On/Off Fluorescence Emission Induced by Encapsulation, Exchange and Reversible Encapsulation of a BODIPY-Guest in Self-Assembled Organometallic Cages

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–Supporting Information–

Table of contents

1. Description of synthetic procedures

Materials and methods. All manipulations and reactions were performed under a nitrogen atmosphere by using standard Schlenk techniques. Glasswares were dried in an oven at 120 °C before operation. However, once the reactions were finished, subsequent processing requires no special attention, owing to compounds are stable in air. Solvents were further purified according to standard method prior to use. ^{1}H NMR spectra were monitored on Bruker AVANCE III 400 spectrometers in CD_3OD (δ = 3.31 ppm), all coupling constants are expressed in Hz. Mass spectra were obtained with a Bruker microTOF-Q II mass spectrometer (Bruker Daltonics Corp., USA) in the electrospray ionization (ESI) mode. UV-Vis spectra were measured using an Agilent Cary-100 spectrophotometer. Fluorescence spectra were recorded on a Horiba Fluorolog-3 spectrometer. All chemicals were purchased through commercial resources, and all are used without purification.

Synthesis of 3

This compound was synthesized according to the reported literature.[S1]

Yield: (215 mg, 68%), ^{1}H NMR (400 MHz, CD_3OD): δ = 6.13 (s, 2H), 2.66 (s, 3H), 2.45 (d, J = 4.0 Hz, 12H). ^{19}F NMR (376 MHz, CD_3OD): δ = -147.5 (q, J = 32.8 Hz, 2F).

Self-assembly of 1 and 2

1 and **2** were synthesized according to our reported procedures.[S2]

Data for **1**

Yield: (33.9 mg, 76%), ^{1}H NMR (400 Hz, CD_3OD): δ = 8.76 (d, J = 6.4 Hz, 12H), 8.64 (d, J = 6.4 Hz, 12H), 1.75 (s, 90H; Cp*). ^{13}C NMR (100 MHz, CD_3OD): δ = 178.14, 170.96, 153.66, 146.59, 126.85, 107.37, 98.10, 8.75. ^{19}F NMR (376 MHz, CD_3OD): δ = -80.23 (s, 3F). ESI-MS (positive ions): m/z = 743.0219 (calcd. for [**1** − 4OTf]$^{4+}$, 743.0027), m/z = 1040.3486 (calcd. for [**1** − 3OTf]$^{3+}$, 1040.3226). IR (KBr) ν = 1528 cm^{-1} (C=O).

Data for **2**

Yield: (40.3 mg, 83%); ^{1}H NMR (400 Hz, CD_3OD): δ = 8.89 – 8.62 (m, 24H), 8.43 (s, 12H), 7.98 (s, 12H), 1.73 (s, 90H, Cp*). ^{13}C NMR (100 MHz, CD_3OD): δ = 170.92, 152.77, 135.83,

134.14, 128.01, 126.00, 123.32, 120.15, 107.94, 96.50, 8.45. ^{19}F NMR (376 MHz, CD_3OD): δ = -79.96 (s, 3F). ESI-MS (positive ions): m/z = 1121.7832 (calcd. for [**2** − 3OTf]$^{3+}$, 1121.7832), m/z = 1757.2012 (calcd. for [**2** − 2OTf]$^{2+}$, 1757.1511). IR (KBr) ν =1530 cm^{-1} (C=O).

Synthesis of 3 ⊂ 1

To a solution of cage **1** (26.7 mg, 0.01 mmol) in CH_3OH (15 mL), guest **3** (2.6 mg, 0.01 mmol) was added in one proportion. The color of the reaction mixture gradually changed from intense green to dark brown. The mixture was allowed to stir for 3 h at ambient temperature and subsequently filtered. The filtration was concentrated (2 mL) and was precipitated by the addition of diethyl ether (15 mL).

Data for **3 ⊂ 1**

Yield: (22.9 mg, 78%), ^{1}H NMR (400 MHz, CD_3OD): δ = 8.88 – 8.56 (m, 24H), 4.37 (s, 2H, encapsulated guest **3**), 1.74 (s, 90H, Cp*), 1.38 (s, 3H, encapsulated guest **3**), 0.93 (d, J = 26.5 Hz, 12H, encapsulated guest **3**). ^{13}C NMR (100 MHz, CD_3OD): δ =178.71 (encapsulated guest **3**), 177.96, 169.95, 153.56, 146.04, 126.71, 123.31 (encapsulated guest **3**), 120.15 (encapsulated guest **3**), 116.99 (encapsulated guest **3**), 107.45, 98.18, 96.39 (encapsulated guest **3**), 30.72 (s, br, encapsulated guest **3**), 19.46 (encapsulated guest **3**), 8.88. ^{19}F NMR (376 MHz, CD_3OD): δ = -80.2 (s, 3F), -143.0 (br, 2F, encapsulated guest **3**). ESI-MS (positive ions): m/z = 854.2715 (calcd for [[**3** ⊂ **1**] − 4OTf + 3CH_3CN + 3H_2O]$^{4+}$, 854.3301), m/z = 1188.6801 (calcd. for [[**3** ⊂ **1**] − 3OTf + 3CH_3CN + 3H_2O]$^{3+}$, 1188.7577). IR (KBr) ν =1534 cm^{-1} (C=O).

Synthesis of 3 ⊂ 2

AgOTf (25.7 mg, 0.1 mmol) was added to a solution of complex [$Cp^*_2Rh_2(\mu$-DHNA$)_3Cl_2$] (41.7 mg, 0.05 mmol) in CH_3OH (15 mL). Immediately a white precipitate formed. The reaction mixture was further stirred for 3 h and filtered to give a clear solution. After that, BODIPY derivative **3** (4.5 mg, 0.017 mmol) and tpt (10.4 mg, 0.034 mmol) were subsequently added to the solution and the reaction mixture was further stirred for 12 h at the ambient temperature. After filtration, the solution was concentrated to 2 mL. Addition of diethyl ether precipitates the solid **3 ⊂ 2**.

Data for **3 ⊂ 2**

Yield: (39.8 mg, 75%), ^{1}H NMR (400 MHz, CD_3OD): δ = 8.82 (dd, J = 6.1, 3.4 Hz, 12H), 8.69 (d, J = 5.6 Hz, 12H), 8.29 (d, J = 5.6 Hz, 12H), 8.02 (dd, J = 6.0, 3.5 Hz, 12H), 5.36 (s, 2H, encapsulated guest **3**), 2.02 (s, 3H, encapsulated guest **3**), 1.75 (br, J = 3.1 Hz, 12H, encapsulated guest **3**), 1.70 (s, 90H, Cp*).^{13}C NMR (100 MHz, CD_3OD): δ = 171.02, 169.98 (encapsulated guest **3**), 152.73, 145.57 (encapsulated guest **3**), 141.35 (encapsulated guest **3**), 135.77, 134.30, 128.08, 126.51, 124.87 (encapsulated guest **3**), 122. 82, 120.17, 118.58 (encapsulated guest **3**), 107.97, 96.53, 30.39 (s, br, encapsulated guest **3**), 15.7 (encapsulated guest **3**), 8.44. ^{19}F NMR (376 MHz, CD_3OD): δ = -79.84 (s, 3F), -144.5 (br, 2F, encapsulated guest **3**). ESI-MS (positive ions): m/z = 1209.1936 (calcd. for $[[\mathbf{3} \subset \mathbf{2}] - 3OTf]^{3+}$, 1209.1669, m/z = 1888.2612 (calcd. for $[[\mathbf{3} \subset \mathbf{2}] - 2OTf]^{2+}$, 1888.2288). IR (KBr) ν =1534 cm^{-1} (C=O).

Exchange of guest 3 from 3 ⊂ 1 and 3 ⊂ 2 by 4

To a solution of **3** ⊂ **1** (49.9 mg, 0.017 mmol) or **3** ⊂ **2** (54.0 mg, 0.017 mmol)**, 4** (5.1 mg, 0.017 mmol) was added and the mixture was stirred for 3 h at ambient temperature. Then, the solvent was removed under vacuum and the residue was extracted with CH_2Cl_2 and added diethyl ether to precipitate the solid.

Data for **4** ⊂ **1** + **3**

Yield: (33.7 mg, 68%), ^{1}H NMR (400 MHz, CD_3OD): δ = 8.46 – 8.41 (m, 12H), 7.55 (s, 12H, encapsulated guest **4**), 7.35 – 7.30 (m, 12H), 6.13 (s, 2H, free guest **3**) 2.65 (s, 3H, free guest **3**), 2.45 (d, J = 3.9 Hz, 12H, free guest **3**), 1.71 (s, 90H, Cp*).

Data for **4** ⊂ **2** + **3**

Yield: (37.5 mg, 70%), ^{1}H NMR (400 MHz, CD_3OD): δ = 9.04 (dd, J = 6.1, 3.4 Hz, 12H), 8.55 – 8.42 (m, 12H), 8.26 (dd, J = 7.5, 3.8 Hz, 12H), 7.04 – 6.94 (m, 12H), 6.54 (s, 12H, encapsulated guest **4**), 6.12 (s, 2H, free guest **3**), 2.64 (s, 3H, free guest **3**), 2.44 (d, J = 4.2 Hz, 12H, free guest **3**), 1.68 (s, 90H, Cp*).

Exchange of guest 3 from 3 ⊂ 1 and 3 ⊂ 2 by 5

To a solution of **3** ⊂ **1** (49.8 mg, 0.017 mmol) or **3** ⊂ **2** (55.0 mg, 0.017 mmol)**, 5** (3.4 mg, 0.017 mmol) was added and the mixture was stirred for 3 h at ambient temperature. Then, the solvent was removed and residue was extracted with CH_2Cl_2. Then diethyl ether was added to

precipitate the solid of **5** ⊂ **1** and **5** ⊂ **2**.

Data for **5** ⊂ **1** + **3**

Yield: (40.0 mg, 73%), ^{1}H NMR (400 MHz, CD_3OD): δ = 8.47 (d, J = 5.9 Hz, 12H), 8.37-8.04 (br, 10H, encapsulated guest **5**), 8.02 (d, J = 5.8 Hz, 12H), 6.13 (s, 2H, free guest **3**), 2.60 (s, 3H, free guest **3**), 2.44 (d, J = 12.2 Hz, 12H, free guest **3**), 1.67 (s, 90H, Cp*).

Data for **5** ⊂ **2** + **3**

Yield: (37.4 mg, 72%), ^{1}H NMR (400 MHz, CD_3OD-d_4): δ = 8.81 (dd, J = 6.0, 3.4 Hz, 12H), 8.38 (d, J = 5.7 Hz, 12H), 8.08 (dd, J = 6.0, 3.6 Hz, 12H), 8.21 – 7.72 (m, 10H, encapsulated guest **5**), 7.59 (d, J = 5.6 Hz, 12H), 6.04 (s, 2H, free guest **3**), 2.61 (s, 3H, free guest **3**), 2.43 (d, J = 3.9 Hz, 12H, free guest **3**), 1.45 (s, 90H, Cp*).

Dissociation of 3 ⊂ 1 and 3 ⊂ 2

NaCl (1.1 mg, 0.02 mmol) was added to the NMR tube containing **3** ⊂ **1** and the mixture was stirred for 10 min at room temperature, a brick-red precipitate was obtained immediately, and the solution turns to green. Following the similar procedure, **3** ⊂ **2** can also be dissociated.

Data for dissociation of **3** ⊂ **1**

^{1}H NMR (400 MHz, CD_3OD): δ = 6.13 (s, 2H, free guest **3**), 2.65 (s, 3H, free guest **3**), 2.45 (d, J = 3.3 Hz, 12H, free guest **3**).

Data for dissociation of **3** ⊂ **2**

^{1}H NMR (400 MHz, CD_3OD): δ = 8.89 (dd, J = 6.1, 3.4 Hz, 12H), 8.70 (d, J = 5.6 Hz, 12H), 8.30 (d, J = 5.6 Hz, 12H), 8.04(dd, J = 6.0, 3.5 Hz, 12H), 6.13 (s, 2H, free guest **3**), 2.50 (s, 3H, free guest **3**), 2.30 (d, J = 3.3 Hz, 12H, free guest **3**), 1.72 (s, 90H, Cp*).

Reversible self-assembly of complexes 3 ⊂ 1 and 3 ⊂ 2

AgOTf (17.7 mg, 0.05 mmol) was added to the NMR tube into the dissociated **3** ⊂ **1** or **3** ⊂ **2**. After that, the reaction mixture was stirred for 1 h at room temperature. The precipitate disappeared and the solution turned again to a brown solution gradually (**3** ⊂ **1**). Because **L2** is dark purple and has good solubility in CD_3OD, so the color change is not obvious.

Data for reversible self-assembly of **3** ⊂ **1**

^{1}H NMR (400 MHz, CD_3OD): δ = 8.86-8.50 (m, 24H), 4.35 (s, 2H, encapsulated guest **3**), 1.74 (s, 90H, Cp*) 1.35 (s, 3H, encapsulated guest **3**), 0.95 (d, J = 26.3 Hz, 12H, encapsulated guest **3**).

Data for reversible self-assembly of **3** ⊂ **2**

^{1}H NMR (400 MHz, CD_3OD): δ = 8.84 (dd, J = 6.1, 3.4 Hz, 12H), 8.71 (d, J = 5.6 Hz, 12H), 8.27 (d, J = 5.6 Hz, 12H), 8.05 (dd, J = 6.0, 3.5 Hz, 12H), 5.39 (s, 2H, encapsulated guest **3**), 2.04 (s, 3H, encapsulated guest **3**), 1.77 (d, J = 3.1 Hz, 12H, encapsulated guest **3**) 1.70 (s, 90H, Cp*).

2. Spectroscopic data.

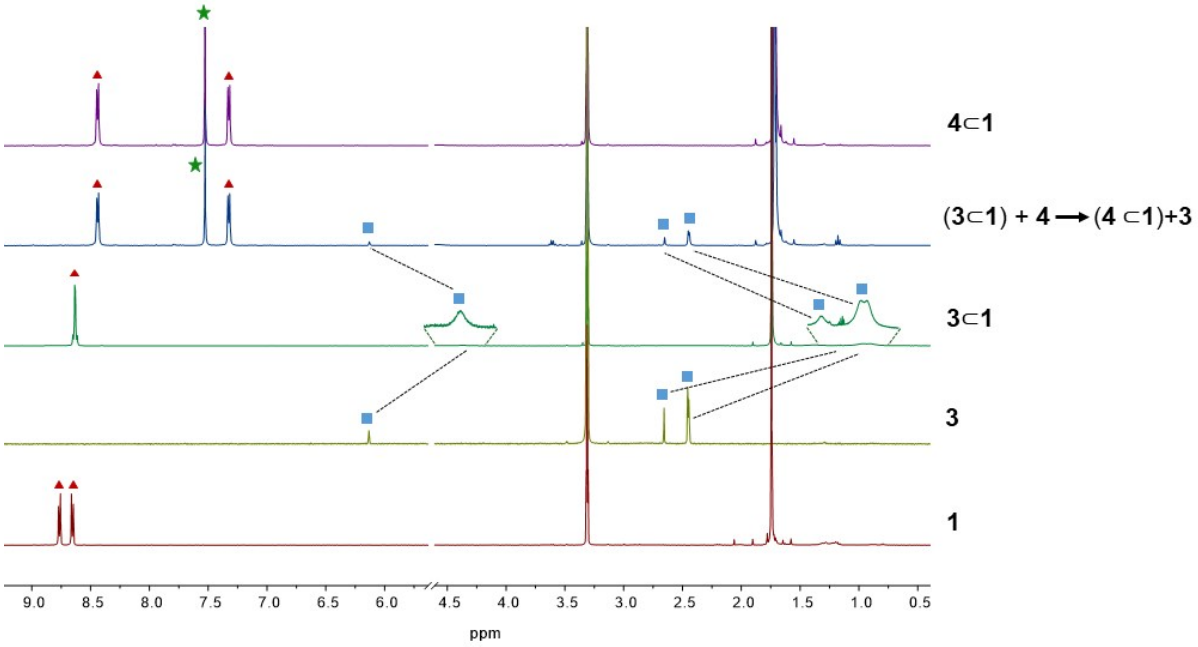

Figure S1. ^{1}H NMR spectra (298 K, 400 MHz, CD_3OD) of inclusion and exchange of **3** by **4** in **3** ⊂ **1** (▲= **1**; ■ = **3**; ★ = **4**).

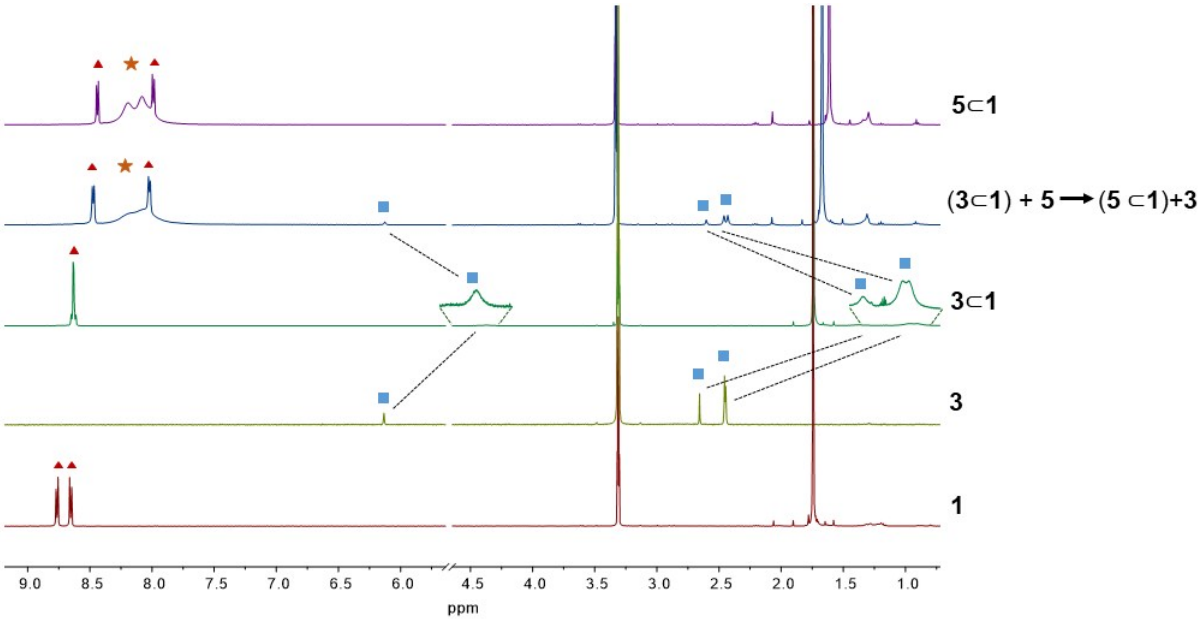

Figure S2. ^{1}H NMR spectra (298 K, 400 MHz, CD_3OD) of inclusion and exchange of **3** by **5** in **3** ⊂ **1** (▲= **1**; ■ = **3**; ★ = **5**)

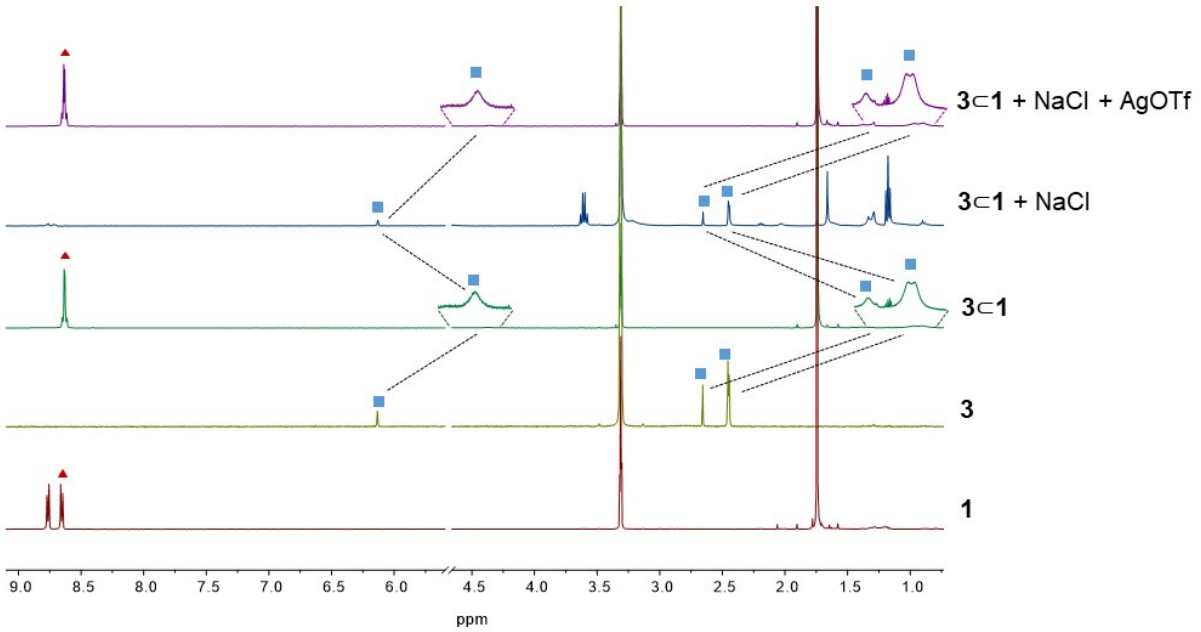

Figure S3. ^{1}H NMR (298 K, 400 MHz, CD_3OD) for dissociation and reassembly of **3** ⊂ **1**(▲= **1**;■ = **3**)

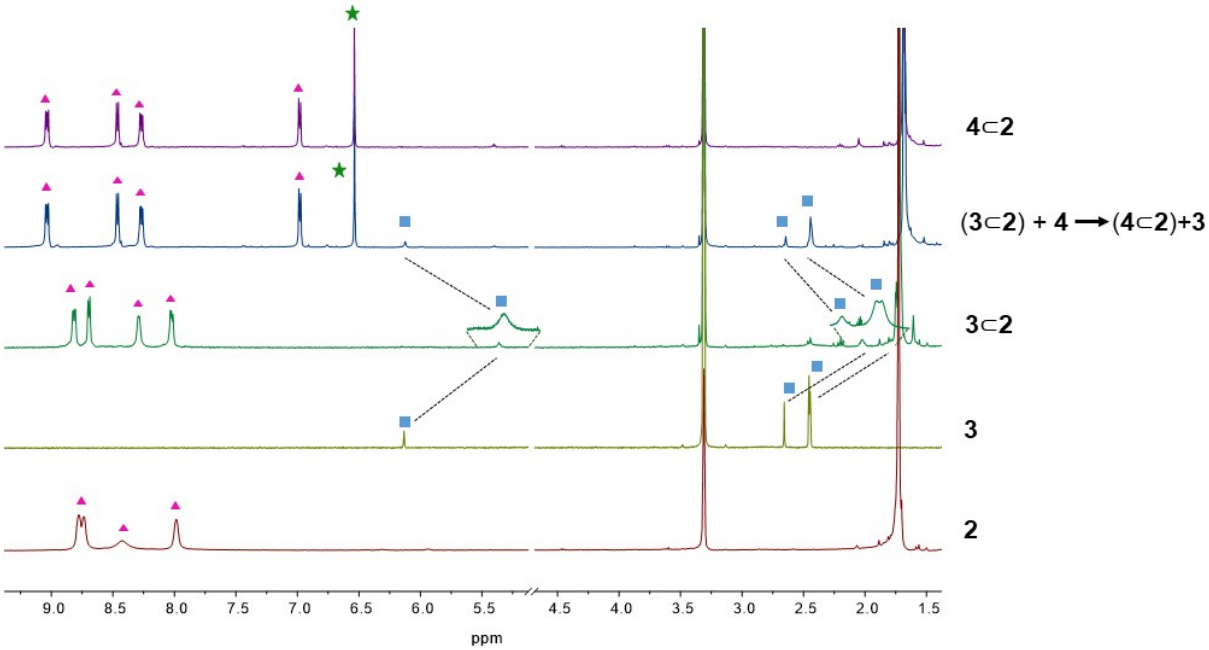

Figure S4. ^{1}H NMR (298 K, 400 MHz, CD_3OD) for the exchange of **3** by **4** in **3** ⊂ **2** (▲= **2**; ■ = **3**; ★ = **4**)

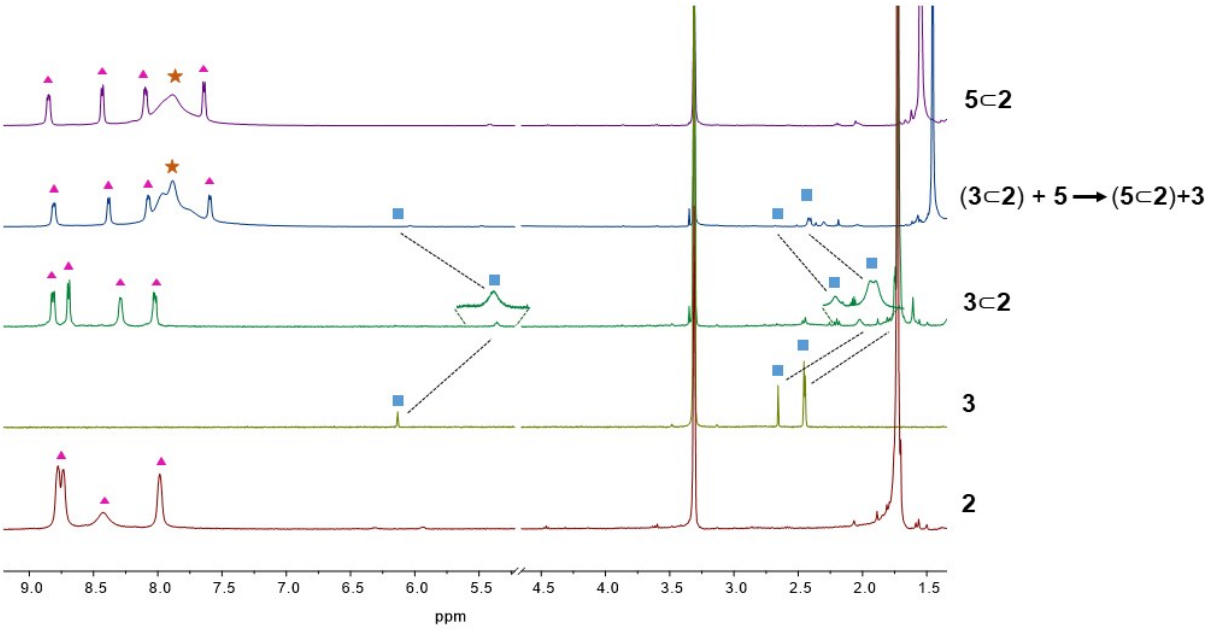

Figure S5. ^{1}H NMR spectra (298 K, 400 MHz, CD_3OD) for the exchange of **3** by **5** in **2** (▲= **2**; ■ = **3**; ★ = **5**).

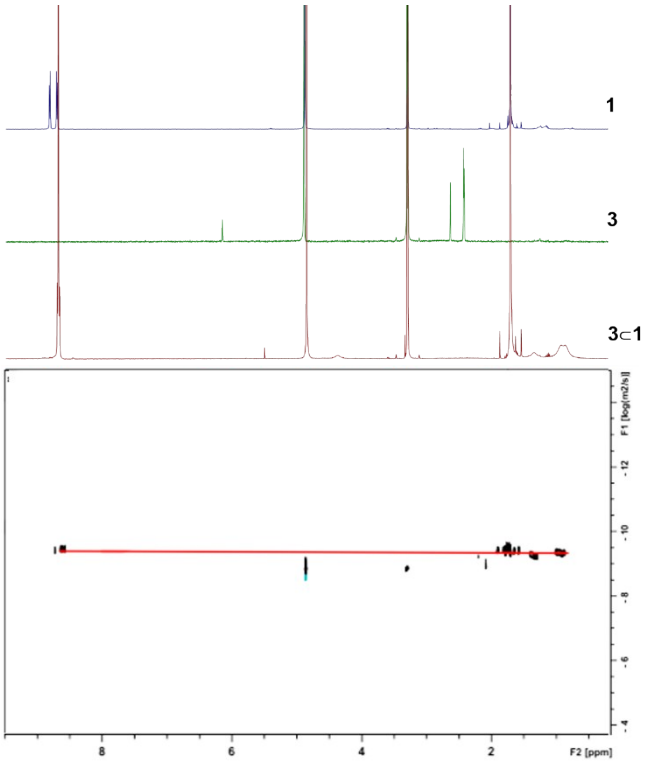

Figure S6. ^{1}H NMR spectra (298 K, 400 MHz, CD_3OD) of **1**, **3**, **3** ⊂ **1**, and the DOSY spectrum of **3** ⊂ **1**.

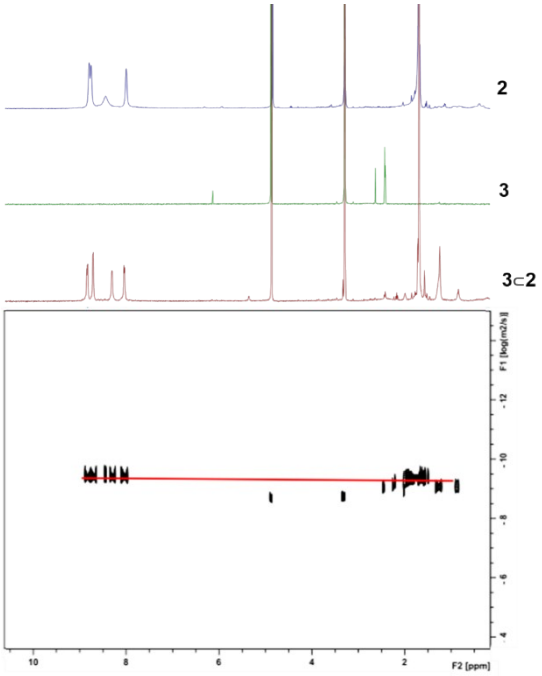

Figure S7. ^{1}H NMR spectra (298 K, 400 MHz, CD_3OD) of **2**, **3**, **3** ⊂ **2** and the DOSY spectrum of **3** ⊂ **2**.

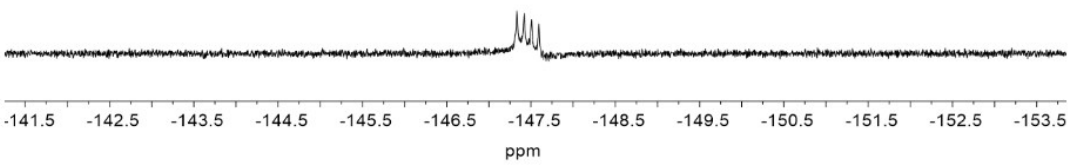

Figure S8. ^{19}F NMR spectrum (298 K, 376 MHz, CD_3OD) of **3**

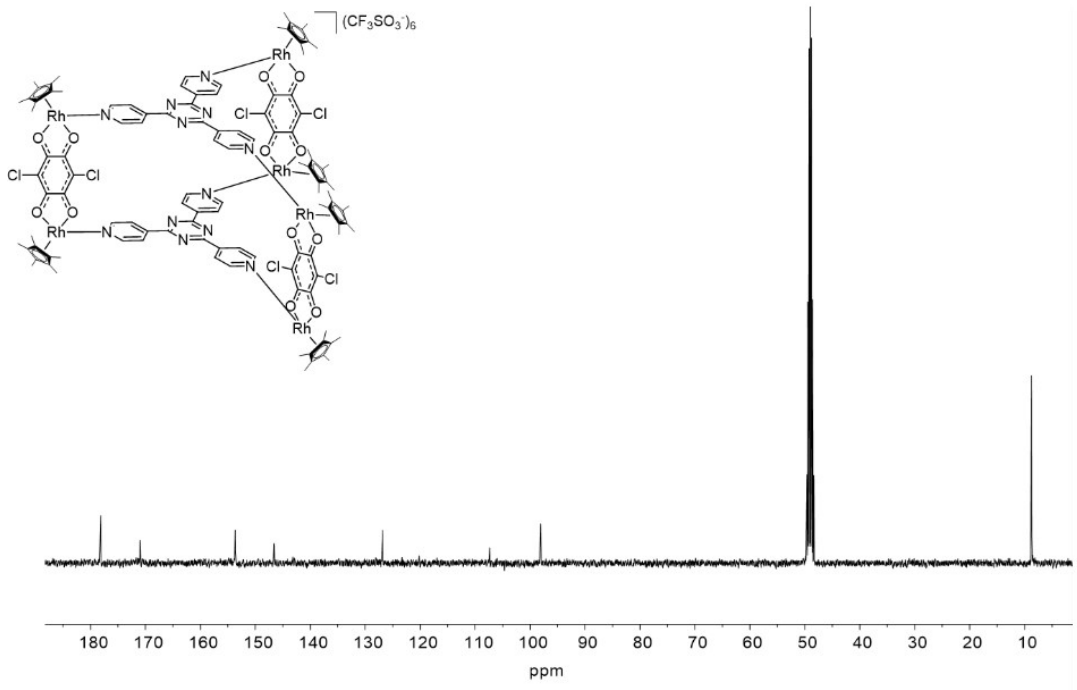

Figure S9. ^{13}C NMR spectrum (298 K, 100 MHz, CD_3OD) of **1**

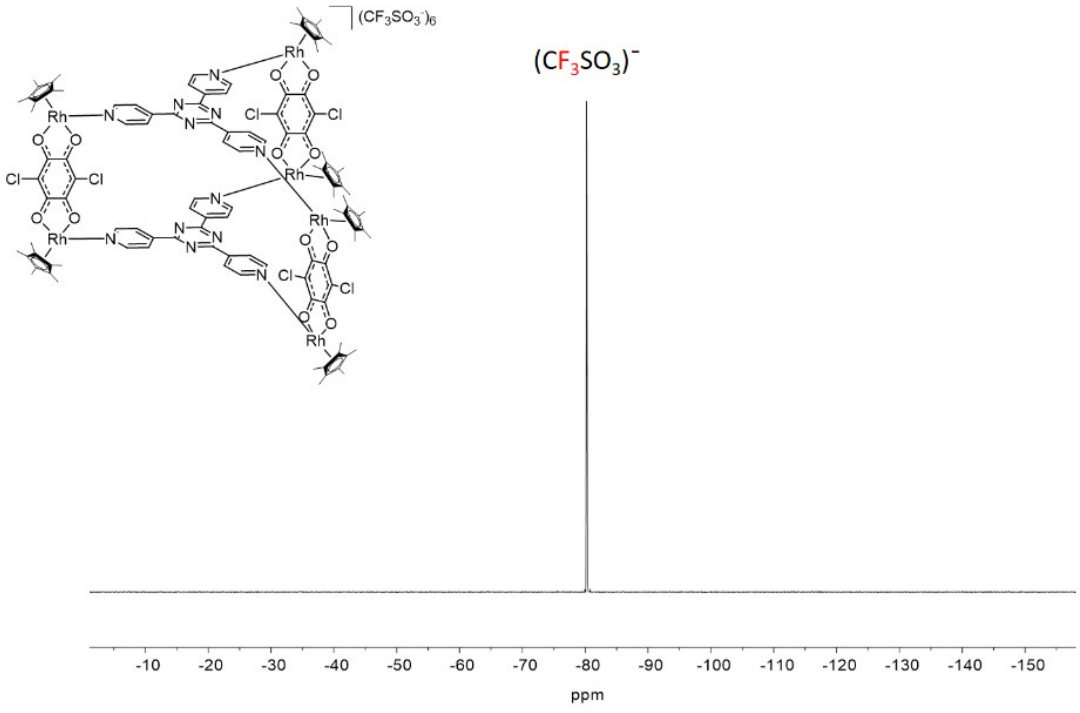

Figure S10. ^{19}F NMR spectrum (298 K, 376 MHz, CD_3OD) of **1**

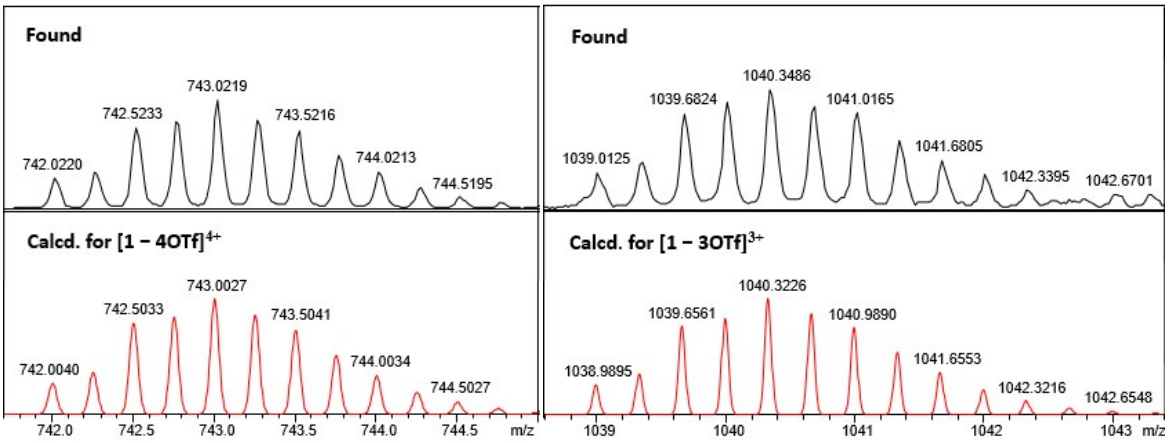

Figure S11. ESI-MS spectrum of **1**, experimentally found is drawn in black (top) and calculated is in red (bottom).

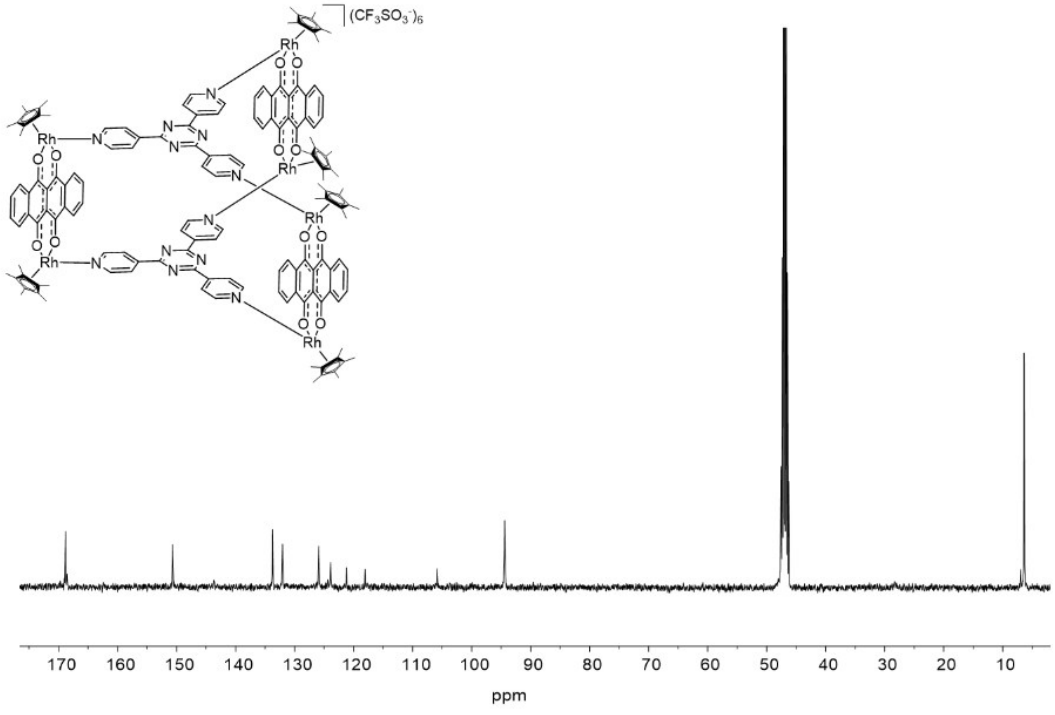

Figure S12. ^{13}C NMR spectrum (298 K, 100 MHz, CD_3OD) of **2**

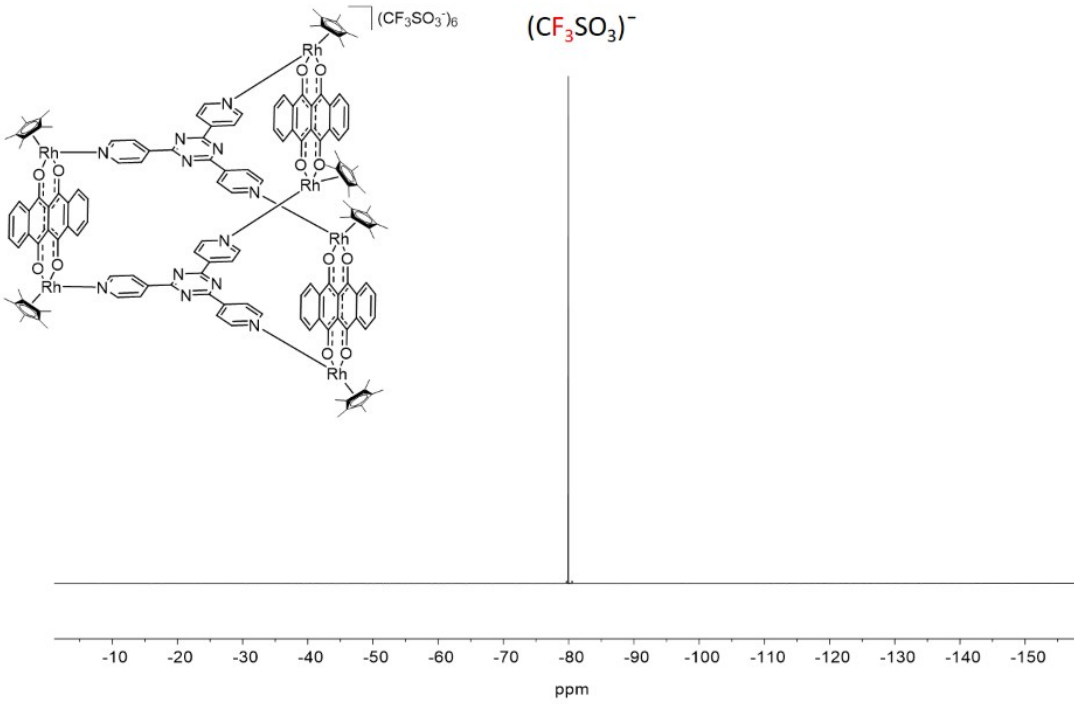

Figure S13. ^{19}F NMR spectrum (298 K, 376 MHz, CD_3OD) of **2**

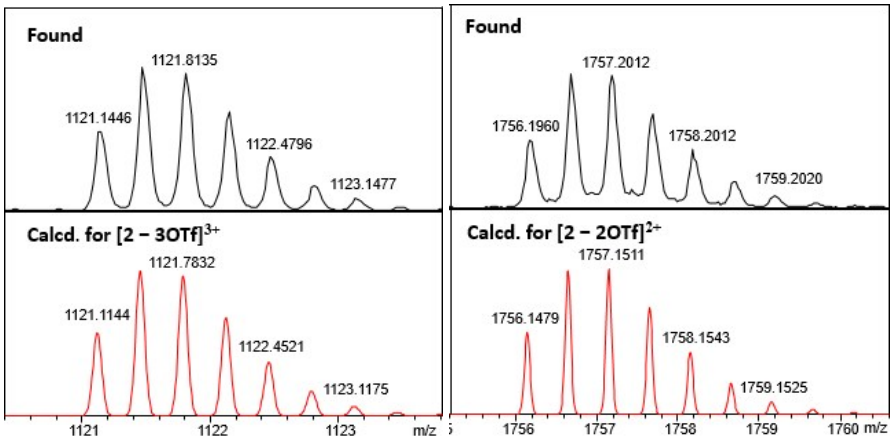

Figure S14. ESI-MS spectrum of **2**, experimentally found is drawn in black (top) and calculated is in red (bottom).

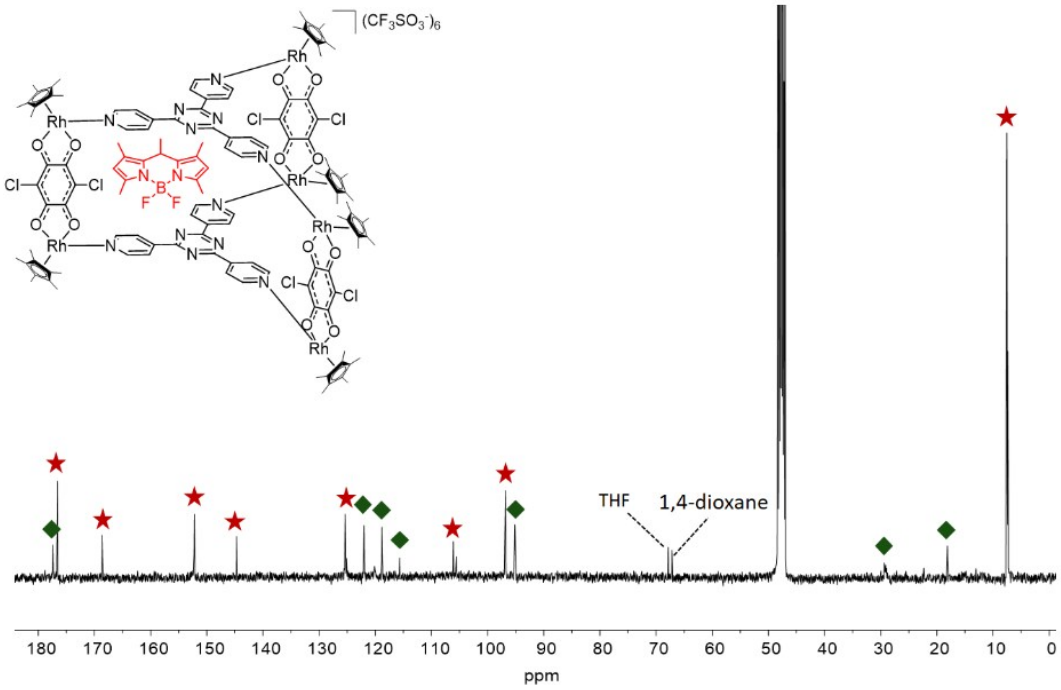

Figure S15. ^{13}C NMR spectrum (298 K, 100 MHz, CD_3OD) of **3** ⊂ **1** (★ = **1**, ◆ = **3**)

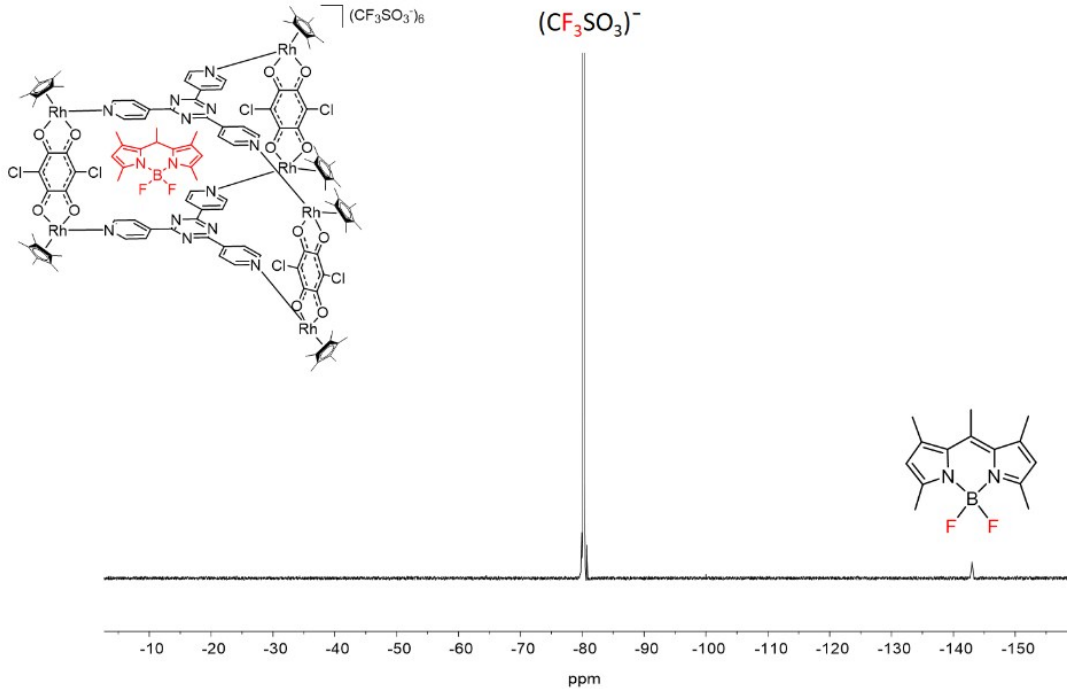

Figure S16. ^{19}F NMR spectrum (298 K, 376 MHz, CD_3OD) of **3** ⊂ **1**

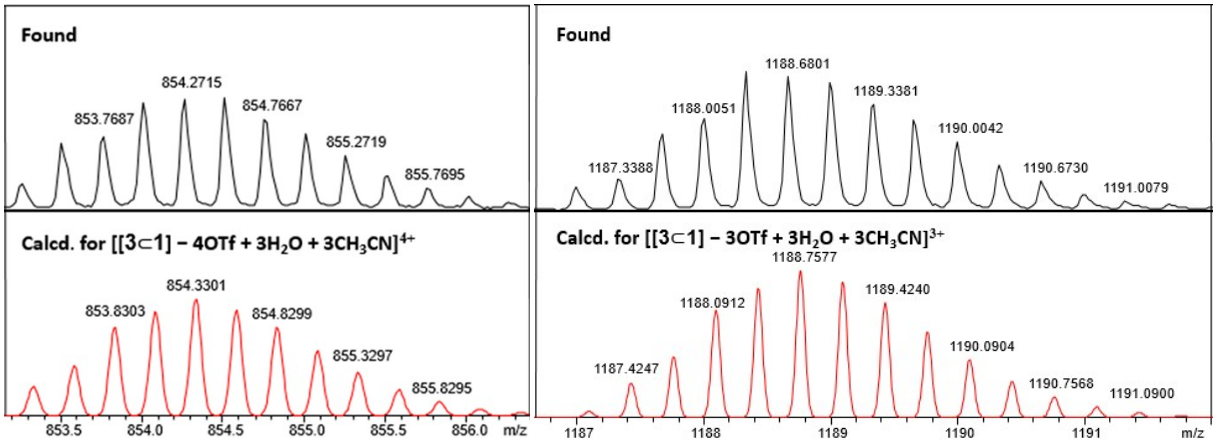

Figure S17. ESI-MS spectrum of **3** ⊂ **1**, experimentally found is drawn in black (top) and calculated is in red (bottom).

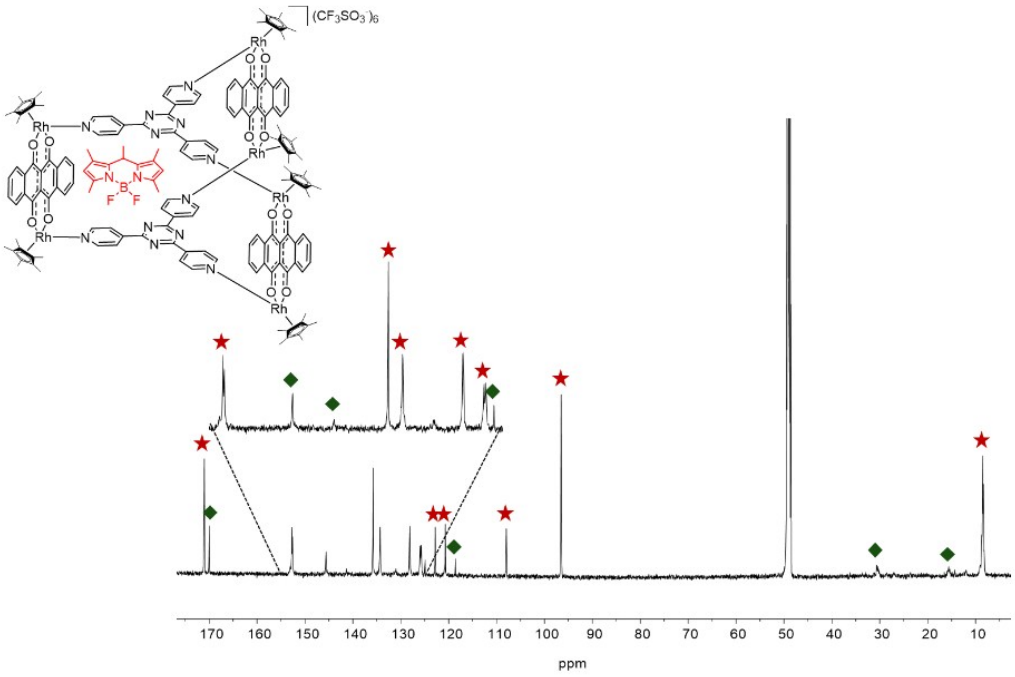

Figure S18. ^{13}C NMR spectrum (298 K, 100 MHz, CD_3OD) of **3** ⊂ **2** (★ = **2**, ◆ = **3**)

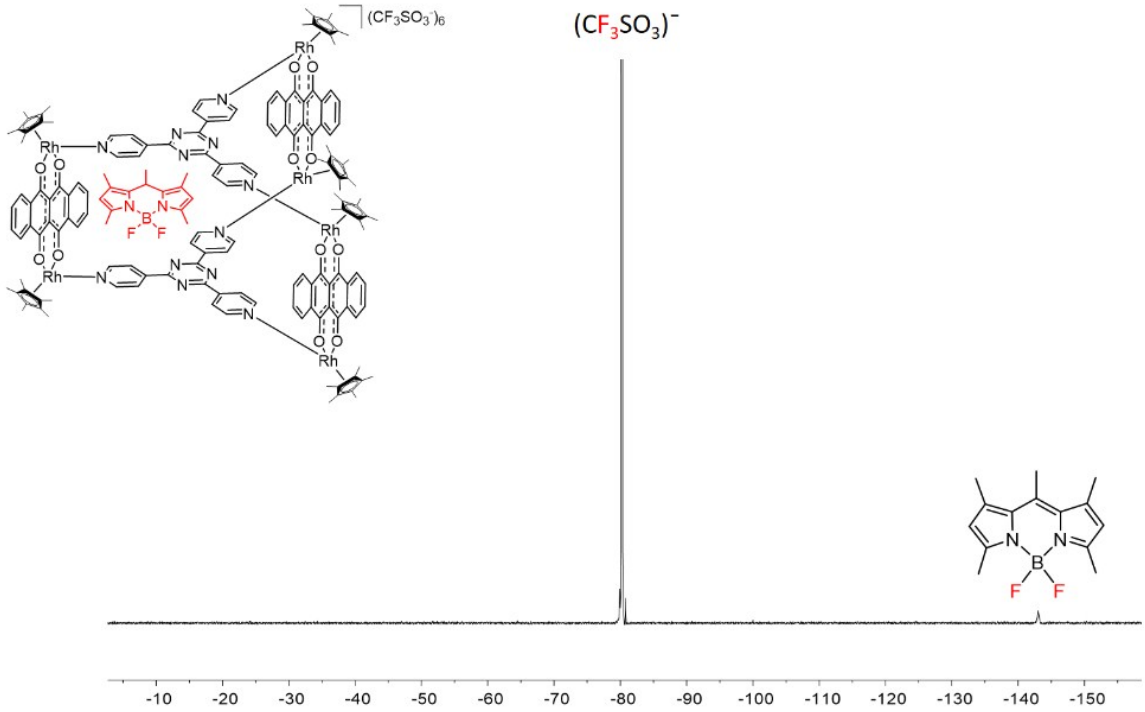

Figure S19. ^{19}F NMR spectrum (298 K, 376 MHz, CD_3OD) of **3** ⊂ **2**

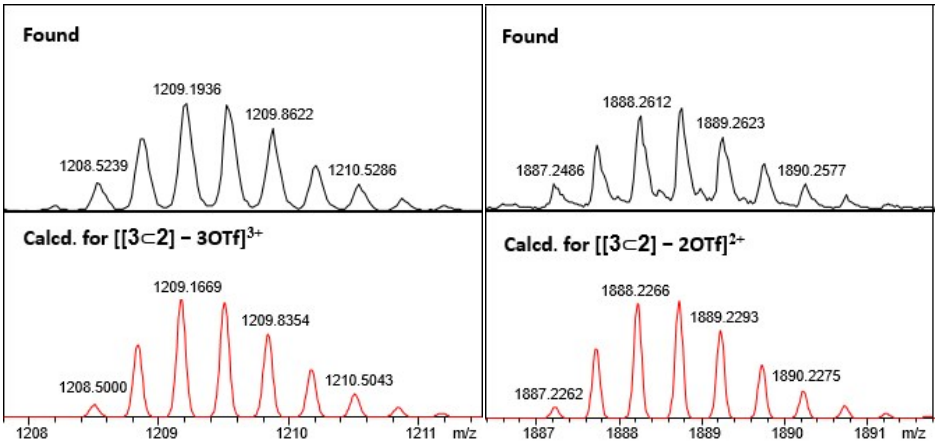

Figure S20. ESI-MS spectrum of **3** ⊂ **2**, experimentally found is drawn in black (top) and calculated is in red (bottom).

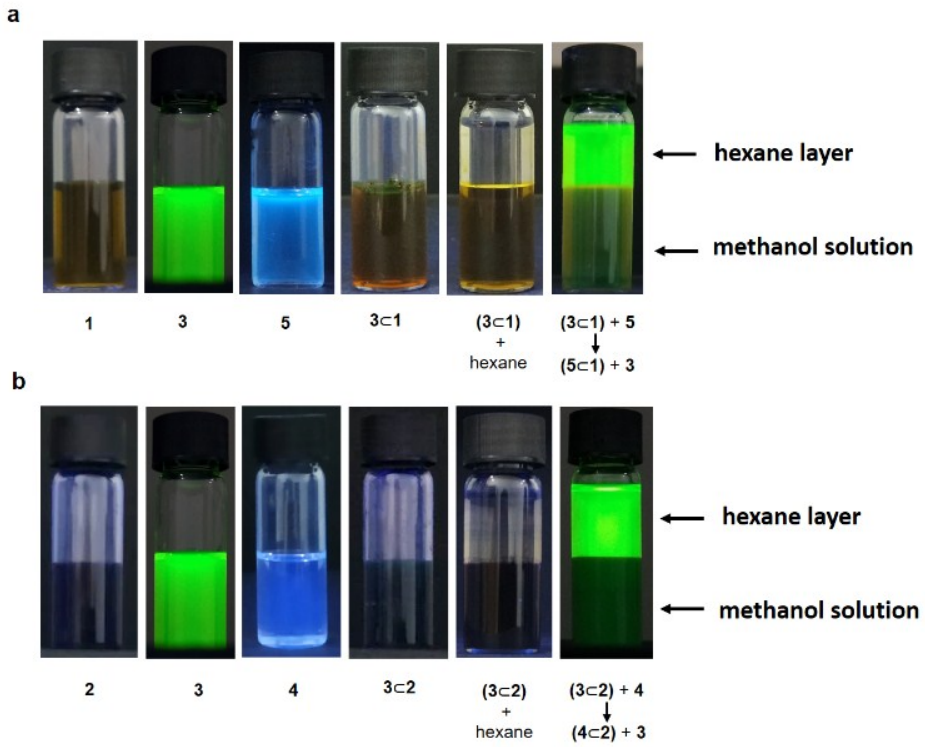

Figure S21. Observable color changes of through inclusion and guest-exchange process. Inset pictures were taken under fluorescence light λ_{ex} = 365 nm; a) experiments were performed in cage **1**; b) experiments were performed in cage **2**.

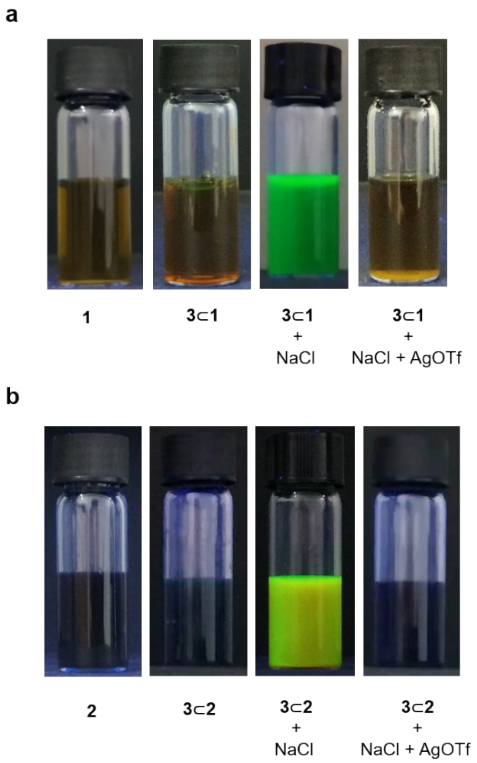

Figure S22. Observable color changes of dissociation and reversible self-assembly of a) **3** ⊂ **1** and b) **3** ⊂ **2**.

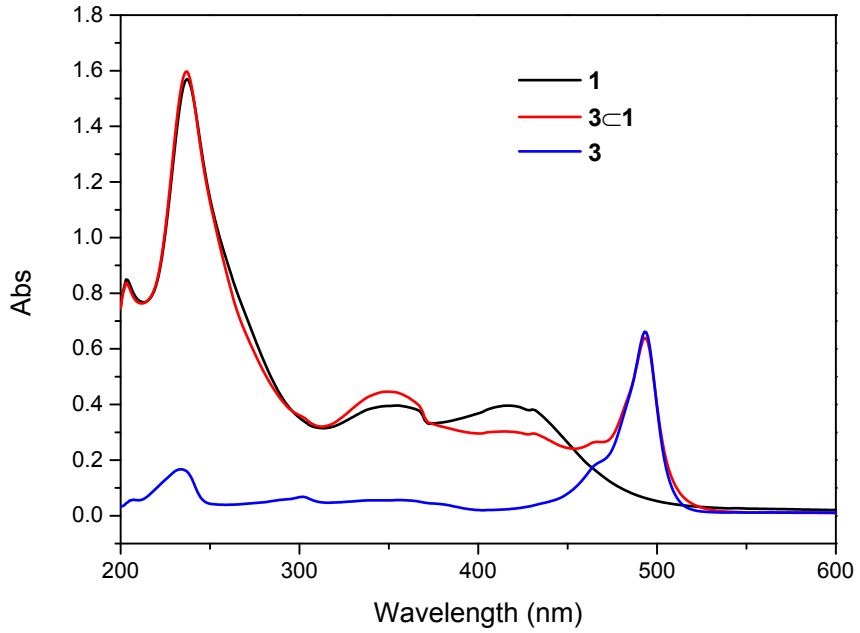

Figure S23 UV-visible absorption spectra of **1**, **3** ⊂ **1** and **3**.

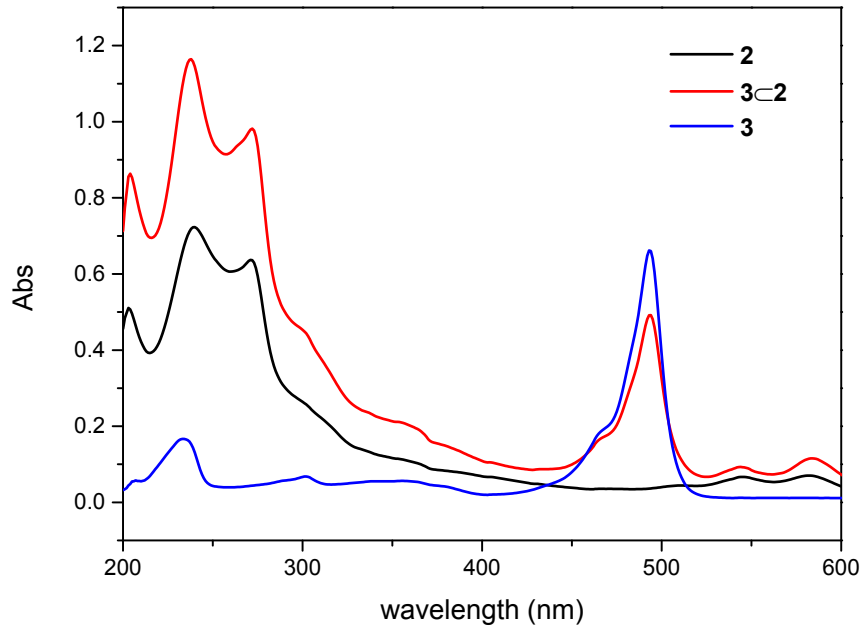

Figure S24. UV-visible absorption spectra of **2**, **3** ⊂ **2** and **3**.

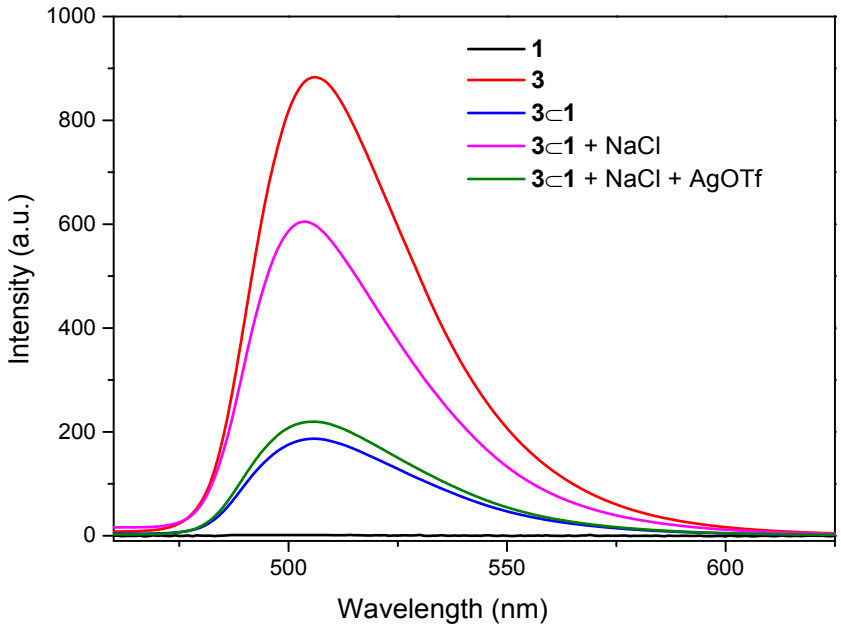

Figure S25. Fluorescence spectrum of the dissociation and reassembly of **3** ⊂ **1** (c = 1 x 10^{-5} M, T = 298 K, λ_{em}= 505 nm, λ_{ex}= 470 nm).

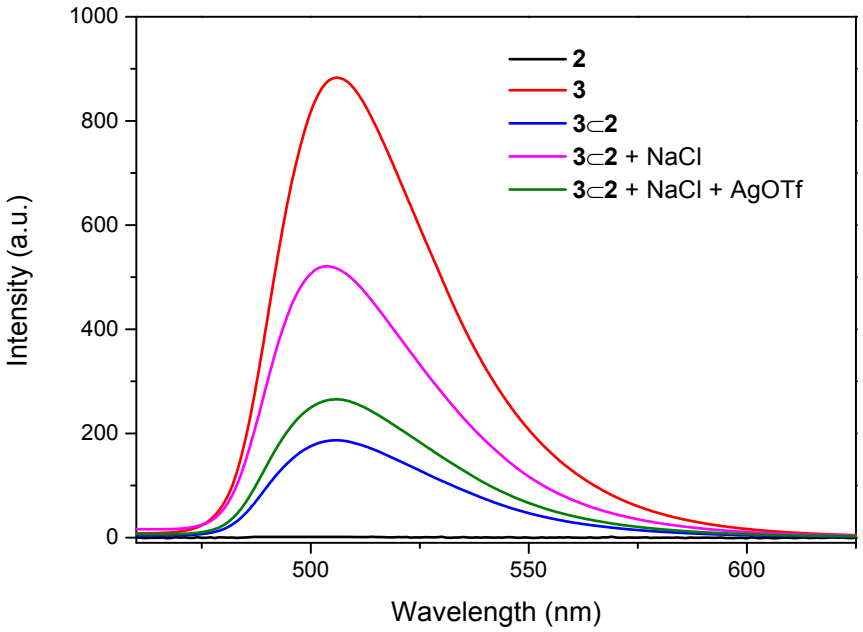

Figure S26. Fluorescence spectrum of the dissociation and reassembly of **3** ⊂ **2** (c = 1 x 10^{-5} M, T = 298 K, λ_{em}= 505 nm, λ_{ex}= 470 nm).

3. References

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S2. Y.-F. Han, H. Li, Z.-F. Zheng and G.-X. Jin, *Chem. Asian J.*, 2012, **7**, 1243-1250.