Supplementary Information

Reversible Encapsulation of a Nitrate Guest via Hydrogen bonded Self-Assembled Capsule Formation by Flexible Tripodal Receptor in Polar Solvent through Dynamic Self-Assembly

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Fig. S1-S47  Spectral characterization of receptors and anion complexes.
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Fig. S86-S93  Titration spectra of perchlorate complexes of the corresponding receptors 1-7 and 1’ with TBANO$_3$ in acetone-d$_6$.
Fig. S94  Spectroscopic curves of titration of perchlorate complexes with TBANO$_3$ in acetone-d$_6$. 
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**Table S1** Crystallographic data and structure refinements for 1a.

**Table S2** Hydrogen bonding distances and Bond angles in complex 6a.

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**Fig. S1** $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of receptor 1.
Fig. S2 $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 °C) spectrum of receptor 1.
Fig. S3 $^1$H NMR (400 MHz, DMSO-$d_6$, 20 $^\circ$C) spectrum of a mixture of complexes 1a (peaks represented by red circles) and 1b (peaks represented by green circles) obtained by treating receptor 1 with nitric acid in CHCl$_3$/MeOH (v/v = 1/1). The circle in blue color represents water peak from DMSO-$d_6$. 
**Fig. S4** $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 1a.
Fig. S5 $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 1a.
**Fig. S6** $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 1b.
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Fig. S9 The HSQC spectrum of nitrate complex 1b in DMSO-\textit{d}$_6$. 
Fig. S10 The HMBC spectrum of nitrate complex 1b in DMSO-$d_6$. 

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Fig. S11 The ROESY spectrum of nitrate complex 1b in DMSO-$d_6$. 

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Fig. S12 $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of receptor 1'.
**Fig. S13** $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 °C) spectrum of receptor 1'.
Fig. S14 $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) spectrum of receptor 1'.
Fig. S15 $^{13}$C NMR (100 MHz, CDCl$_3$, 20 °C) spectrum of receptor 1’.
Fig. S16 $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of receptor 2.
**Fig. S17** $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 °C) spectrum of receptor 2.
Fig. S18 $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 2a.
**Fig. S19** $^{13}$C NMR (100 MHz, DMSO-$_d_6$, 20 °C) spectrum of nitrate complex 2a.
**Fig. S20** $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of receptor 3.
Fig. S21 $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20°C) spectrum of receptor 3.
Fig. S22 $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 3a.
Fig. S23 $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 3a.
**Fig. S24** $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of receptor 4.
Fig. S25 $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 °C) spectrum of receptor 4.
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Fig. S27 $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 $^\circ$C) spectrum of nitrate complex 4a.
Fig. S28 $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of receptor 5.
Fig. S29 $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 ºC) spectrum of receptor 5.
Fig. S30 $^1$H NMR (400 MHz, CDCl$_3$, 20 ºC) spectrum of receptor 5.
**Fig. S31** $^{13}$C NMR (100 MHz, CDCl$_3$, 20 ºC) spectrum of receptor 5.
Fig. S32 $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 5a.
**Fig. S33** $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 5a.
Fig. S34 $^1$H NMR (400 MHz, DMSO-$d_6$, 20 ºC) spectrum of receptor 6.
**Fig. S35** $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 °C) spectrum of receptor 6.
Fig. S36 $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 6a.
**Fig. S37** $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 6a.
**Fig. S38** $^1$H NMR (400 MHz, DMSO-d$_6$, 20 ºC) spectrum of receptor 6'. 
**Fig. S39** $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20°C) spectrum of receptor 6'.

Receptor 6'
Fig. S40 $^1$H NMR (400 MHz, CDCl$_3$, 20 °C) spectrum of receptor 6'.
Fig. S41 $^{13}$C NMR (100 MHz, CDCl$_3$, 20 °C) spectrum of receptor 6'.
Fig. S42 $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 6b.
Fig. S43 $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 6b.
Fig. S44 $^1$H NMR (400 MHz, DMSO-$d_6$, 20°C) spectrum of receptor 7.
**Fig. S45** $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 °C) spectrum of receptor 7.
Fig. S46 $^1$H NMR (400 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 7a.
Fig. S47 $^{13}$C NMR (100 MHz, DMSO-$d_6$, 20 °C) spectrum of nitrate complex 7a.
Fig. S48 HRESI mass spectrum of complex 1a.

Elemental Composition Report

**Single Mass Analysis**

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
9 formulae/ions evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:
C: 0-1000 H: 0-4000 N: 5-5 O: 12-12

1224.428-192.27 (2.056)

Minimum: 5.0  10.0  -1.5
Maximum: 1000.0

Mass  Calc. Mass  mDa  PPM  DBE  i-FIT  i-FIT (Norm)  Formula
886.3306  886.3259  0.7  0.0  27.5  62.0  0.0  C48 H40 N4 O12

Complex 1a

Chemical Formula: C48H40N4O12
Molecular Weight: 887.9290
For [M-H]-: 886.9210
Theoretical value for [M-H]-: 886.3299 (100%)
Fig. S49 HRESI mass spectrum of complex 1b.
Fig. S50 HRESI mass spectrum of complex 2a.
Fig. S51 HRESI mass spectrum of complex 3a.

Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0
Element prediction: Off
Number of isotopic peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron ions
9 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:
C: 0-1000  H: 0-4000  N: 5-5  O: 12-12
CA-65-1
0513_GK-66-1 7 (0.703)

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889.3219
894.3292
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Mass Calculated

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Chemical Formula: C_{48}H_{40}N_{5}O_{12}
Molecular Weight: 887.9290
For [M-H]⁻: 886.9210
Theoretical value for [M-H]⁻: 886.3299 (100%)
Fig. S52 HRESI mass spectrum of complex 4a.

**Elemental Composition Report**

**Single Mass Analysis**

Tolerance = 100.0 PPM / DBE: min = -1.5, max = 1000.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monotopic Mass, Even Electron Ions

18 formulae evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-1000  H: 0-4000  N: 7-8  O: 15-15

C41H25N3O14

0.26 MCH 195.25 (2.002)

Complex 4a

Chemical Formula: C41H25N3O14

Molecular Weight: 932.8437

For [M-H]: 931.8358

Theoretical value for [M-H]: 931.2535 (100%)
Fig. S53 HRESI mass spectrum of complex 5a.

Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ion
9 formula(s) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used
C: 0-1000  H: 0-4000  N: 8-8  O: 15-15

CX-66-2

0513_CX-66-2.0 (0.040) Cm (9-41)

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Chemical Formula: C_{45}H_{40}N_{8}O_{15}
Molecular Weight: 932.8437

For [M-H]^+ : 931.8358
Theoretical value for [M-H]^+ : 931.2535 (100%)
Fig. S54 HRESI mass spectrum of complex 6a.

Elemental Composition Report

Single Mass Analysis
Tolerance = 100.0 PPM / DBE: min = -1.5, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron Ions
9 formula(s) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-1000  H: 0-4000  N: 5-5  O: 9-9

CK-1948

0224_CK-1948_264 (3.418)

Minimum: 5.0  100.0  1600.0
Maximum: 100.0  1000.0

Mass  Calc. Mass  nDa  PDB  i-FIT  i-FIT (Norm)  Formula
638.3452  638.3452  0.1  0.1  57.5  54.0  0.0  C48 H48 N5 O9

Complex 6a

Chemical Formula: C48H48N5O9
Molecular Weight: 839.9308
For [M+H]+: 838.9228
Theoretical value for [M-H]-: 838.3452 (100%)
Fig. S5 HRESI mass spectrum of complex 6b.

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, From Electron Ions
9 formula(s) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-1000  H: 0-4000  N: 0-8  O: 15-15

Complex 6b
Chemical Formula: C_{46}H_{46}N_{6}O_{15}
Molecular Weight: 974.9234
For [M-H]: 973.9155
Theoretical value for [M-H]: 973.3004 (100%)
Fig. S6. HRESI mass spectrum of complex 7a.

**Elemental Composition Report**

**Single Mass Analysis**

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 1000.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron ions

6 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

Elements Used:

C: 0-1000  H: 0-4000  N: 5-5  O: 9-9

CK-122-2

1118 CK-122-2 13 (1,327) Cm (13-1)

100

%  

50  750  755  760  765  770  775  780  785  790  795  800  805  810  815  820  825  830  835  840  845  850

0  749.3025  757.9260  761.5108  771.8665  774.0896  776.6578  785.8210  792.9924

796.2977  797.2967  798.3042  799.2914  800.0464  813.7084  821.5923  826.7084  834.2786  842.8303  848.4924

m/z

Minimum: 5.0  20.0  1000.0

Maximum: 1.5

**Mass**  **Calc. Mass**  **zm/z**  **DBE**  **i-FIT**  **i-FIT (Nons)**  **Formula**

796.2977  796.2963  -0.6  -0.9  27.5  35.4  0.0  C41 H42 N8 O9

**Chemical Formula:** C41H42N8O9

**Molecular Weight:** 797.8510

For [M-H]: 796.8431

Theoretical value for [M-H]: 796.2983 (100%)
Fig. S57 HRESI mass spectrum of the self-assembled capsule (1'2) recorded after dissolving nitrate complex 1b in a mixture solution of DMSO/CHCl₃ (1:1).
Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 1000.0
Element prediction: Off
Number of isotopic peaks used for i-FIT = 2

Monoisotopic Mass, Even Electron ions
17 formula(s) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 0-1000 H: 0-4000 N: 1-14 O: 30-30 Na: 1-1

Chemical Formula for [M+Na]^+: C_{96}H_{90}N_{14}NaO_{30}
Molecular Weight: 1942.8074
Theoretical value for [M+Na]^+: 1942.5879 (100%)

Fig. S58 HRESI mass spectrum of the self-assembled capsule (1') recorded after dissolving receptor 1' in a mixture solution of DMSO/CHCl3 (1:1).
Fig. S59 HRESI mass spectrum of the self-assembled capsule (1') recorded by dissolving receptor 1' to a mixture solution of DMSO/acetone (1:1, v/v).
Fig. S60 HRESI mass spectrum of the self-assembled capsule (1') recorded by dissolving receptor 1 to a mixture solution of DMSO/CH$_3$NO$_2$ (1:1, v/v).

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**Fig. S61** HRESI mass spectrum of the self-assembled capsule (5) recorded after dissolving nitrate complex 5a in mixture solution of DMSO/CHCl₃ (1:1).

**Elemental Composition Report**

**Single Mass Analysis**

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**Element prediction**: Off

**Number of isotope peaks used for i-FIT**: 2

**Monoisotopic Mass, Even Electron ion**

15 formula(s) evaluated with 1 results within limits (up to 50 closest results for each mass)

**Elements Used**

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**CX-19-28**

0467_CX-19-28 11 (1.057) Cm (11-1)

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**Chemical Formula**: C₈₀H₇₈N₁₄O₂₄

**Molecular Weight**: 1739.6617

**Theoretical value for [M+H]+**: 1739.5392 (100%)
Fig. S62. HRESI mass spectrum of the self-assembled capsule (5) recorded by dissolving receptor 5 to a mixture solution of DMSO/CHCl₃ (1:1, v/v).

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Fig. S63 HRESI mass spectrum of the self-assembled capsule (5) recorded by dissolving receptor 5 to a mixture solution of DMSO/acetone-d₆ (1:1, v/v).

**Elemental Composition Report**

**Single Mass Analysis**

Tolerance = 40.0 PPM / DBE: min = -1.5, max = 1000.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 2

**Monoisotopic Mass, Even Electron Ion:**

10 formula(e) evaluated with 1 result within limits (all results up to 1000) for each mass

**Elements Used:**

C: 0-400  H: 0-1000  N: 14-14  O: 24-24  Na: 1-1

CX:183-4

0030 CX:183-4 24 (1.940)

**Minimum:**

Calc. Mass  mDa  PPM  DBE  i-FIT  i-FIT (Norm)  Formula

1761.5193  1761.5211  -1.0  -1.0  58.5  12.6  0.0  C₉₀ H₇₈ N₁₄ O₂₄ Na

**Self-assembled molecular capsule (5₂)**

Chemical Formula: C₉₀H₇₈N₁₄O₂₄

Molecular Weight: 1739.6817

Theoretical value for [M+Na⁺]: 1761.5211 (100%)
Fig. S4. HRESI mass spectra of the self-assembled capsule (52) recorded by dissolving receptor 5 to a mixture solution of DMSO/CH3NO2 (1:1, v/v).
Fig. S65 HRESI mass spectrum of the self-assembled capsule (6b) recorded after dissolving the nitrate complex 6b in a mixture solution of DMSO/CHCl₃ (1:1).

Elemental Composition Report

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Minimum: 5.0  50.0  1000.0
Maximum: 17.4

Chemical Formula: C₉₀H₁₀₀N₁₄O₂₄
Molecular Weight: 1823.6212

Theoretical value for M⁺: 1823.6286 (100%)
Theoretical value for [M+H]⁺: 1824.6364 (100%)
Fig. S6. HRESI mass spectra of the self-assembled capsule (6') recorded by dissolving receptor 6' to a mixture solution of DMSO/acetone (1:1, v:v).
**Fig. S67** HRESI mass spectra of the self-assembled capsule (6’2) recorded by dissolving receptor 6’ to a mixture solution of DMSO/CH$_3$NO$_2$ (1:1, v/v).
Fig. S68 $^1$H NMR titration spectra of a mixture of nitrate complexes (in DMSO-$d_6$ with varying amount of CDCl$_3$) obtained after addition of nitric acid in aqueous methanol to a suspension of receptor 1 in CHCl$_3$. The star marks in green and red color represent the peaks for DMSO-$d_6$ (as solvent) and DMSO-$d_6$ (as internal reference, TMS in DMSO-$d_6$), respectively. The circles in green and red color represent water peaks from DMSO-$d_6$ (as solvent) and from DMSO-$d_6$ (as internal reference, TMS in DMSO-$d_6$), respectively. The triangles in red and blue color represent amide N-H peaks of nitrate complexes 1b and 1a, respectively. The circle in blue color represents peak for CDCl$_3$. 

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Fig. S69 $^1$H NMR (400 MHz, 20 °C) titration spectra of receptor $1'$ (10.3 mM) in DMSO-$d_6$ with varying amount of CDCl$_3$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-$d_6$ and from internal reference, respectively. A star mark in blue color represents peak for CDCl$_3$. The spectrum in red color was recorded after partial evaporation of CDCl$_3$ from the mixture solution, showing reversible capsule formation through dynamic self-assembly of receptor $1'$. 
**Fig. S70** $^1$H NMR (400 MHz, 20 °C) titration spectra of receptor 1’ (10.3 mM) in DMSO-$d_6$ with varying amount of acetone-$d_6$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-$d_6$ and from internal reference, respectively. Star marks in blue color represent the peaks for acetone-$d_6$. The spectrum in red color was recorded after partial evaporation of acetone-$d_6$ from the mixture solution, showing reversible capsule formation through dynamic self-assembly of receptor 1’.
Fig. S71 ¹H NMR (400 MHz, 20 °C) titration spectra of receptor 1’ (10.3 mM) in DMSO-­d₆ with varying amount of CD₃NO₂ with TMS (in DMSO-­d₆) as the internal reference. Green stars represent the peaks of DMSO-­d₆ used as solvent. Red stars represent the peaks of DMSO-­d₆ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-­d₆ and from internal reference, respectively. A star mark in blue color represents peak for CD₃NO₂.
**Fig. S72** $^1$H NMR (400 MHz, 20 °C) titration spectra of nitrate complex 1b (10.3 mM) in DMSO-$d_6$ with varying amount of CDCl$_3$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-$d_6$ and from internal reference, respectively. A star mark in blue color represents peak for CDCl$_3$. The spectrum in red color was recorded after partial evaporation of CDCl$_3$ from the mixture solution, showing reversible binding of nitrate anion by receptor 1'.
**Fig. S73** $^1$H NMR (400 MHz, 20 °C) titration spectra of nitrate complex 1b (10.3 mM) in DMSO-$d_6$ with varying amount of acetone-$d_6$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-$d_6$ and from internal reference, respectively. A star mark in blue color represents the peak for acetone-$d_6$. The spectrum in red color was recorded after partial evaporation of acetone-$d_6$ from the mixture solution, showing reversible binding of nitrate anion by receptor $1'$. 
**Fig. S74** $^1$H NMR (400 MHz, 20 °C) titration spectra of nitrate complex 1b (10.3 mM) in DMSO-$d_6$ with varying amount of CD$_3$NO$_2$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-$d_6$ and from internal reference, respectively. A star mark in blue color represents the peak for CD$_3$NO$_2$. 

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**Fig. S75** $^1$H NMR (400 MHz, 20 °C) titration spectra of receptor 5 (10.3 mM) in DMSO-$d_6$ with varying amount of acetone-$d_6$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-$d_6$ and from internal reference, respectively. A star mark in blue color represents the peak for acetone-$d_6$. 
Fig. S76 $^1$H NMR (400 MHz, 20 °C) titration spectra of receptor 5 (10.3 mM) in DMSO-$d_6$ with varying amount of CD$_3$NO$_2$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-$d_6$ and from internal reference, respectively. A star mark in blue color represents the peak for CD$_3$NO$_2$. 
Fig. S77 ¹H NMR (400 MHz, 20 °C) titration spectra of nitrate complex 5a (10.3 mM) in DMSO-­d₆ with varying amount of CDCl₃ with TMS (in DMSO-­d₆) as the internal reference. Green stars represent the peaks of DMSO-­d₆ used as solvent. Red stars represent the peaks of DMSO-­d₆ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-­d₆ and from internal reference, respectively. A star mark in blue color represents the peak for CDCl₃. The spectrum in red color was recorded after partial evaporation of CDCl₃ from the mixture solution, showing reversible binding of nitrate anion by receptor 5.
Fig. S78 $^1$H NMR (400 MHz, 20 °C) titration spectra of nitrate complex 5a (10.3 mM) in DMSO-$d_6$ with varying amount of acetone-$d_6$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-$d_6$ and from internal reference, respectively. A star mark in blue color represents the peak for acetone-$d_6$. The spectrum in red color was recorded after partial evaporation of acetone-$d_6$ from the mixture solution, showing reversible binding of nitrate anion by receptor 5.
Fig. S79 $^1$H NMR (400 MHz, 20 °C) titration spectra of nitrate complex 5a (10.3 mM) in DMSO-$d_6$ with varying amount of CD$_3$NO$_2$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-$d_6$ and from internal reference, respectively. A star mark in blue color represents peak for CD$_3$NO$_2$. 
Fig. S80 ¹H NMR titration spectra of mixture of nitrate complex (in DMSO-ç with varying amount of CDCl₃), obtained after addition of nitric acid in an aqueous methanol to the suspension of receptor 6 in CHCl₃. The star marks in green and red color represents peak corresponding to DMSO-ç (as solvent) and DMSO-ç (as internal reference, TMS in DMSO-ç), respectively. Circle in green color represents water peak from DMSO-ç (as solvent) and the same in red color represents water peak from DMSO-ç (as internal reference, TMS in DMSO-ç). A star mark in blue color represents peak for CDCl₃.
Fig. S81 $^1$H NMR (400 MHz, 20 °C) titration spectra of receptor 6$^*$ (10.3 mM) in DMSO-$d_6$ with varying amount of CD$_3$NO$_2$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-$d_6$ and from internal reference, respectively. A star mark in blue color represents the peak for CD$_3$NO$_2$. 

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Fig. S82 $^1$H NMR (400 MHz, 20 °C) titration spectra of nitrate complex 6b (10.3 mM) in DMSO-$d_6$ with varying amount of CDCl$_3$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-$d_6$ and from internal reference, respectively. A star mark in blue color represents the peak for CDCl$_3$. The spectrum in red color was recorded after partial evaporation of CDCl$_3$ from the mixture solution, showing reversible binding of nitrate anion by receptor 6•.
Fig. S83 $^1$H NMR (400 MHz, 20 °C) titration spectra of nitrate complex 6b (10.3 mM) in DMSO-$d_6$ with varying amount of acetone-$d_6$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-$d_6$ and from internal reference, respectively. A star mark in blue color represents peak for acetone-$d_6$. The spectrum in red color was recorded after partial evaporation of acetone-$d_6$ from the mixture solution, showing reversible binding of nitrate anion by receptor 6'.
**Fig. S84** $^1$H NMR (400 MHz, 20 °C) titration spectra of nitrate complex 6b (10.3 mM) in DMSO-$d_6$ with varying amount of CD$_3$NO$_2$ with TMS (in DMSO-$d_6$) as the internal reference. Green stars represent the peaks of DMSO-$d_6$ used as solvent. Red stars represent the peaks of DMSO-$d_6$ from the internal reference. Circles in red color represent the peaks for water from DMSO-$d_6$ (internal reference). A star mark in blue color represents the peak for CD$_3$NO$_2$. 

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**Fig. S85** Concentration dependent $^1$H NMR of 5$_2$ in CDCl$_3$ showing the self-assembled capsule exists till $1 \times 10^8$ M concentration without formation of any side products.
**Fig. S86** Partial $^1$H NMR titration spectra of perchlorate complex 1c ($2.96 \times 10^{-3}$ M) with tetrabutylammonium nitrate in acetone-$d_6$.

**Fig. S87** Partial $^1$H NMR titration spectra of perchlorate complex 1’c ($1.48 \times 10^{-3}$ M) with tetrabutylammonium nitrate in acetone-$d_6$. 
**Fig. S88** Partial $^1$H NMR titration spectra of perchlorate complex 2c ($1.48 \times 10^{-3}$ M) with tetrabutylammonium nitrate in acetone-$d_6$.

**Fig. S89** Partial $^1$H NMR titration spectra of perchlorate complex 3c ($1.48 \times 10^{-3}$ M) with tetrabutylammonium nitrate in acetone-$d_6$. 
**Fig. S90** Partial $^1$H NMR titration spectra of perchlorate complex 4c (1.48 × 10^{-3} M) with tetrabutylammonium nitrate in acetone-$d_6$.

**Fig. S91** Partial $^1$H NMR titration spectra of perchlorate complex 5c (1.48 × 10^{-3} M) with tetrabutylammonium nitrate in acetone-$d_6$. 
**Fig. S92** Partial $^1$H NMR titration spectra of perchlorate complex 6c ($1.48 \times 10^{-3}$ M) with tetrabutylammonium nitrate in acetone-$d_6$.

**Fig. S93** Partial $^1$H NMR titration spectra of perchlorate complex 7c ($1.48 \times 10^{-3}$ M) with tetrabutylammonium nitrate in acetone-$d_6$. 
Fig. S94 $^1$H NMR titration curves of perchlorate complexes ($1.48 \times 10^{-3}$ M) with tetrabutylammonium nitrate in acetone-$d_6$. 
pH dependent reversible binding of NO$_3$ anion by compound 1':

![Diagram showing pH dependent reversible binding of NO$_3$ anion by compound 1']

**Fig. S95** $^1$H NMR spectra (400 MHz, DMSO-$d_6$, 20 °C) of complex 1b (49 mM) showing proton-induced reversible binding of nitrate anion. (a) $^1$H NMR spectrum of complex 1b in DMSO-$d_6$. (b) After treating with 2.5 equiv. of KOH. (c) $^1$H NMR spectrum of compound 1' in DMSO-$d_6$. (d) Acidification with trifluoroacetic acid retained its yellow color. (e) Compound 1' in DMSO-$d_6$ in presence of trifluoroacetic acid. The star mark in green and red color represent the peaks for DMSO-$d_6$ and for trifluoroacetic acid.
### Table T1. Crystallographic data and structure refinements for 6a and 52.

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### Table T2. Hydrogen bonding distances (Å) and Bond angles (°) in complex 6a

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