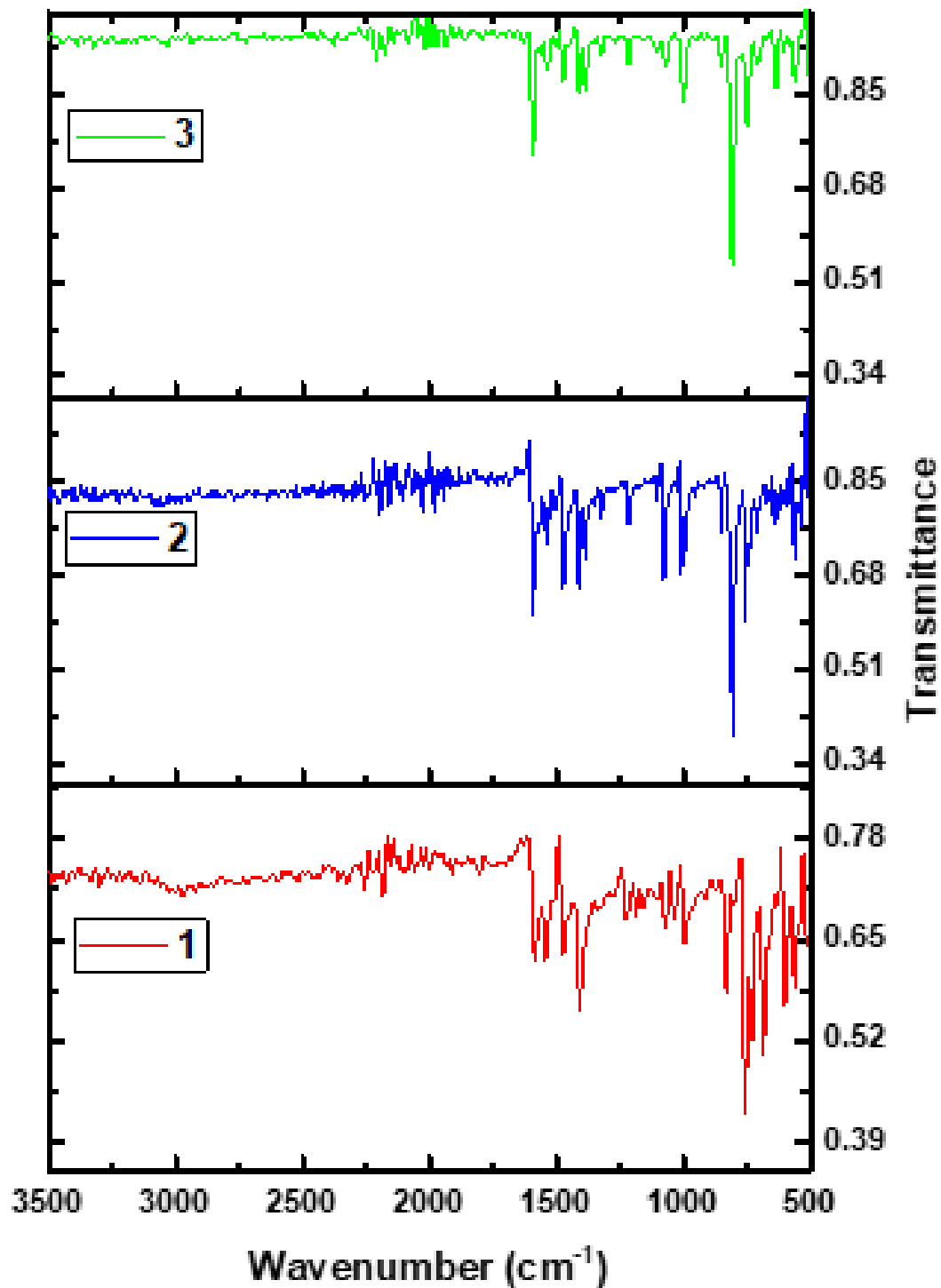
B. HRMS of 2



C. HRMS of 3



6. FTIR Spectra of the Compounds



References

S1. J.-J. Li, Y. Chen, J. Yu, N. Cheng and Y. Liu, *Adv. Mater.*, 2017, **29**, 1701905.