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Differences of solubilities, crystal structures, NMR spectra and fluorescence emissions induced by potassium cation/benzo-21-crown-7 molecular recognition

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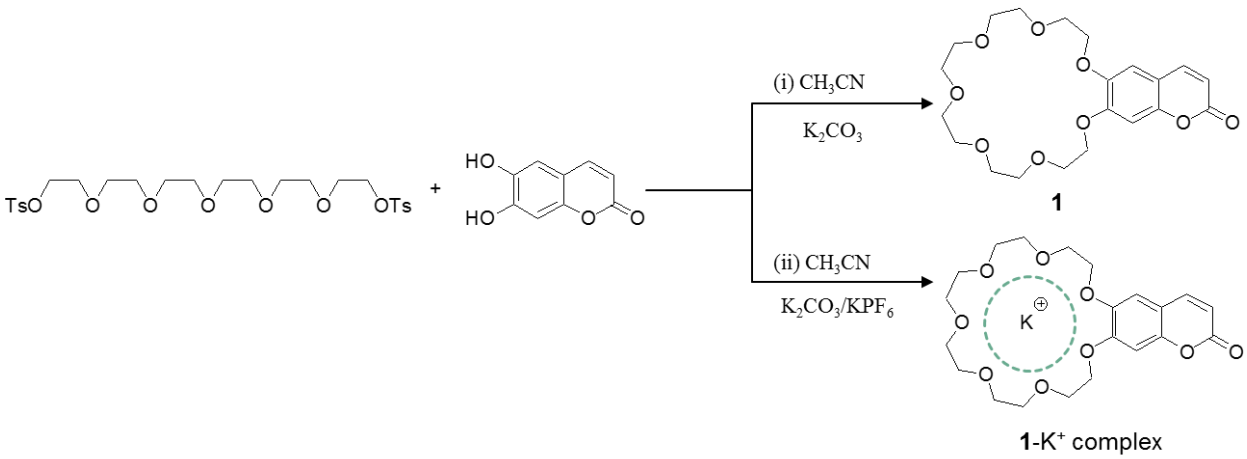
Supporting Information

1. Materials and methods

Detailed in the maintext.

*2. Syntheses of **1** (without potassium cations complexed) and **1**-K^+ complex (with potassium cations complexed)*



Scheme S1. Synthesis of **1** and **1**-K^+ complex: (i) CH_3CN, K_2CO_3, refluxing, 48 h; (ii) CH_3CN, K_2CO_3, KPF_6, refluxing, 48 h.

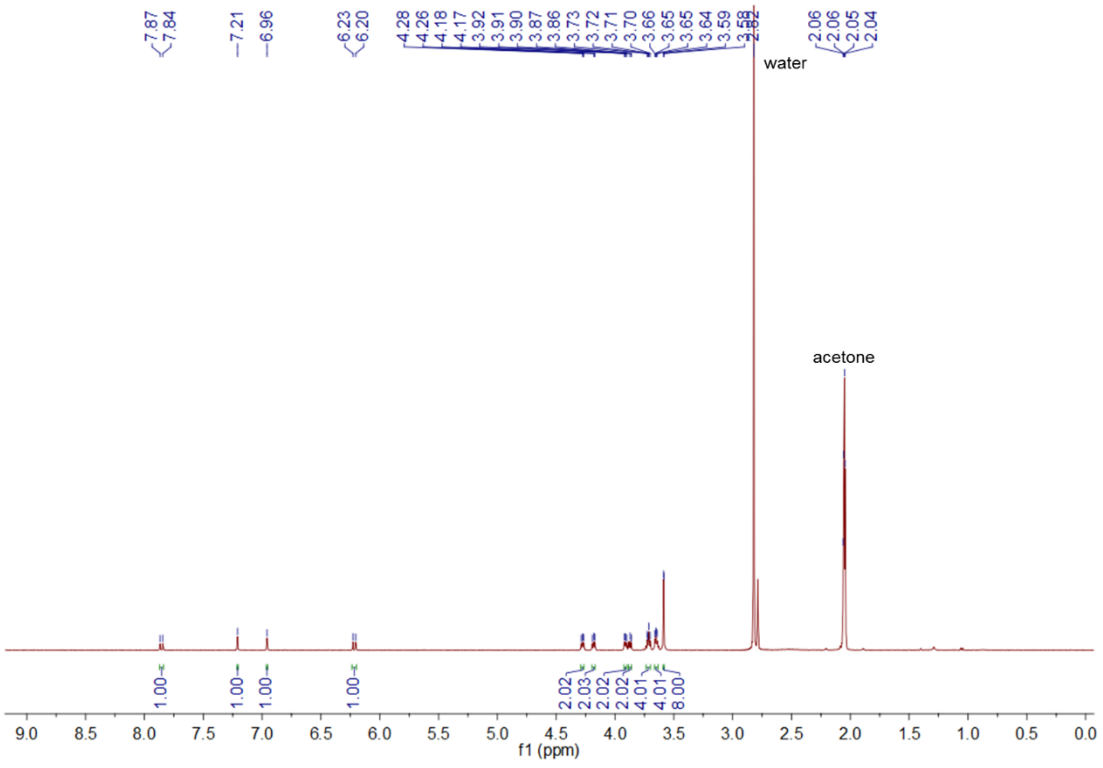


Figure S1. ^1H NMR spectrum (400 MHz, CD_3COCD_3, room temperature) of **1**.

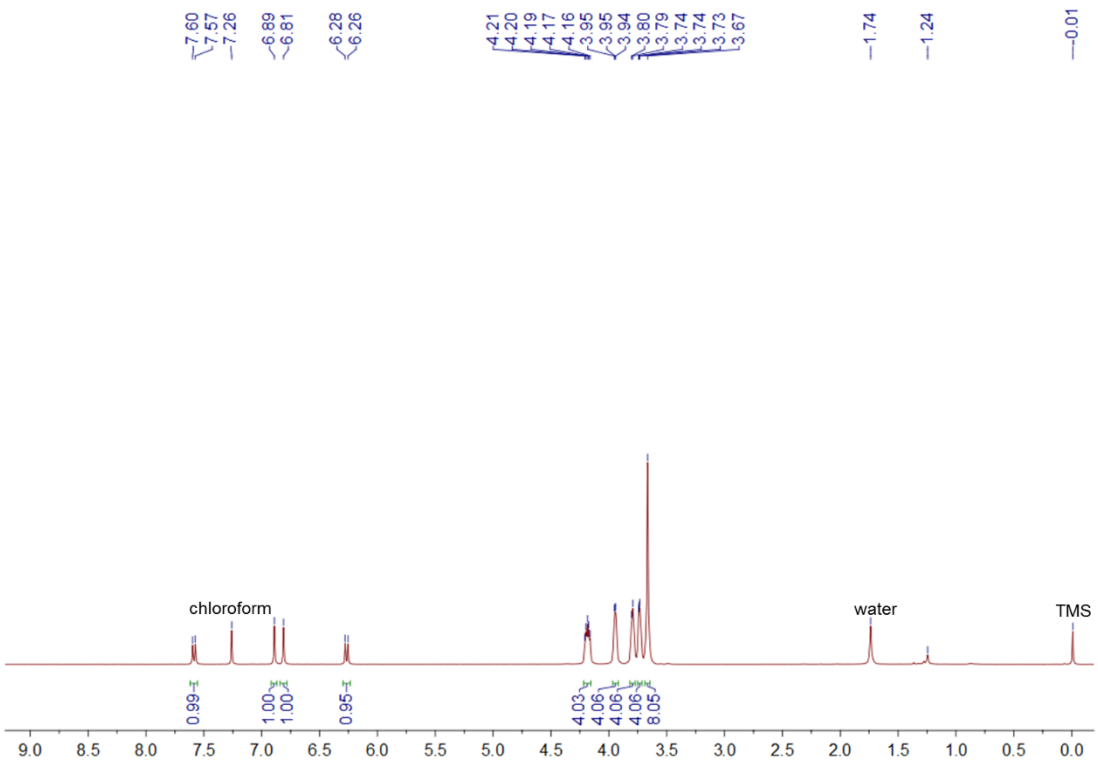


Figure S2. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **1**.

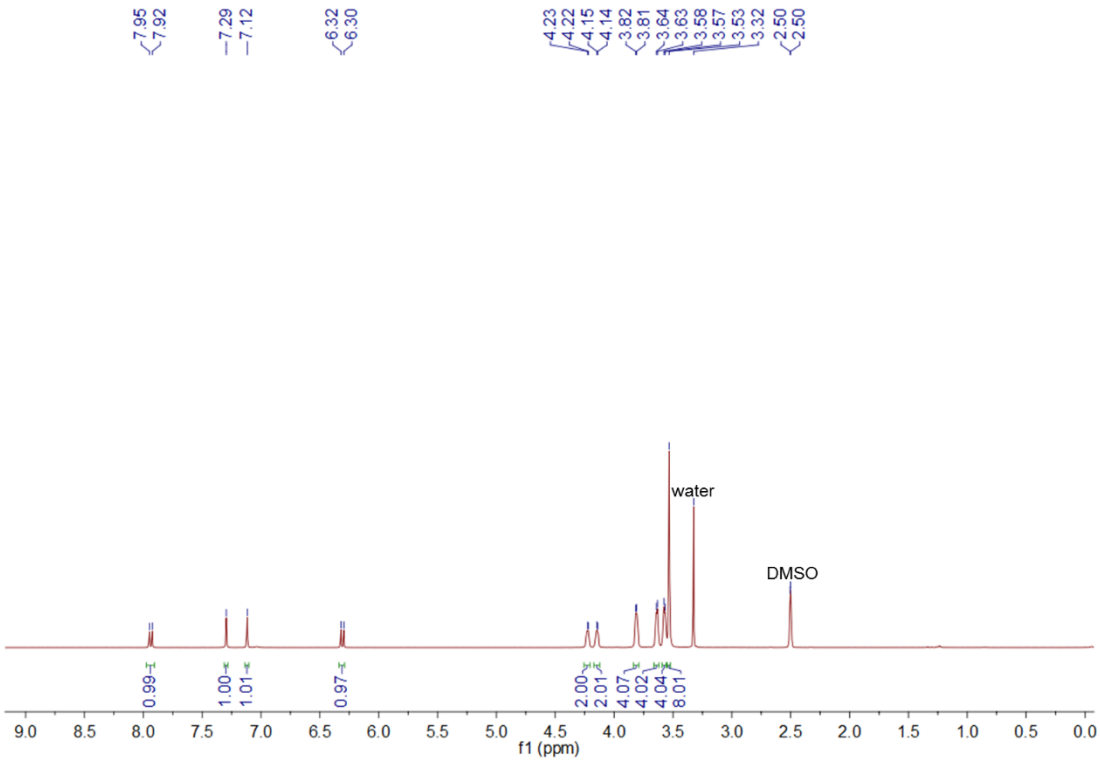


Figure S3. ^{1}H NMR spectrum (400 MHz, CD_3SOCD_3, room temperature) of **1**.

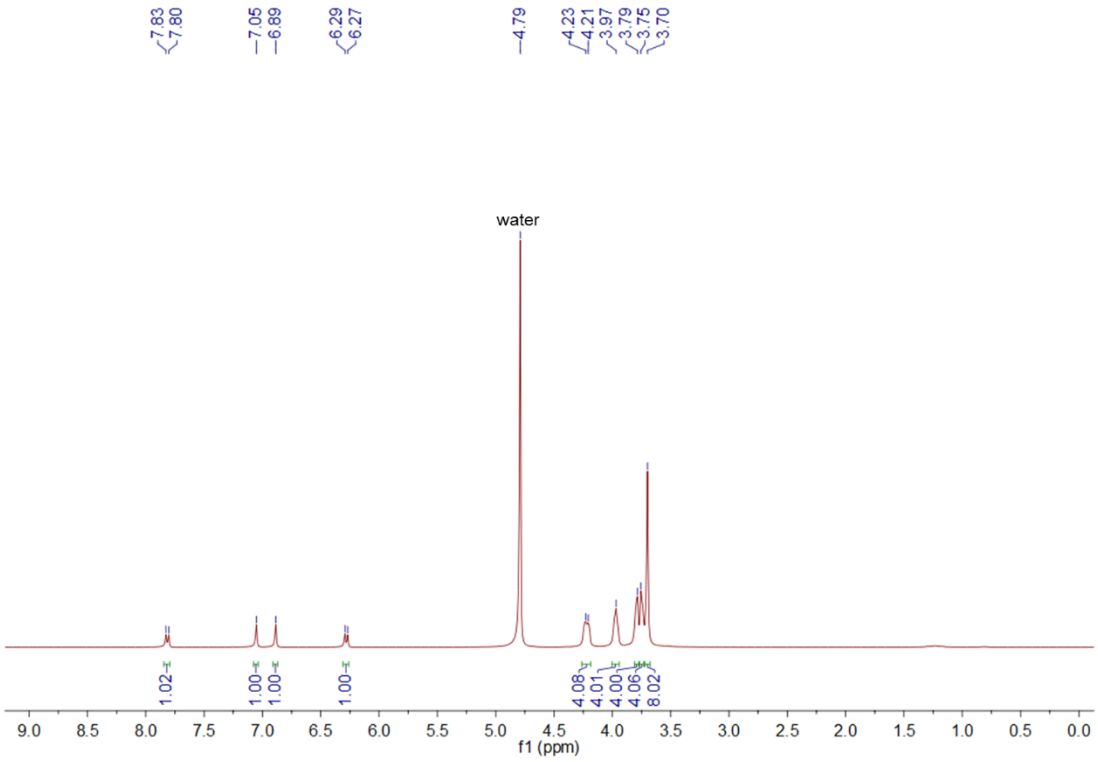


Figure S4. ^{1}H NMR spectrum (400 MHz, D_2O, room temperature) of **1**.

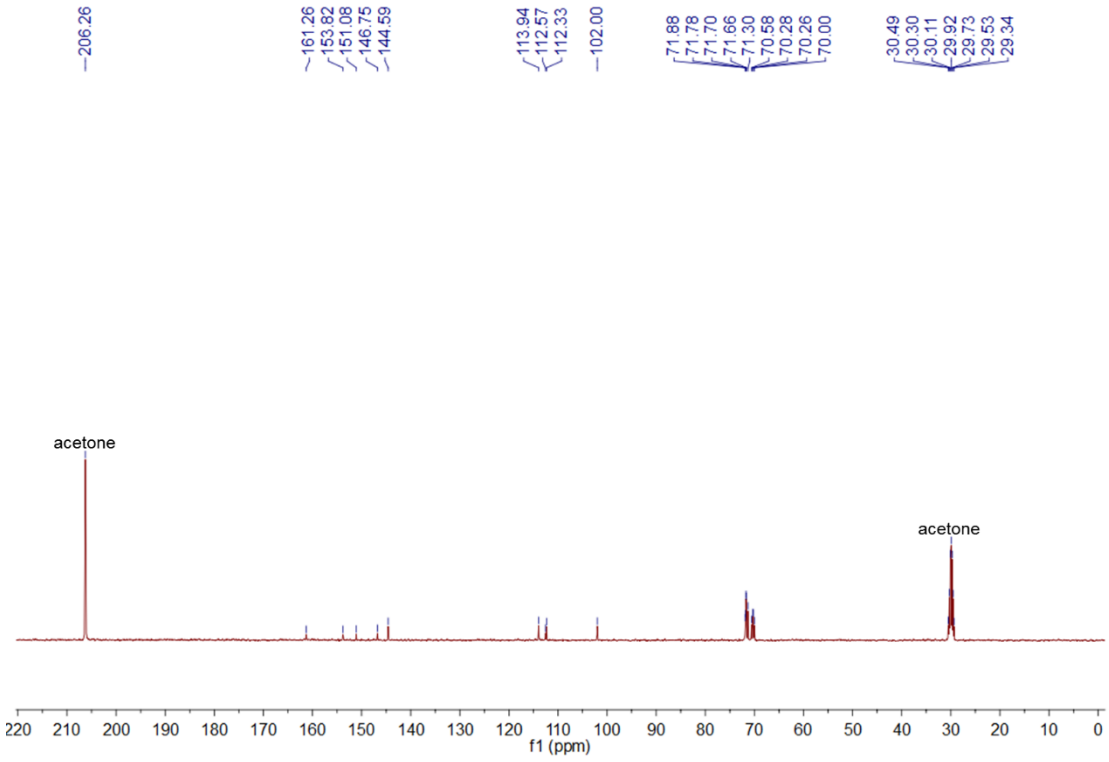


Figure S5. ^{13}C NMR spectrum (125 MHz, CD_3COCD_3, room temperature) of **1**.

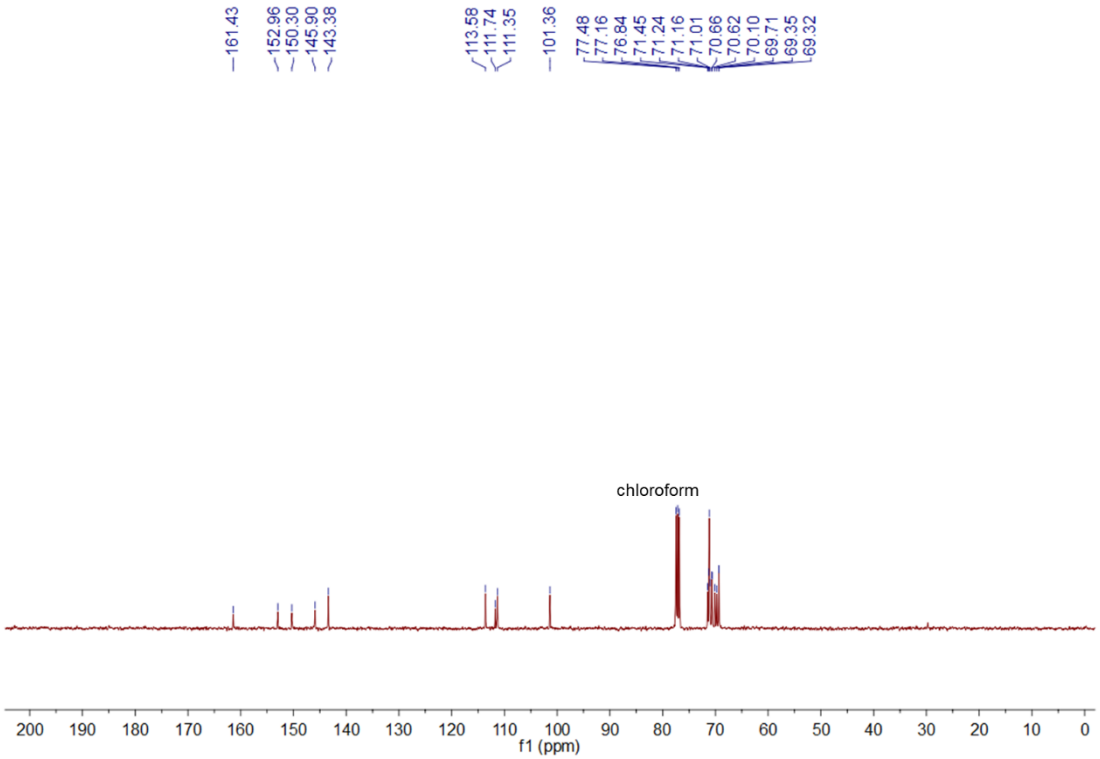


Figure S6. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, room temperature) of **1**.

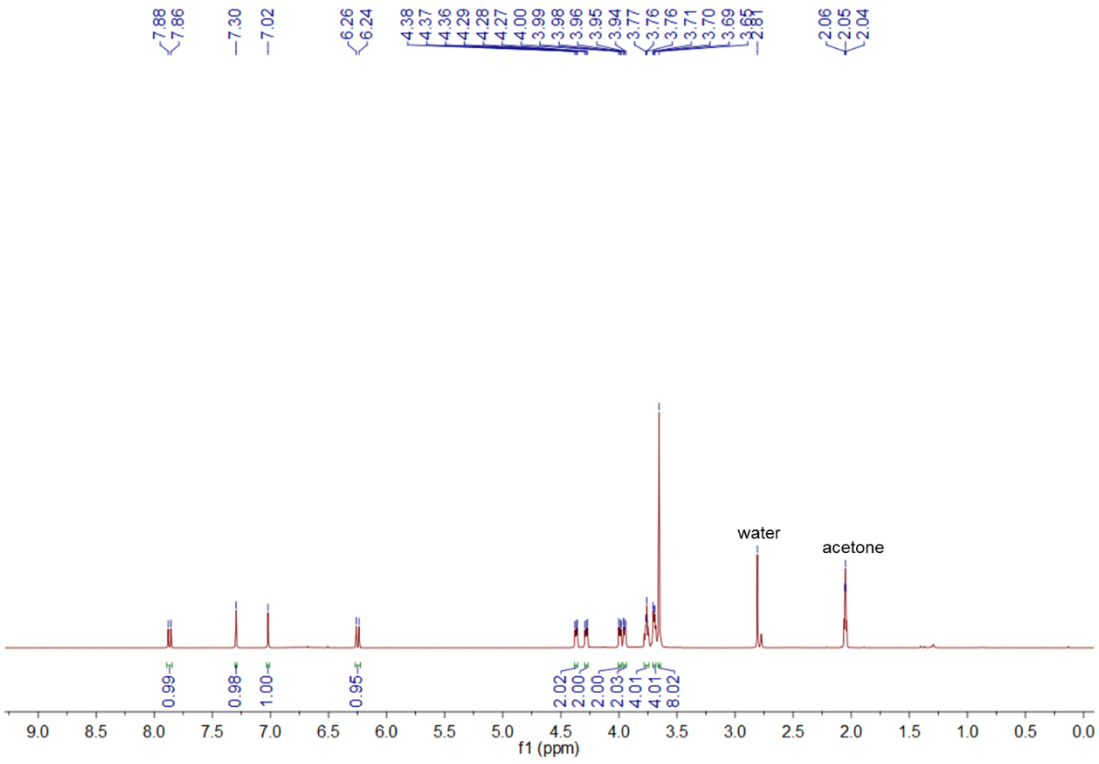


Figure S7. ^{1}H NMR spectrum (400 MHz, CD_3COCD_3, room temperature) of **1**-K^+ complex.

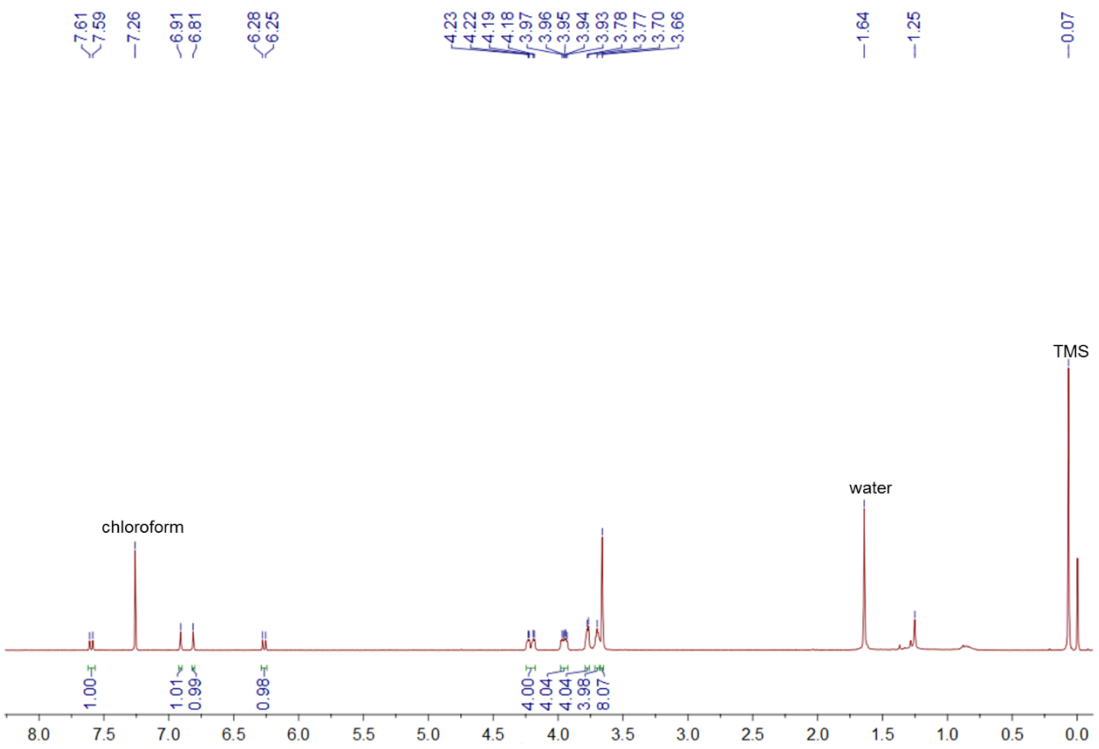


Figure S8. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **1**-K^+ complex.

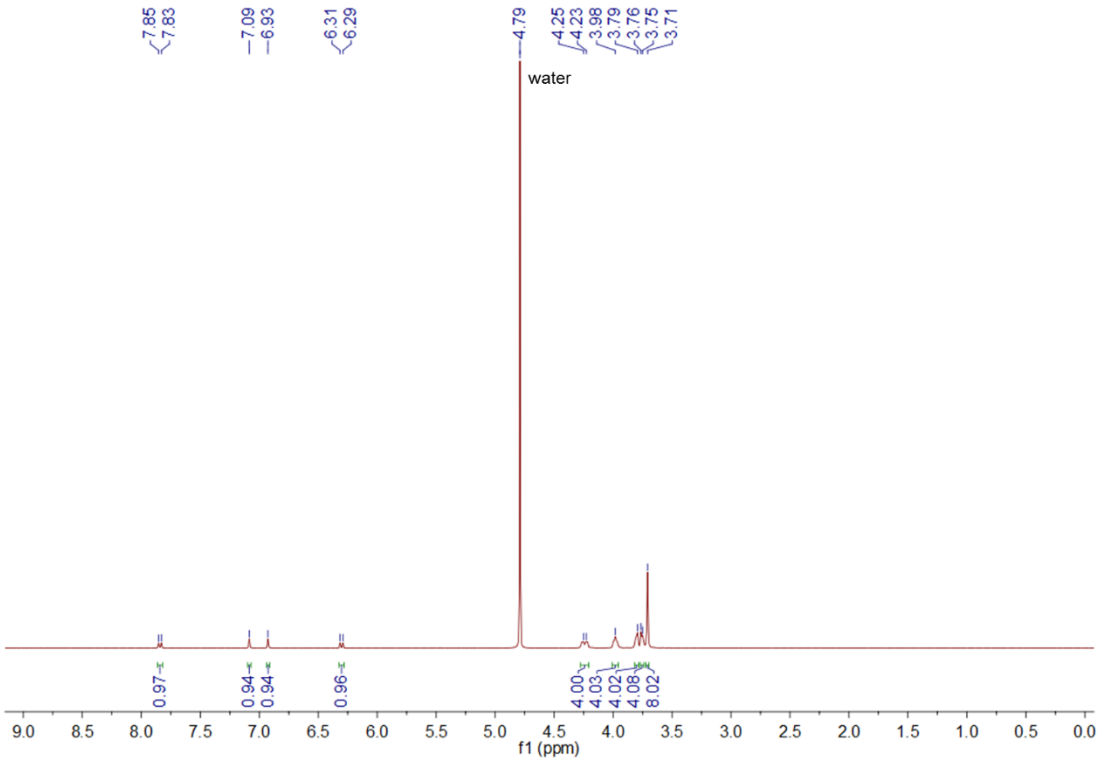


Figure S9. ^{1}H NMR spectrum (400 MHz, D_2O, room temperature) of **1**-K^+ complex.

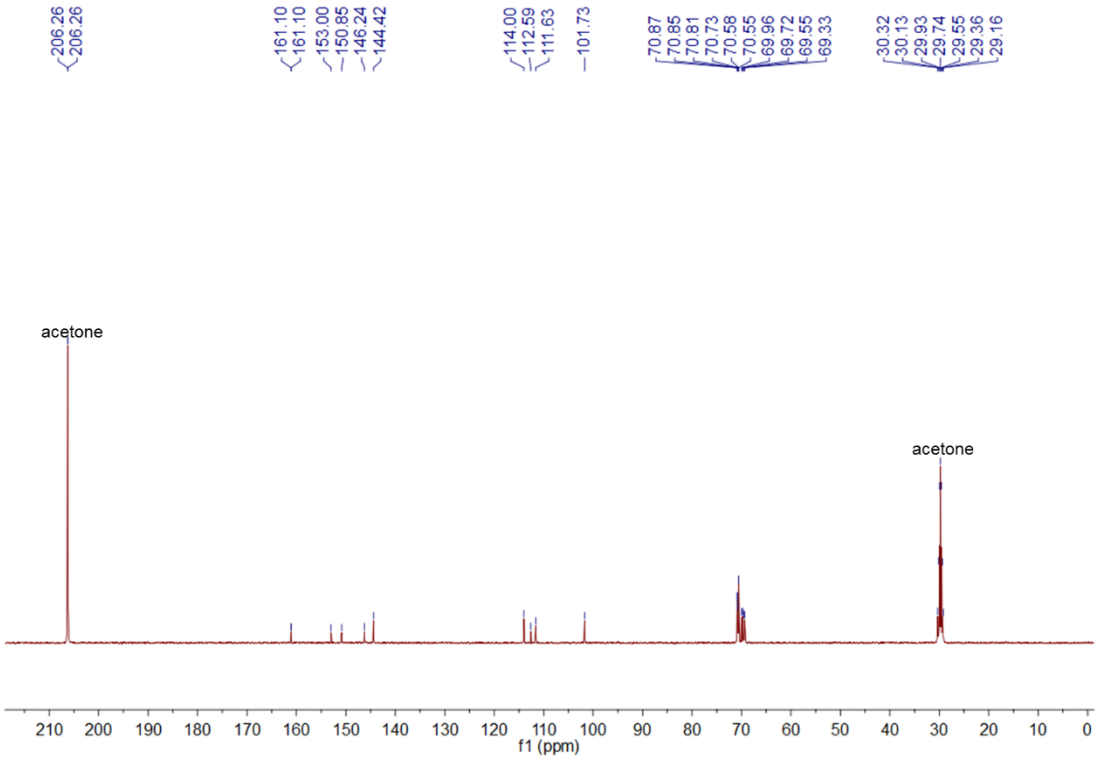


Figure S10. ^{13}C NMR spectrum (125 MHz, CD_3COCD_3, room temperature) of **1**-K^+ complex.

*3. Comparison of ^1H NMR spectra of **1** and **1**-K^+ complex*

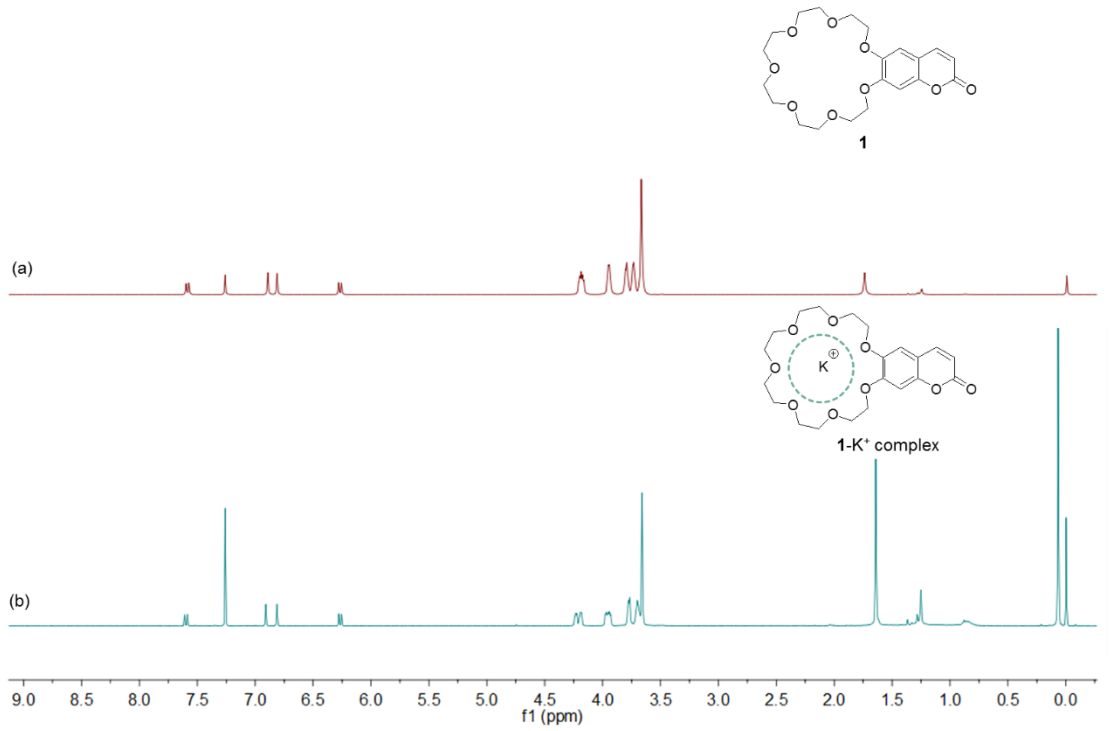


Figure S11. ^1H NMR spectra (400 MHz, $CDCl_3$, room temperature) of (a) **1**, (b) **1**-K^+ complex.

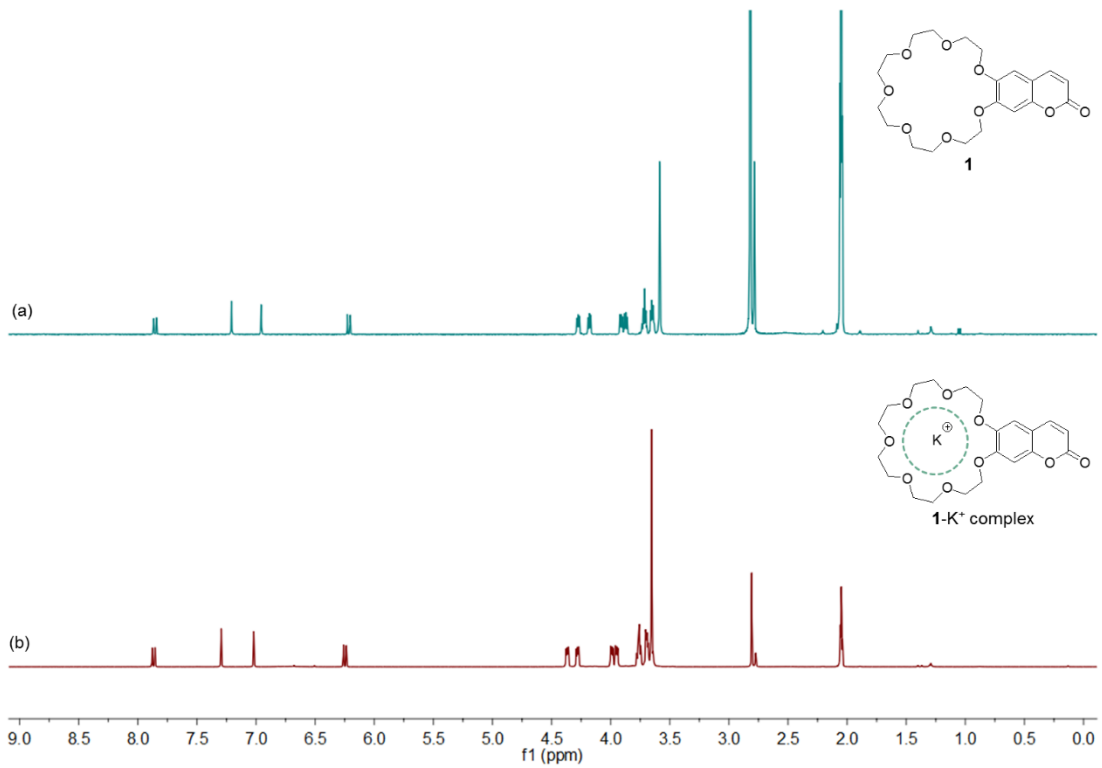


Figure S12. ^{1}H NMR spectra (400 MHz, CD_3COCD_3, room temperature) of (a) **1**, (b) **1**-K^+ complex.

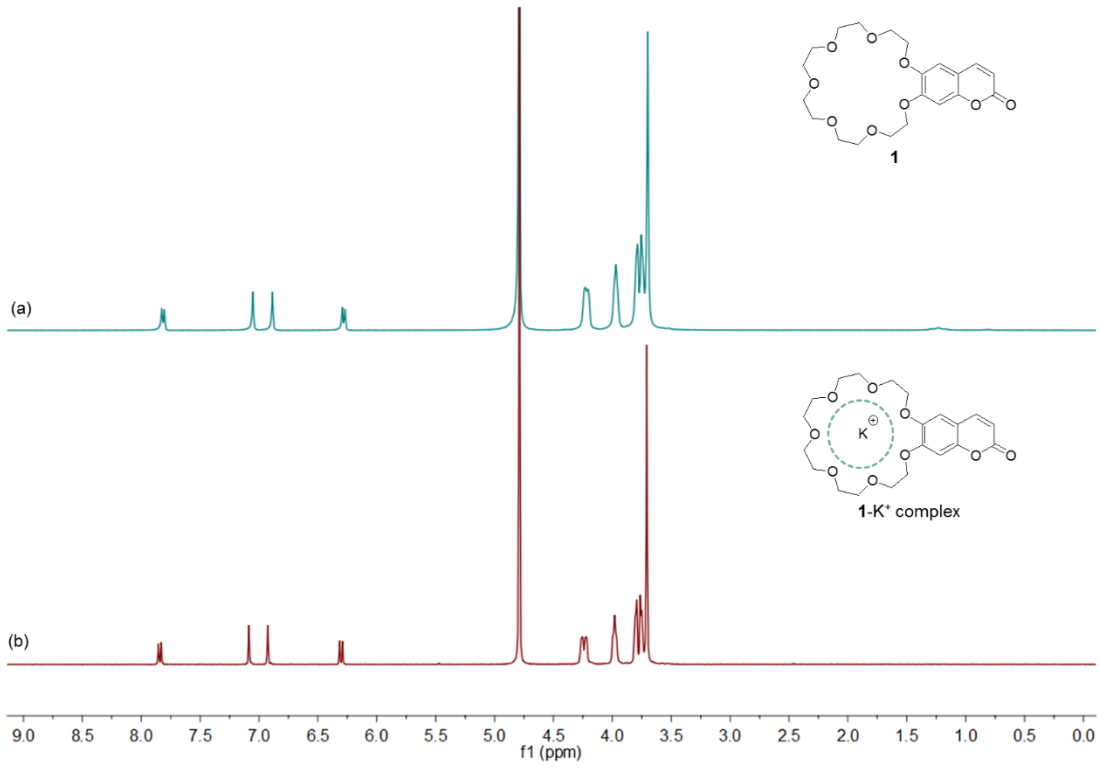


Figure S13. ^{1}H NMR spectra (400 MHz, D_2O, room temperature) of (a) **1**, (b) **1**-K^+ complex.

*4. Comparison of ^{13}C NMR spectra of **1** and **1**-K^+ complex*

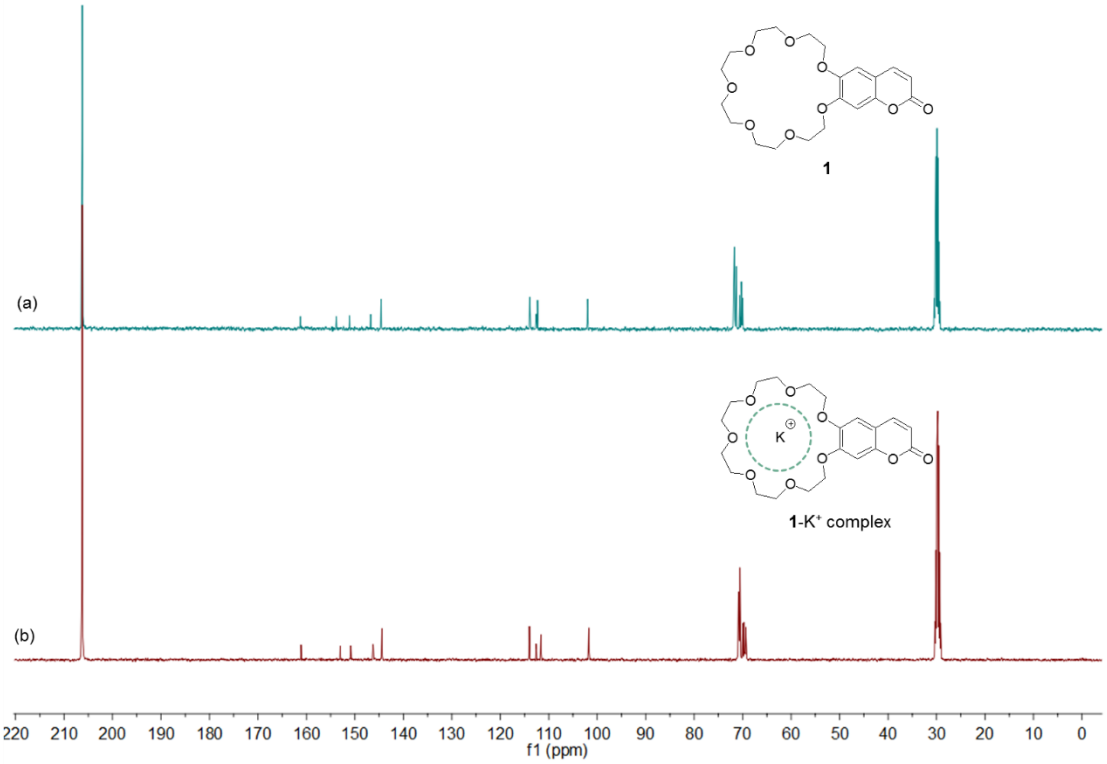
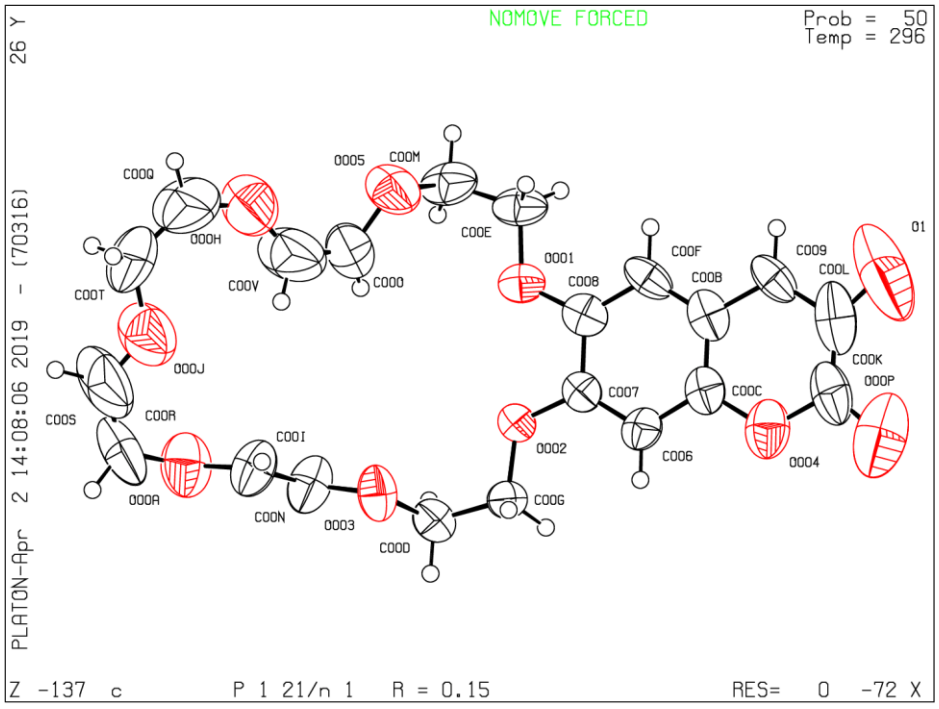
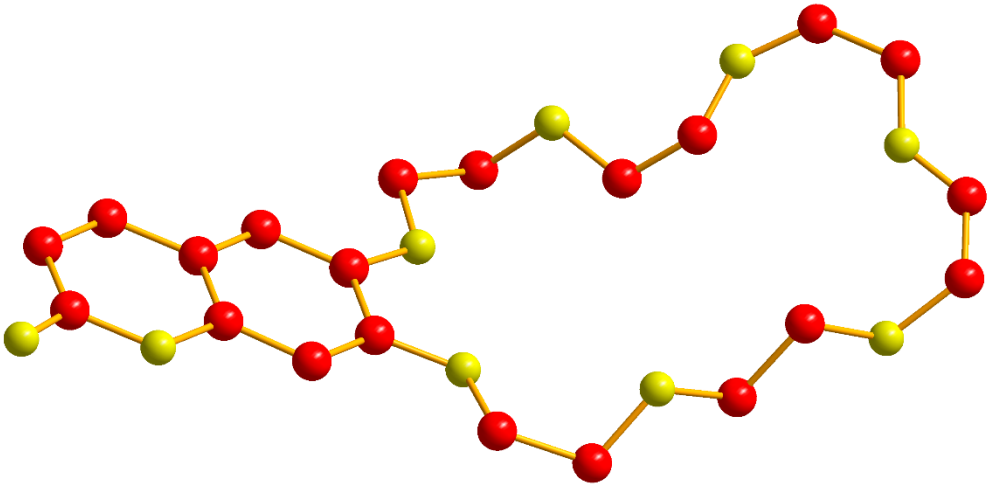


Figure S14. ^{13}C NMR spectra (100 MHz, CD_3COCD_3, room temperature) of (a) **1**, (b) **1**-K^+ complex.

*5. X-ray analysis data of **1***



X-ray crystallographic data: cube, green, $C_{21}H_{20}O_{10}$, *FW* 432.37, triclinic, space group *P* 1 21/n 1, *a* = 15.411 (4), *b* = 4.6612 (13), *c* = 29.404 (8) Å, α = 90.00°, β = 91.133 (8) Å^3, γ = 90.00°, *Z* = 4, *Dc* = 1.360 g cm $^{-3}$, *T* = 296 K, μ = 0.110 mm^{-1}, 17665 measured reflections, 2160 independent reflections, 280 parameters, 4 restraints, *F*(000) = 904, R_1 = 0.2032, wR_2 = 0.4487 (all data), R_1 = 0.1515, wR_2 = 0.4194 [I > 2σ(I)], max. residual density 0.567 e·Å^{-3}, and goodness-of-fit (F^2) = 1.555.



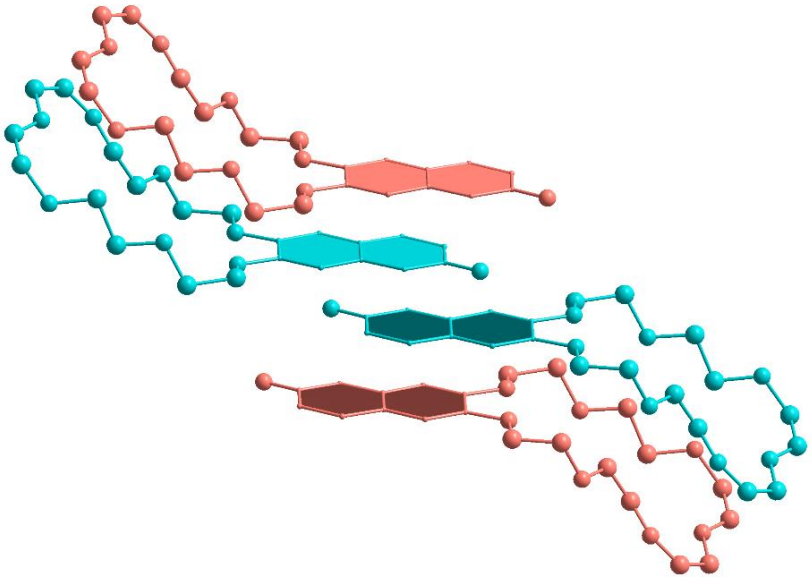
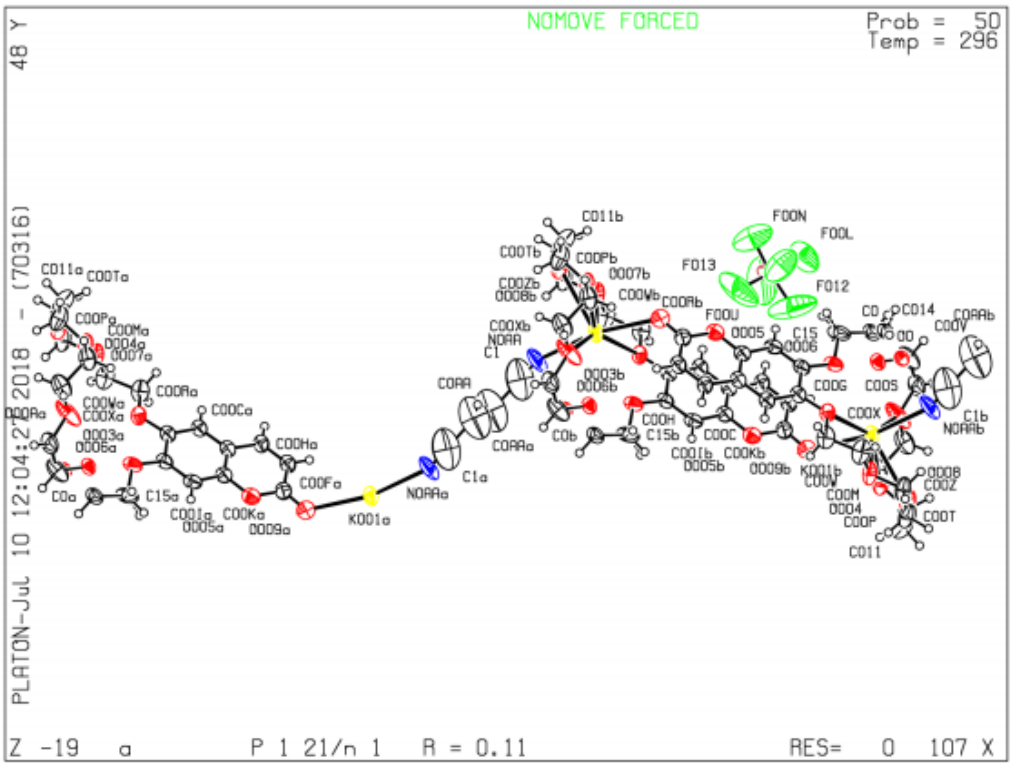


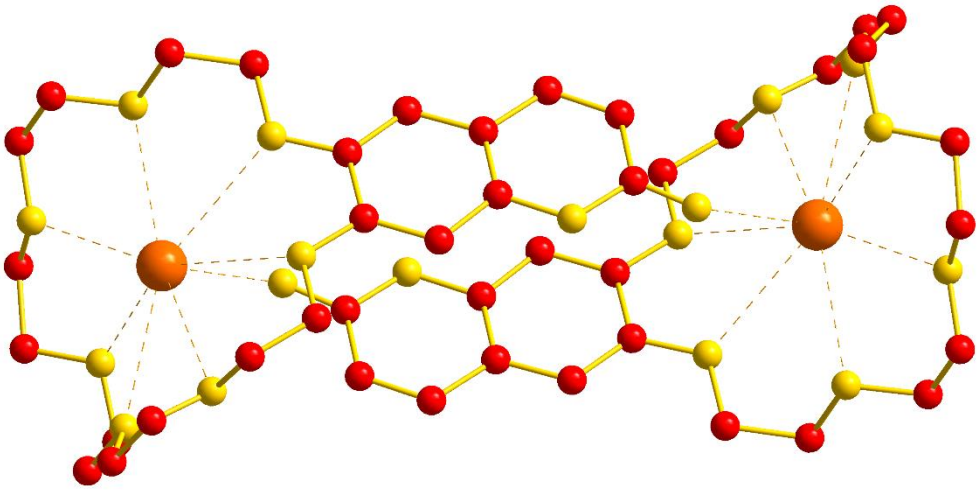
Figure S15. Ball-stick views of the X-ray structure of **1** (top) and the packing structure of **1** (bottom).

*6. X-ray analysis data of **1**-K^+ complex*



X-ray crystallographic data: cube, green, $C_{23}H_{24.5}F_6KNO_9P$, *FW* 643, triclinic, space group *P* 1 21/n 1, *a* = 13.5206 (11), *b* = 14.1906 (12), *c* = 15.6156 (16) Å, *α* = 90.00°, *β* = 113.509 (3) $Å^3$, *γ* = 90.00°, *Z* = 4, *Dc* = 1.555 g cm^{-3}, *T* =

296 K, μ = 0.344 mm^{-1}, 24349 measured reflections, 4700 independent reflections, 390 parameters, 379 restraints, F(000) = 1318, R_1 = 0.1373, wR_2 = 0.3214 (all data), R_1 = 0.1110, wR_2 = 0.2996 [I > 2σ(I)], max. residual density 0.993 e·Å^{-3}, and goodness-of-fit (F^2) = 1.032.



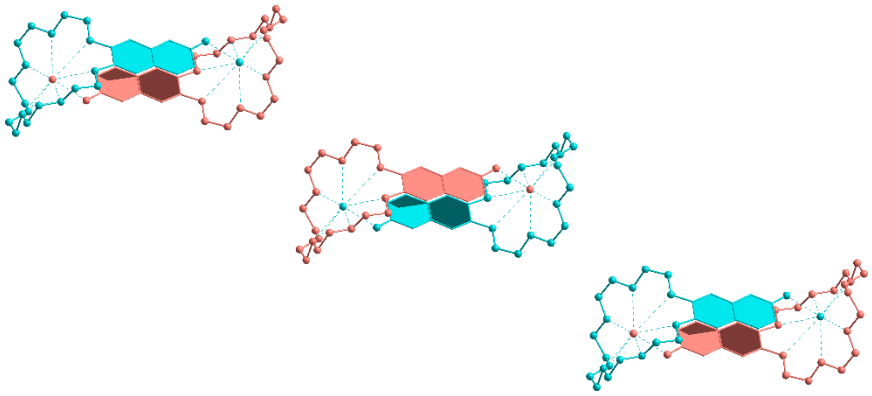


Figure S16. Ball-stick views of the X-ray structure of **1**-K^+ complex (top) and the packing structure of **1**-K^+ complex (bottom).

*7. Solubility of **1** and **1**-K^+ complex in different solvents*

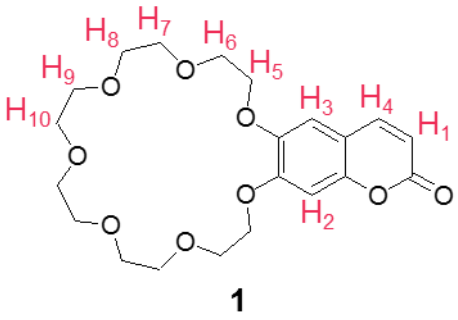
Solubility experiment: Excess of **1** or **1**-K^+ complex was added into the flask which contained 2 mL pure solvent. The solution was stirred at room temperature for one day. The turbid solution was filtered and the solvent was removed in vacuum and the mount of dry precipitate was obtained.

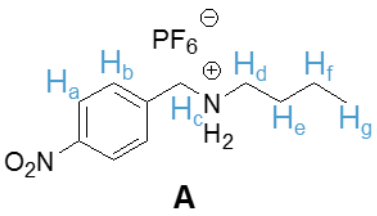
Temperature: 25 °C

solvent	water	acetonitrile	acetone	chloroform	methanol
1 (g/mL)	0.5502	0.0950	0.1009	1.1050	1.9050
1-K^+ complex (g/mL)	0.0021	0.3097	0.1245	0.0027	0.0052

Table S1. Solubility of **1** and **1**-K^+ complex in different solvents. "g/mL" means the mount of **1** or **1**-K^+ complex dissolved in 1 mL solvent.

*8. ^1H NMR spectra of an equimolar acetone solution of **1** and **A***





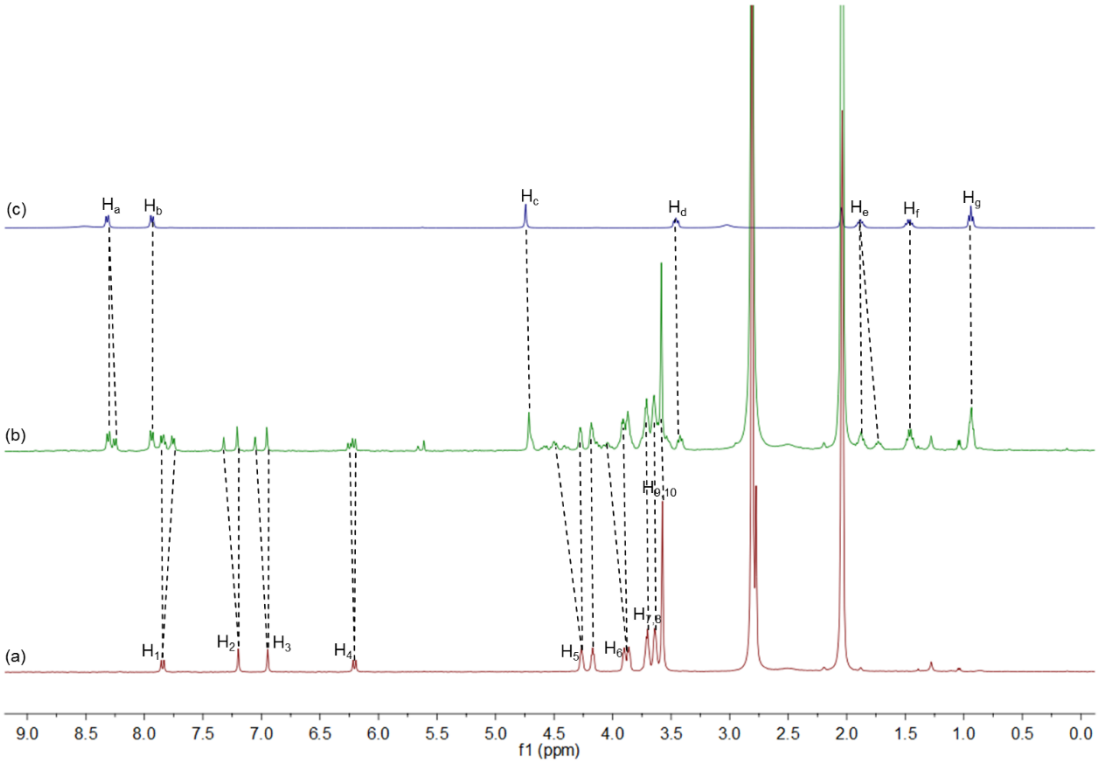


Figure S17. ^{1}H NMR spectra (400 MHz, CD_3COCD_3, room temperature) of (a) 2.00 mM **1**, (b) 2.00 mM **1** and **A**, (c) 2.00 mM **A**.

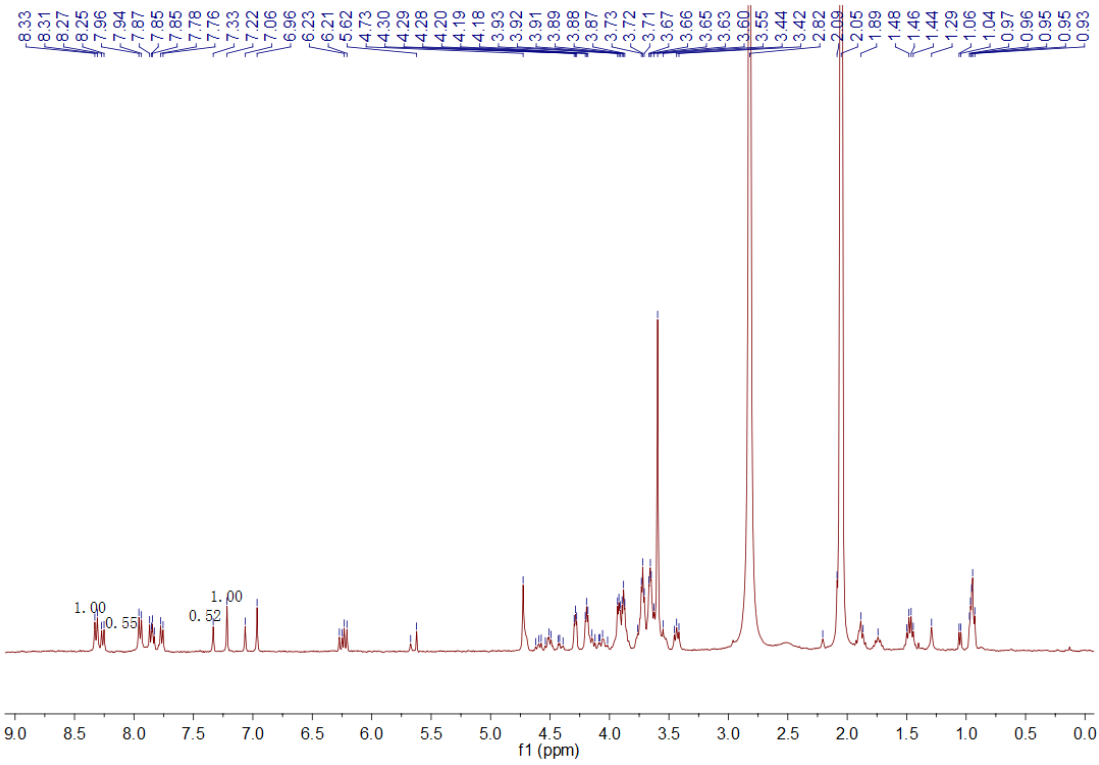


Figure S18. ^{1}H NMR spectra (400 MHz, CD_3COCD_3, room temperature) of 2.00 mM **1** and **A**. The association constant K_a value calculated from integrations of complexed and uncomplexed peaks of H_2 of **1**

is [(0.52/1.52) × 1.00 × 10^{-3}]/[(1 - 0.52/1.52) × 1.00 × 10^{-3}]^2 = 790 M^{-1}. The association constant K_a value calculated from integrations of complexed and uncomplexed peaks of H_a of **A** is [(0.55/1.55) × 1.00 × 10^{-3}]/[(1 - 0.55/1.55) × 1.00 × 10^{-3}]^2 = 853 M^{-1}. Therefore K_a = (790 + 853)/2 = 822 (±32) M^{-1}.

*9. ^1H NMR spectra of an equimolar acetone solution of **1** and **B***

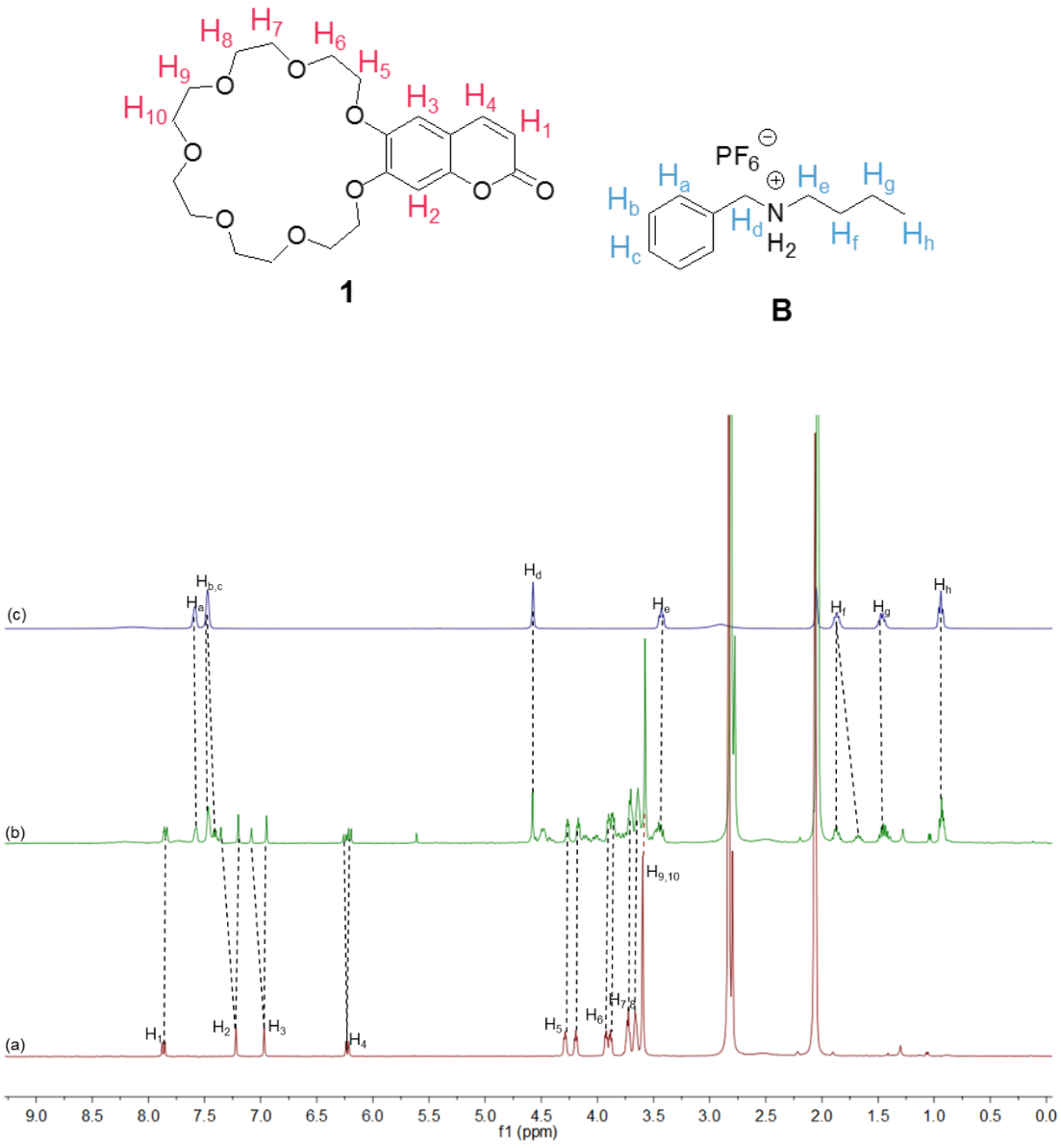


Figure S19. ^1H NMR spectra (400 MHz, CD_3COCD_3, room temperature) of (a) 2.00 mM **1**, (b) 2.00 mM **1** and **B**, (c) 2.00 mM **B**.

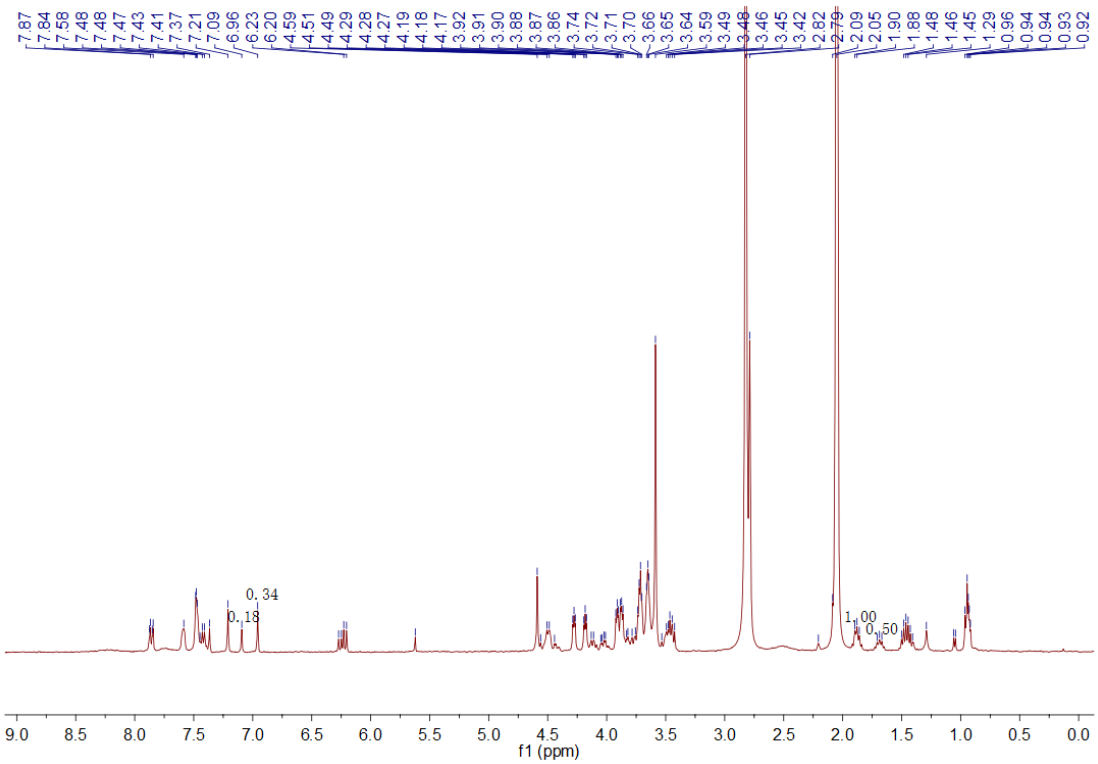
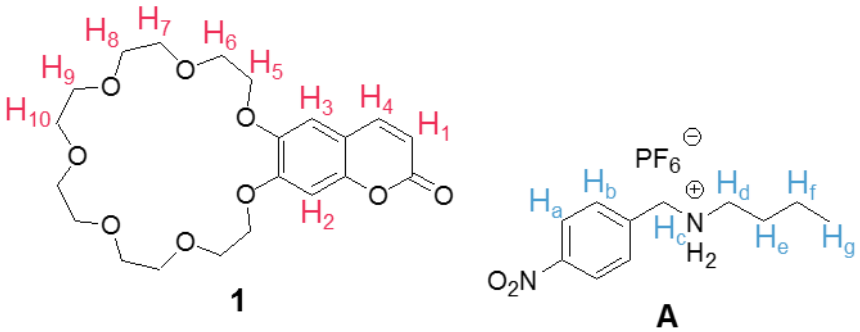


Figure S20. ^{1}H NMR spectra (400 MHz, CD_3COCD_3, room temperature) of 2.00 mM **1** and **B**. The association constant K_a value calculated from integrations of complexed and uncomplexed peaks of H_f of **B** is $[(0.50/1.50) \times 1.00 \times 10^{-3}]/[(1 - 0.50/1.50) \times 1.00 \times 10^{-3}]^2 = 750$ M^{-1}. The association constant K_a value calculated from integrations of complexed and uncomplexed peaks of H_3 of **1** is $[(0.18/0.52) \times 1.00 \times 10^{-3}]/[(1 - 0.18/0.52) \times 1.00 \times 10^{-3}]^2 = 810$ M^{-1}. Therefore $K_a = (750 + 810)/2 = 780$ ($\pm$30) M^{-1}.

*10. ^{1}H NMR spectrum of an equimolar acetonitrile solution of **1** and **A***



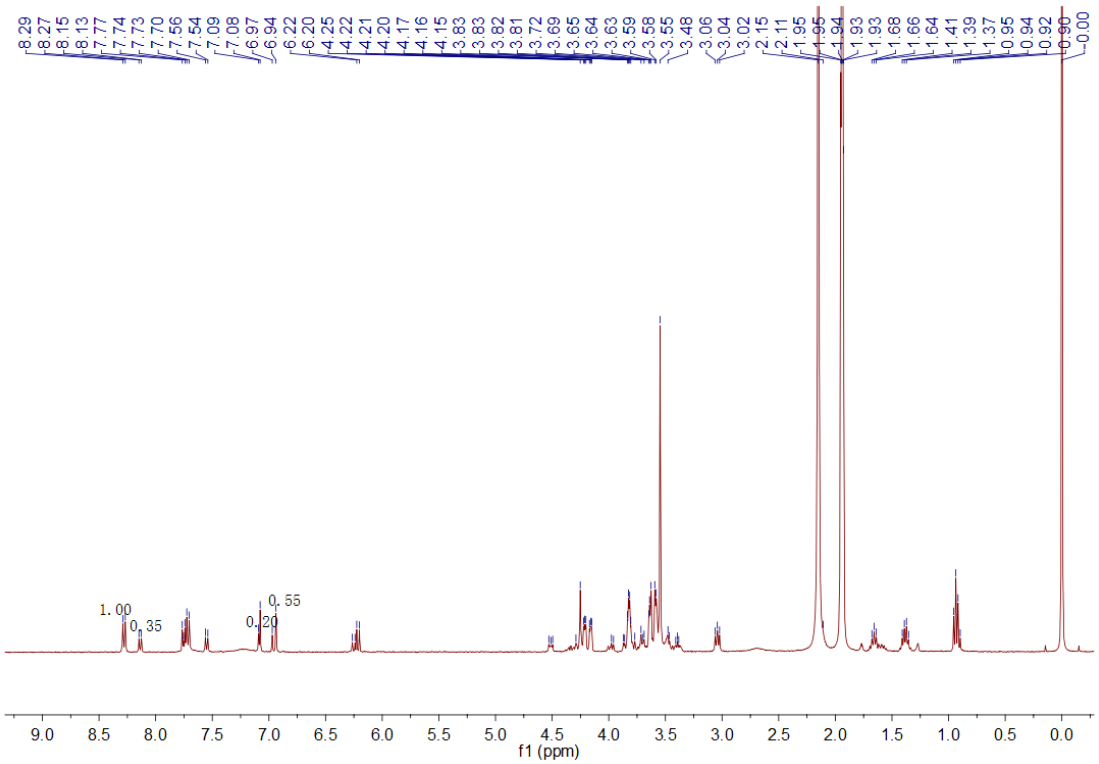
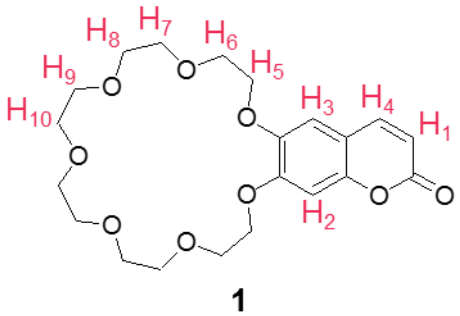
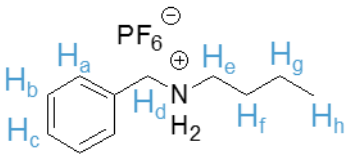


Figure S21. ^{1}H NMR spectra (400 MHz, CD_3CN, room temperature) of 2.00 mM **1** and **A**. The association constant K_a value calculated from integrations of complexed and uncomplexed peaks of H_a of **A** is $[(0.35/1.35) \times 1.00 \times 10^{-3}]/[(1 - 0.35/1.35) \times 1.00 \times 10^{-3}]^2 = 473\ M^{-1}$. The association constant K_a value calculated from integrations of complexed and uncomplexed peaks of H_3 of **1** is $[(0.20/0.75) \times 1.00 \times 10^{-3}]/[(1 - 0.20/0.75) \times 1.00 \times 10^{-3}]^2 = 496\ M^{-1}$. Therefore $K_a = (473 + 496)/2 = 485\ (\pm 12)\ M^{-1}$.

*11. ^{1}H NMR spectrum of an equimolar acetonitrile solution of **1** and **B***



1



B

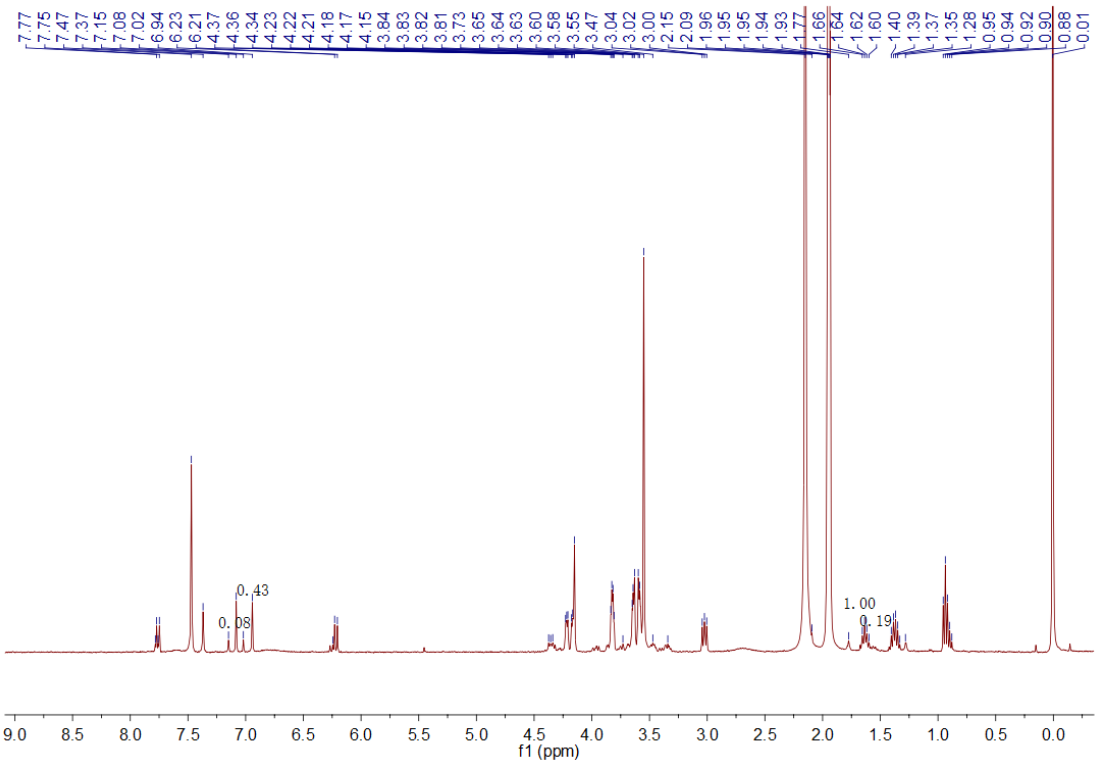
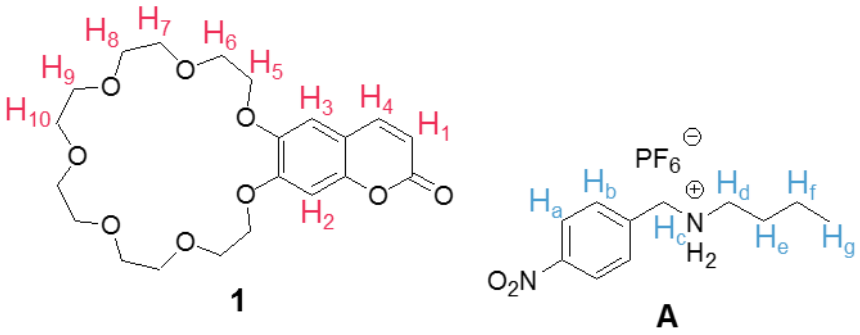


Figure S22. ^{1}H NMR spectra (400 MHz, CD_3CN, room temperature) of 2.00 mM **1** and **B**. The association constant K_a value calculated from integrations of complexed and uncomplexed peaks of H_3 of **1** is [(0.08/0.51) × 1.00 × 10^{-3}]/[(1 - 0.08/0.51) × 1.00 × 10^{-3}]^2 = 221 M^{-1}. The association constant K_a value calculated from integrations of complexed and uncomplexed peaks of H_f of **B** is [(0.19/1.19) × 1.00 × 10^{-3}]/[(1 - 0.19/1.19) × 1.00 × 10^{-3}]^2 = 226 M^{-1}. Therefore K_a = (221 + 226)/2 = 224 (±3) M^{-1}.

*12. ^{1}H NMR spectra of an equimolar methanol solution of **1** and **A***



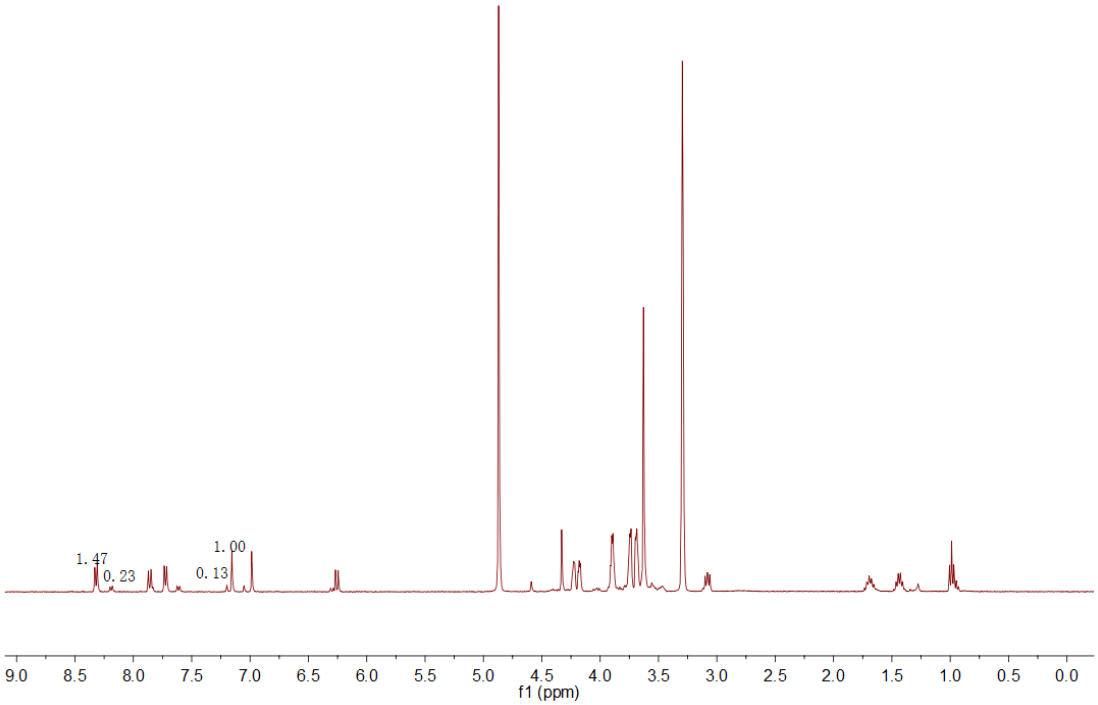


Figure S23. ^{1}H NMR spectra (400 MHz, MeOD, room temperature) of 5.00 mM **1** and **A**. The association constant K_a value calculated from integrations of complexed and uncomplexed peaks of H_a of **A** is $[(0.23/1.70) \times 1.00 \times 10^{-3}]/[(1 - 0.23/1.70) \times 1.00 \times 10^{-3}]^2 = 181\ M^{-1}$. The association constant K_a value calculated from integrations of complexed and uncomplexed peaks of H_2 of **1** is $[(0.13/1.13) \times 1.00 \times 10^{-3}]/[(1 - 0.13/1.13) \times 1.00 \times 10^{-3}]^2 = 147\ M^{-1}$. Therefore $K_a = (147 + 181)/2 = 164\ (\pm 17)\ M^{-1}$.

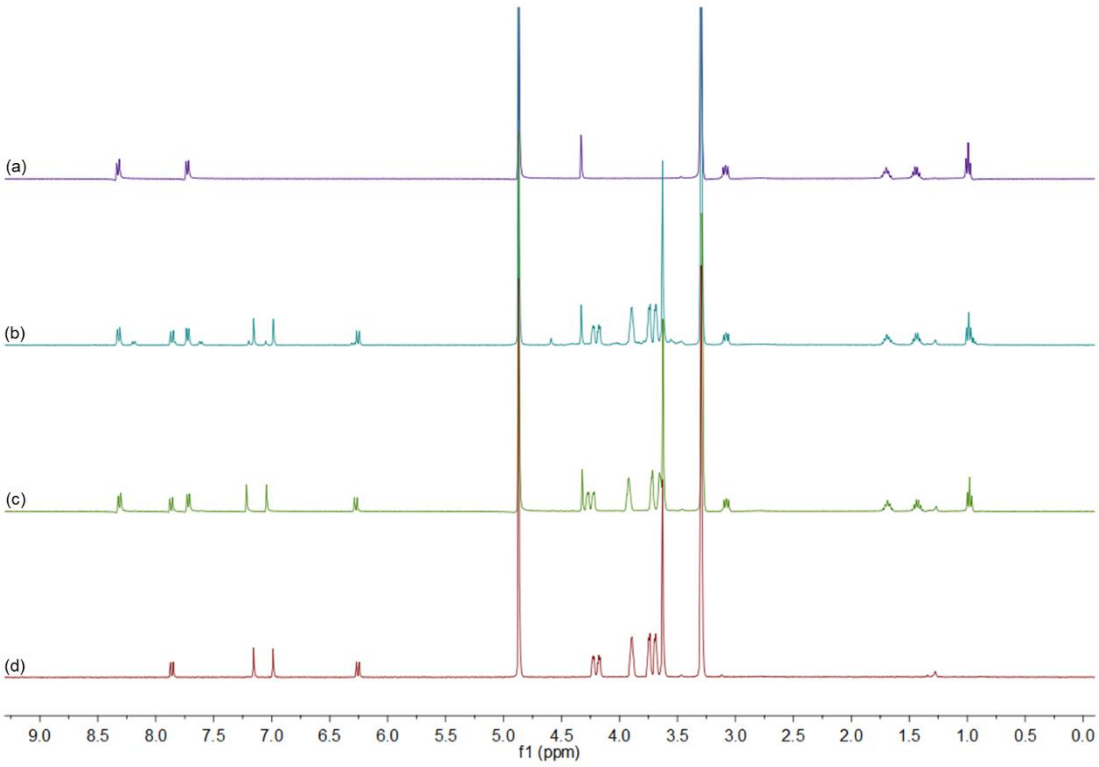
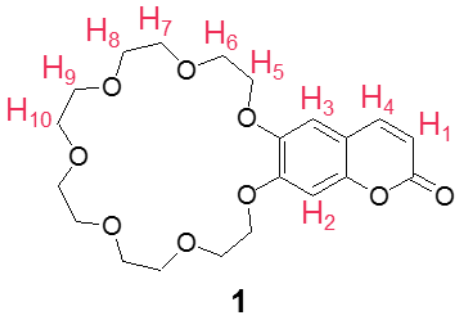
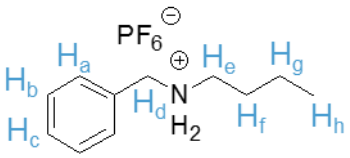


Figure S24. ^{1}H NMR spectra (400 MHz, MeOD, room temperature) of (a) 5 mM **A**, (b) 5 mM **1** and **A**, (c) 5 mM **A**, **1** and KPF_6, (d) 5 mM **1**-K^+ complex.

*13. ^{1}H NMR spectra of an equimolar methanol of **1** and **B***



1



B

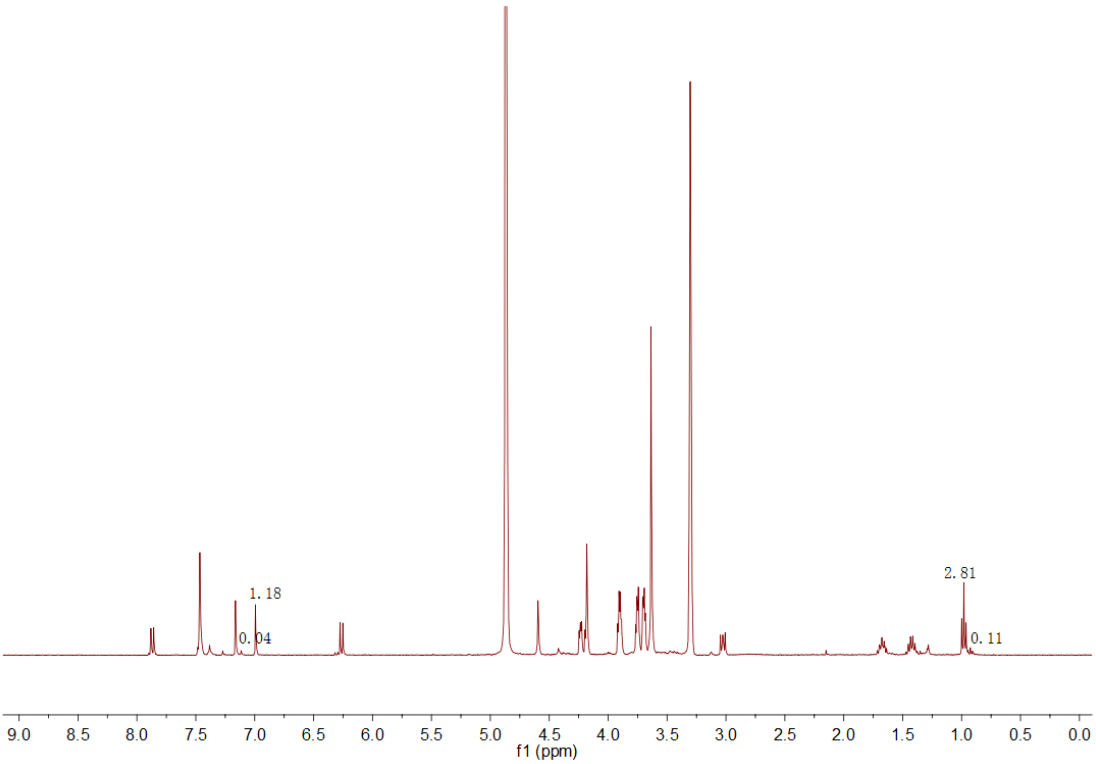


Figure S25. ^{1}H NMR spectra (400 MHz, MeOD, room temperature) of 5.00 mM **1** and **B**. The association constant K_a value calculated from integrations of complexed and uncomplexed peaks of H_3 of **1** is [(0.04/1.22) × 1.00 × 10^{-3}]/[(1 - 0.04/1.22) × 1.00 × 10^{-3}]^2 = 35 M^{-1}. The association constant K_a value calculated from integrations of complexed and uncomplexed peaks of H_h of **B** is [(0.11/2.92) × 1.00 × 10^{-3}]/[(1 - 0.11/2.92) × 1.00 × 10^{-3}]^2 = 41 M^{-1}. Therefore K_a = (35 + 41)/2 = 38 (±3) M^{-1} .

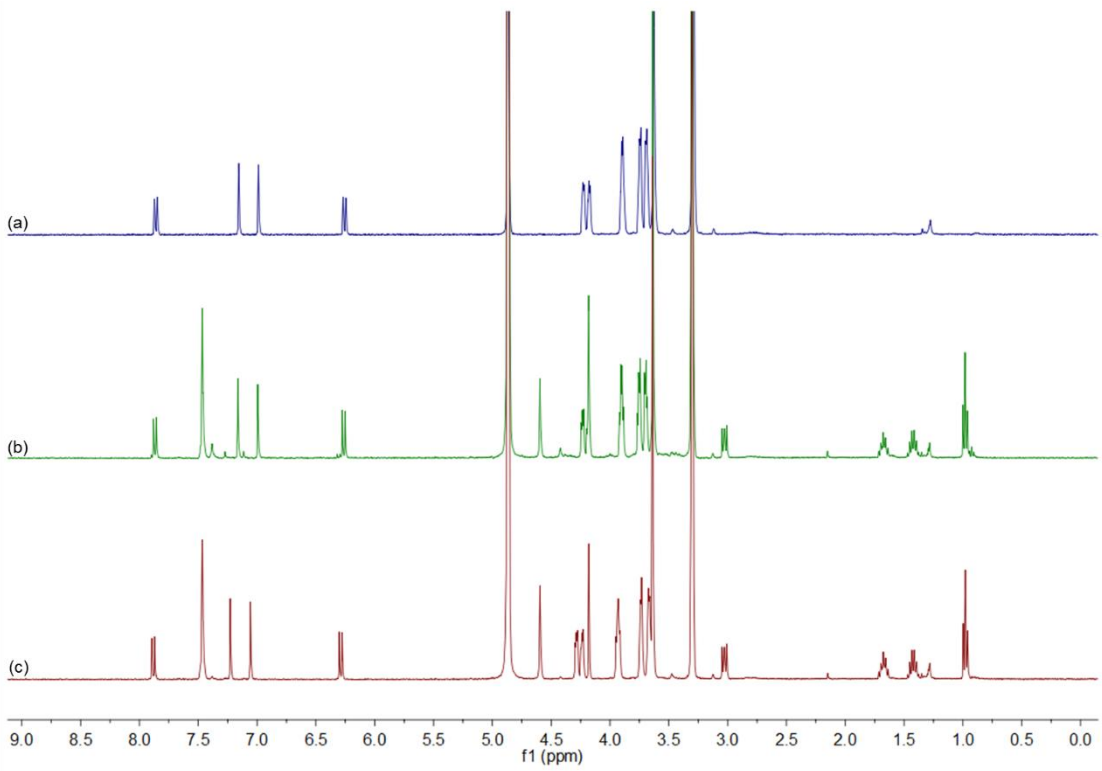


Figure S26. ^{1}H NMR spectra (400 MHz, MeOD, room temperature) of (a) 5 mM **1** and **B**, (b) 5 mM **1** and **B**, (c) 5 mM **1**, **B** and KPF_6.

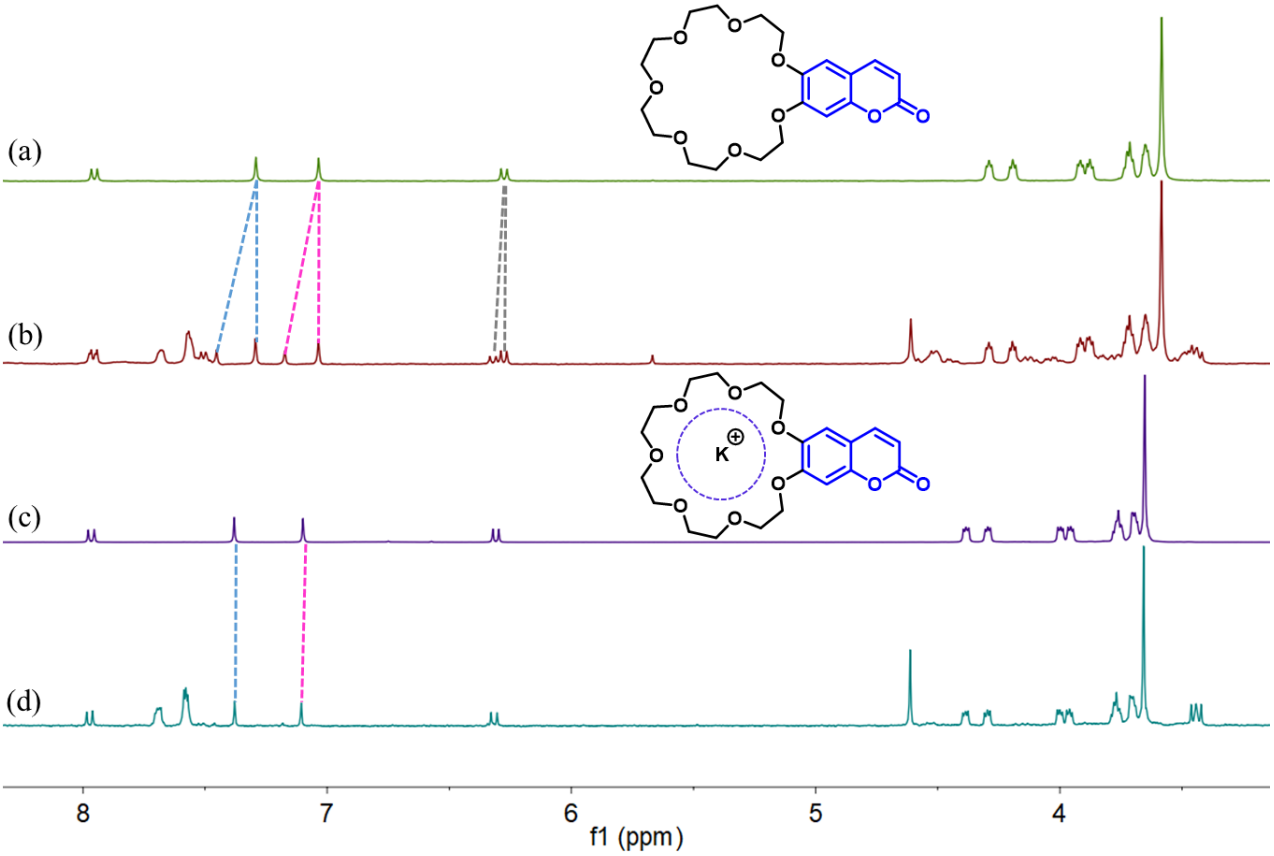
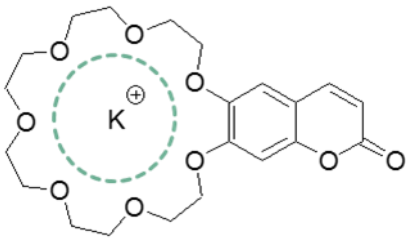
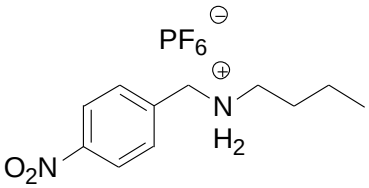


Figure S27. Partial 1H NMR spectra (400 MHz, acetone-d_6, room temperature) of (a) **1**, (b) **1** and **B**, (c) **1**-K^+ complex, and (d) **1**-K^+ complex and **B**. The concentrations for each monomer and guest are 2 mM.

14. *^{1}H NMR spectra of an equimolar acetone solution of **1**-K^+ complex and **A***



1-K^+ complex



A

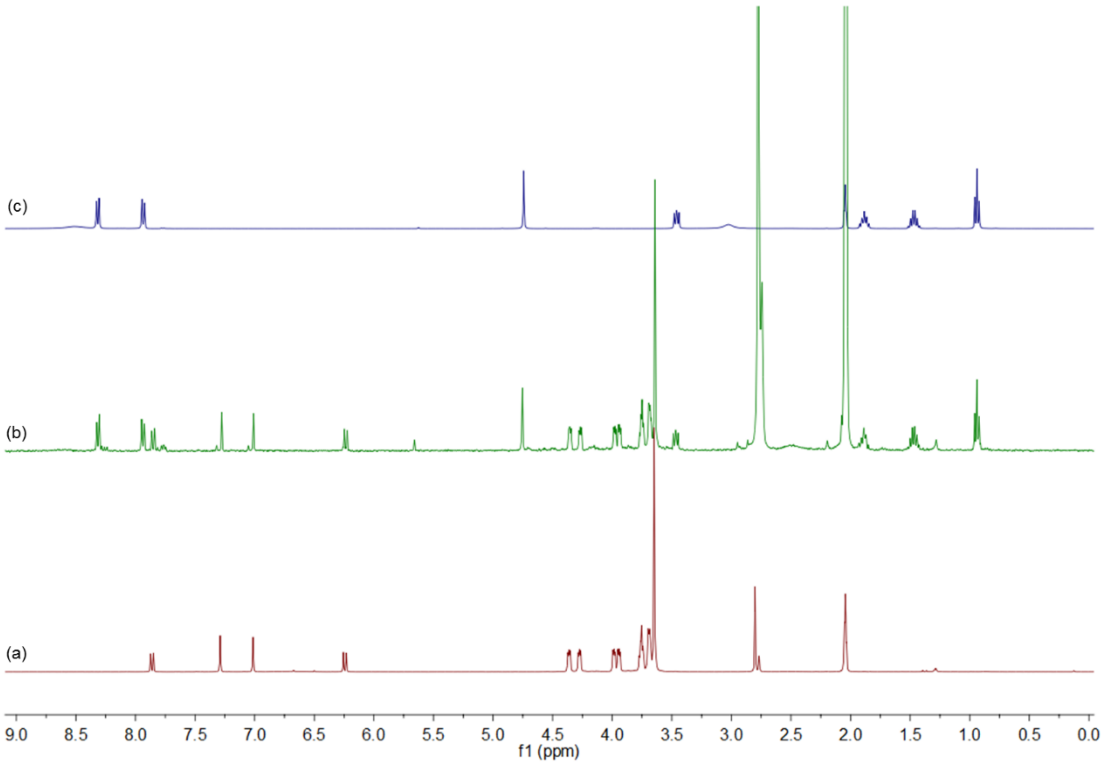


Figure S28. ^{1}H NMR spectra (400 MHz, CD_3COCD_3, room temperature) of (a) 2.00 mM **1**-K^+ complex, (b) 2.00 mM **1**-K^+ complex and **A**, (c) 2.00 mM **A**.

*15. ^{1}H NMR spectra of an equimolar acetone solution of **1**-K^+ complex and **B***

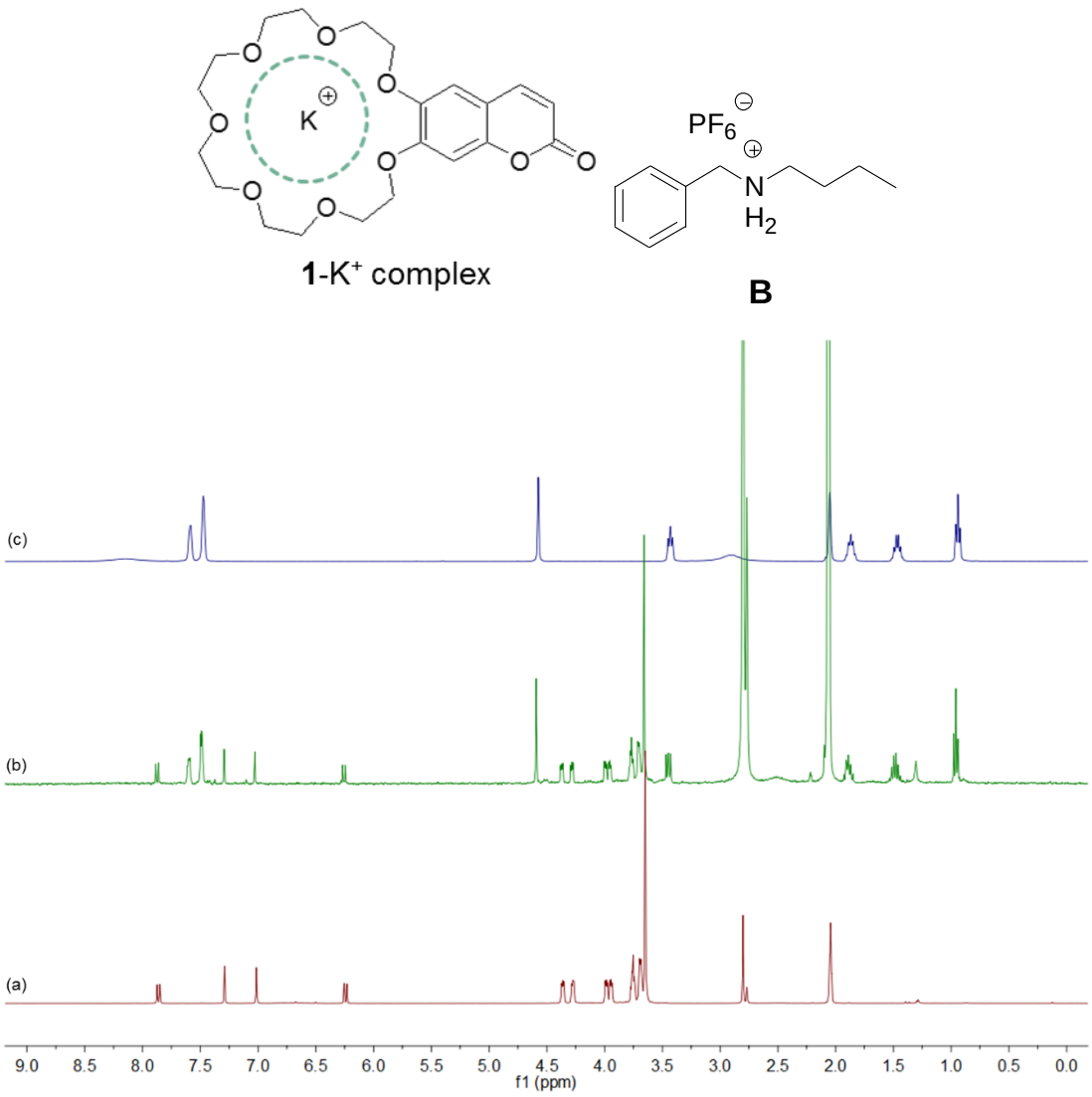


Figure S29. ^{1}H NMR spectra (400 MHz, CD_3COCD_3, room temperature) of (a) 2.00 mM **1**-K^+ complex, (b) 2.00 mM **1**-K^+ complex and **B**, (c) 2.00 mM **B**.

*16. Absorption and emission spectra of **1**.*

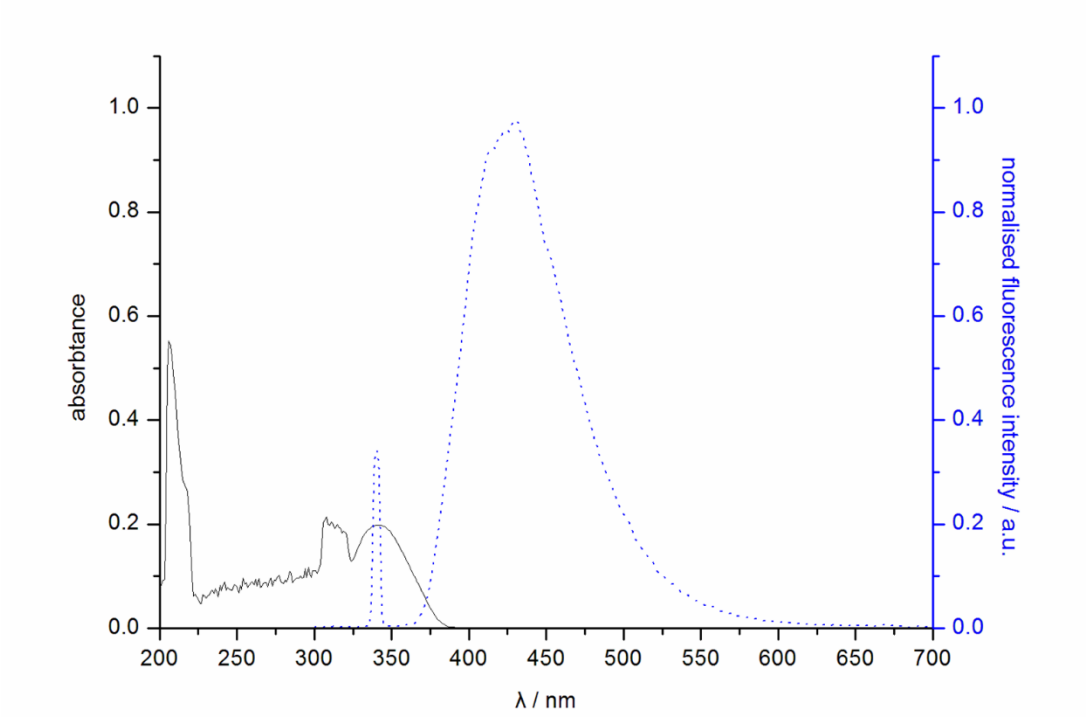


Figure S30. Absorption (—) and emission (---) spectra of **1** in acetone (*c* = 0.02 mM, bandwidth = 1 nm). Raman and Rayleigh peaks have not been removed.

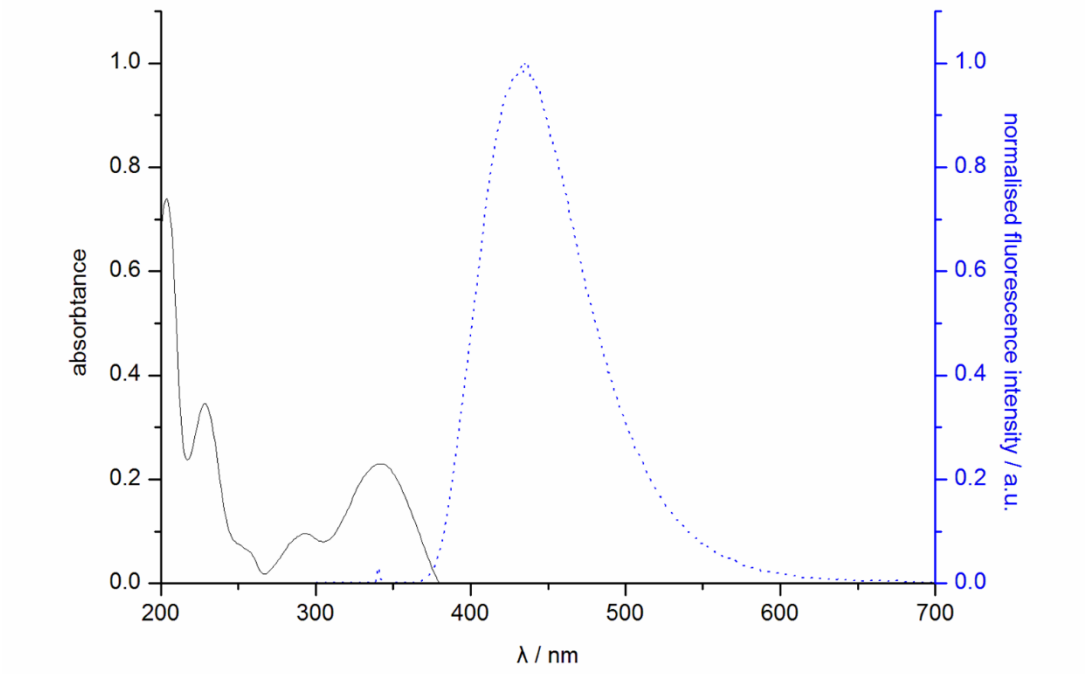


Figure S31. Absorption (—) and emission (---) spectra of **1** in water (*c* = 0.02 mM, bandwidth = 1 nm). Raman and Rayleigh peaks have not been removed.

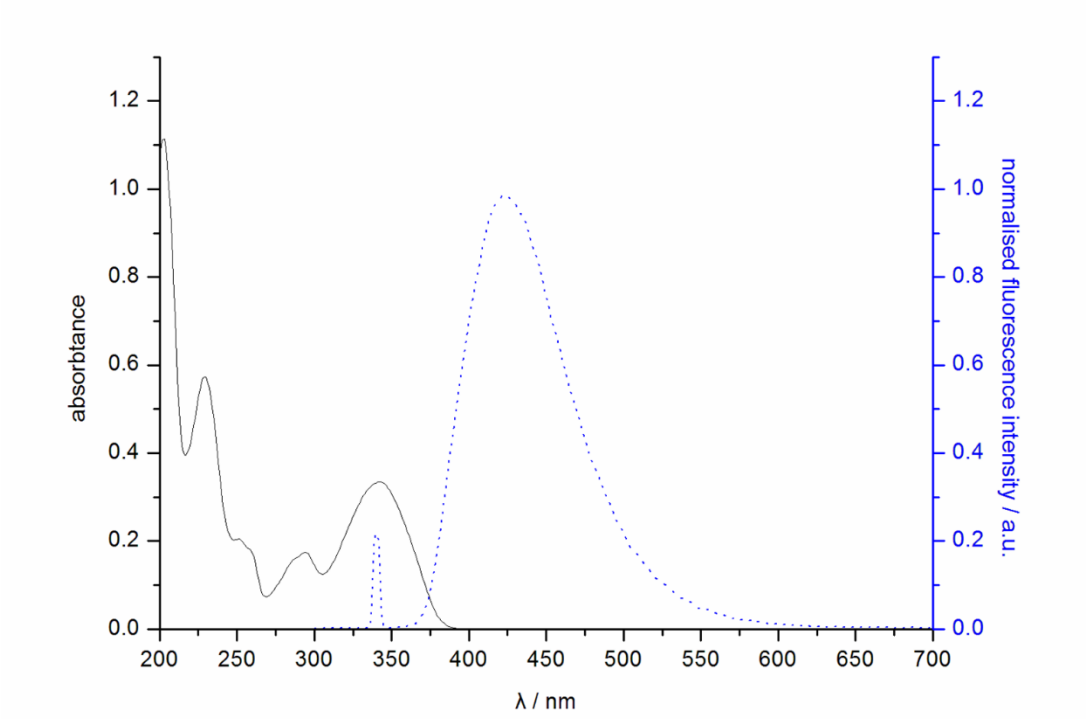


Figure S32. Absorption (—) and emission (---) spectra of **1** in acetonitrile (c = 0.02 mM, bandwidth = 1 nm). Raman and Rayleigh peaks have not been removed.

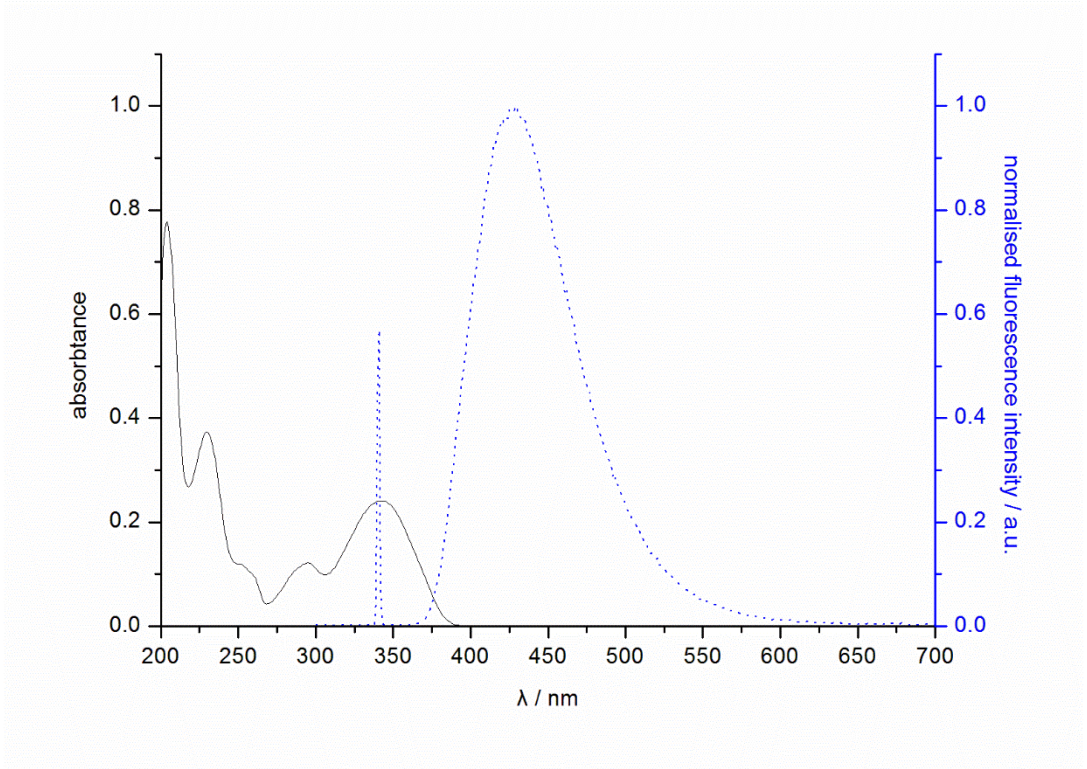


Figure S33. Absorption (─) and emission (---) spectra of **1** in methanol (*c* = 0.02 mM, bandwidth = 1 nm). Raman and Rayleigh peaks have not been removed.

*17. Absorption and emission spectra of **1**-K^+ complex.*

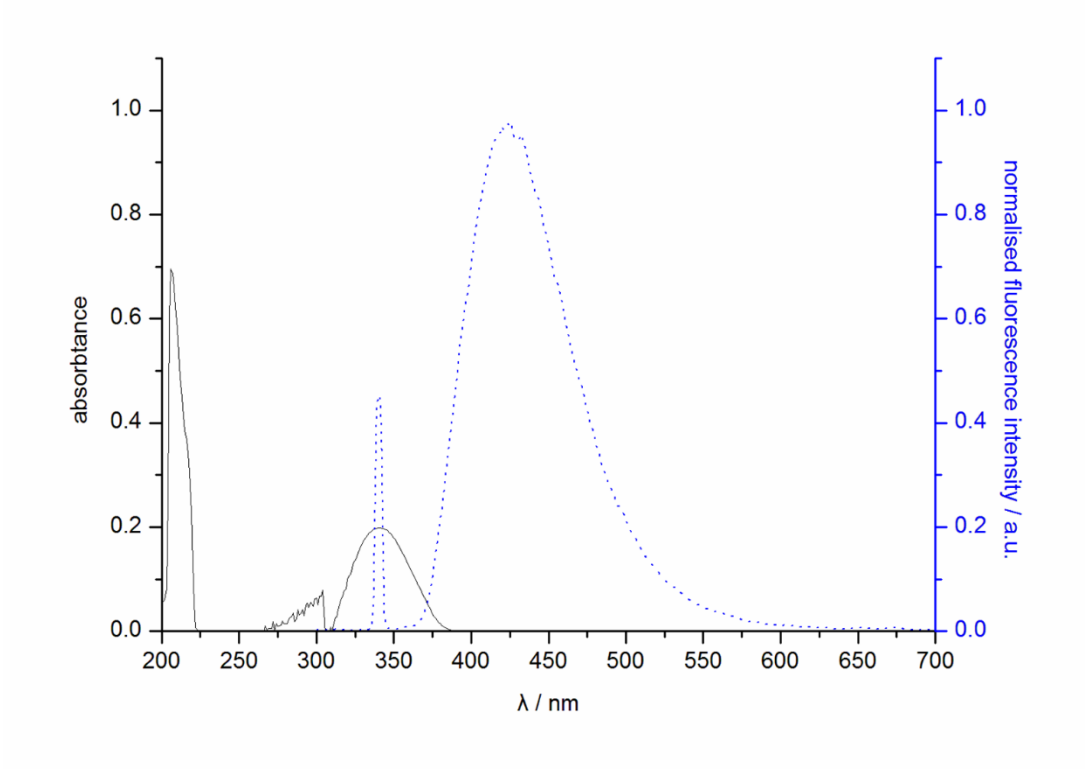


Figure S34. Absorption (─) and emission (---) spectra of **1**-K^+ complex in acetone (*c* = 0.02 mM, bandwidth = 1 nm). Raman and Rayleigh peaks have not been removed.

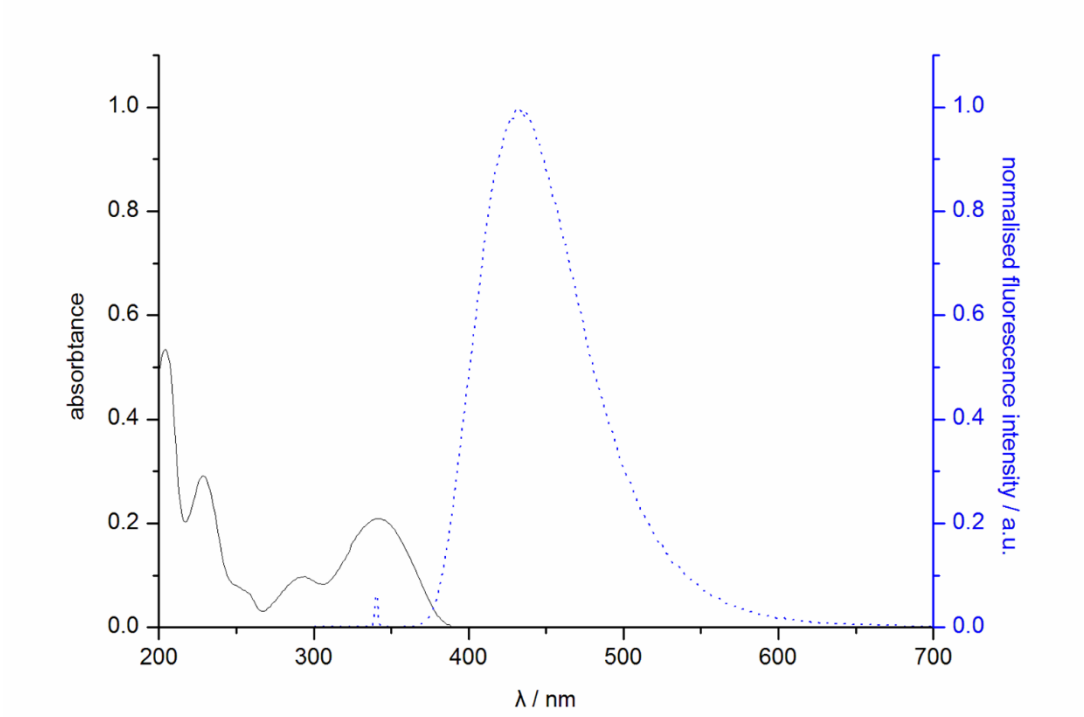


Figure S35. Absorption (—) and emission (---) spectra of **1**-K^+ complex in water (c = 0.02 mM, bandwidth = 1 nm). Raman and Rayleigh peaks have not been removed.

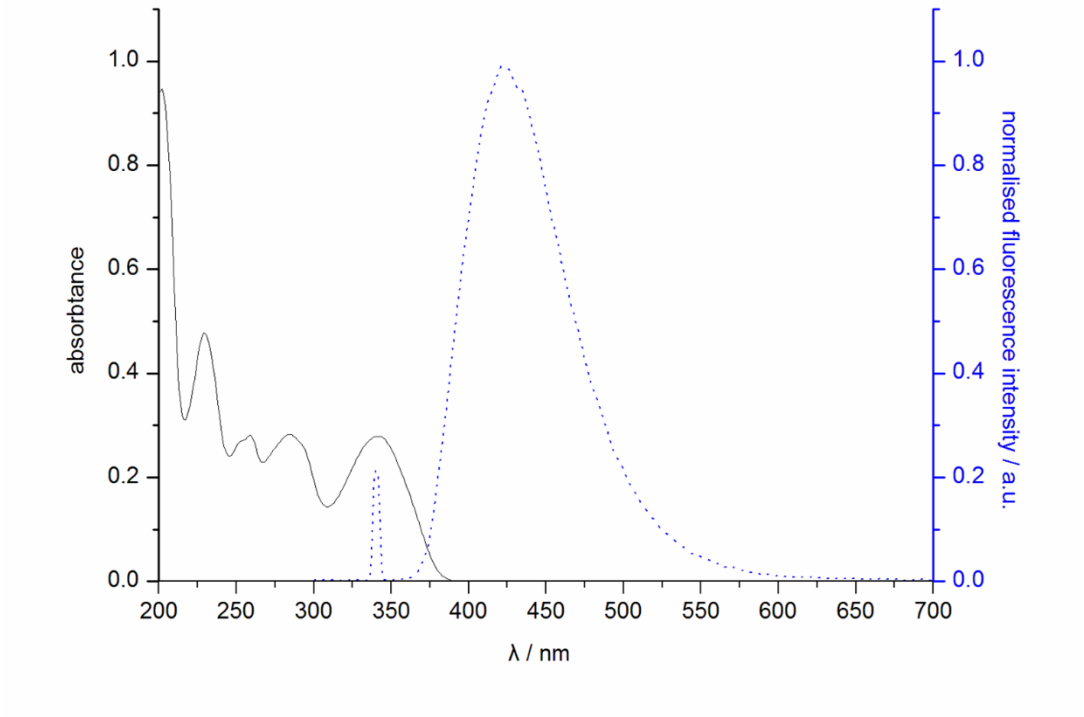


Figure S36. Absorption (—) and emission (---) spectra of **1**-K^+ complex in acetonitrile (c = 0.02 mM, bandwidth = 1 nm). Raman and Rayleigh peaks have not been removed.

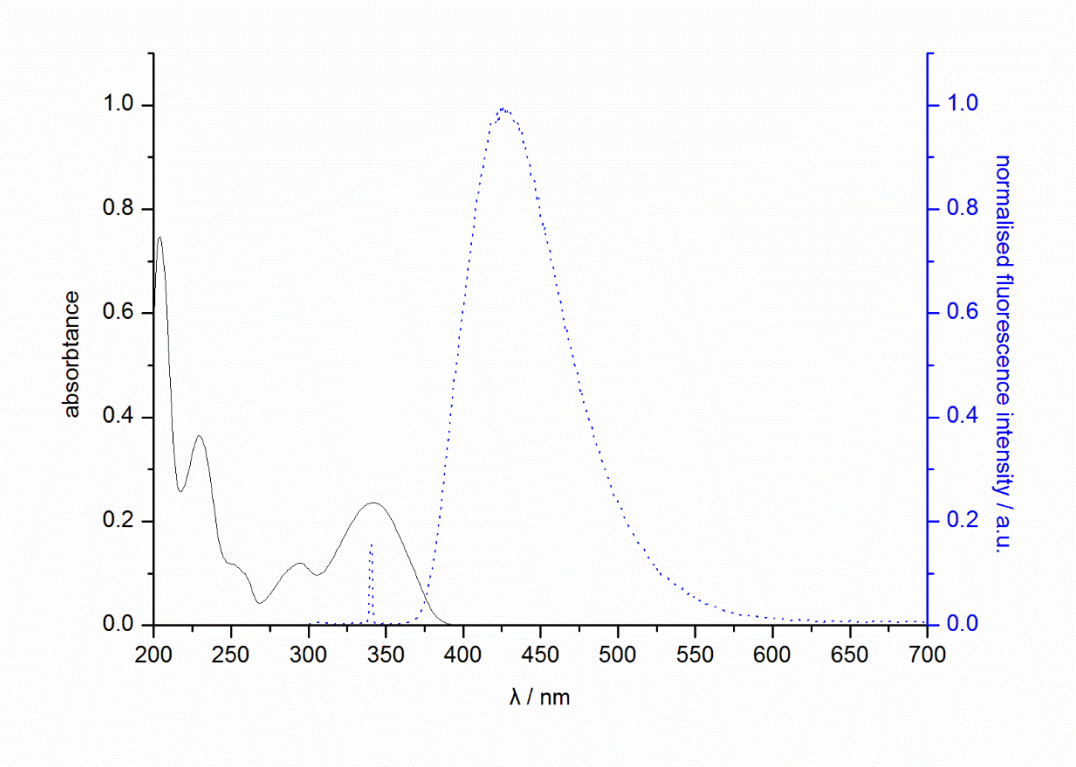


Figure S37. Absorption (—) and emission (---) spectra of **1**-K^+ complex in methanol (*c* = 0.02 mM, bandwidth = 1 nm). Raman and Rayleigh peaks have not been removed.