Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Narcissistic self-sorting of hydrogen-bonded dimeric capsules formed through self-assembly of flexible tripodal receptors in Polar Solvents

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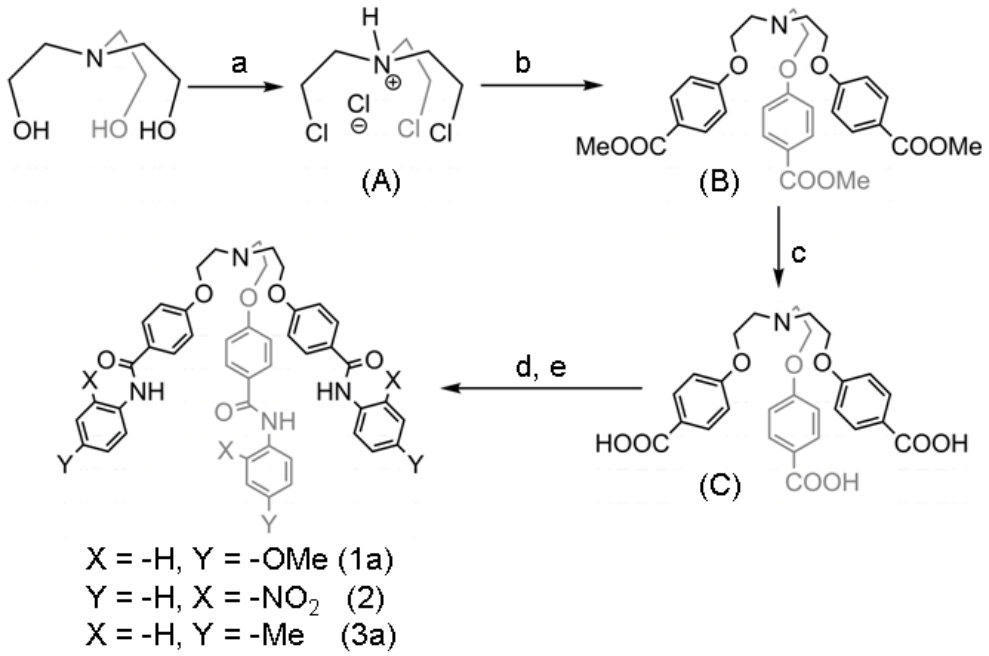
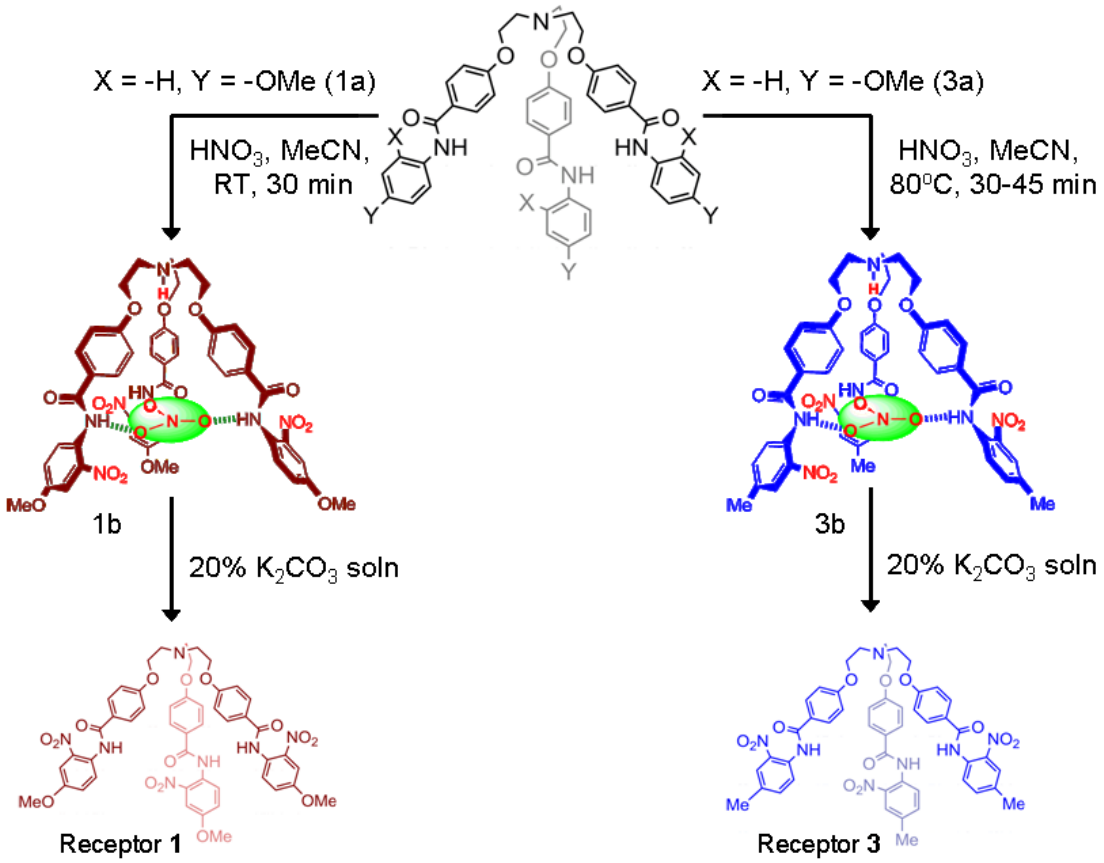
Synthetic Scheme:



(a) $SOCl_2$, $CHCl_3$, 54%. (b) *p*-OH-C_6H_4COOMe, KOH, DMSO, 80 ºC, 75%. (c) 5 N NaOH/MeOH (1:1, v/v), 100 ºC, 12 h, dil HCl, 92%. (d) $SOCl_2$, CH_2Cl_2, DMF (cat.), reflux, 2-3 h. (e) X-$C_6H_4NH_2$, CH_2Cl_2, Et_3N, reflux, 8 h



General procedures for the synthesis of receptors 1–3. Receptors were synthesized from previously reported tris(2-chloroethyl)amine hydrochloride[1] (A) by simple SN_2 substitution with 4-hydroxy methylbenzoate in DMSO followed by basic hydrolysis to yield corresponding triacid (C). Subsequent condensation of triacid with thionyl chloride in dichloromethane yielded corresponding acid chloride. Subsequently, the acid chloride solution in dichloromethane was slowly added to a mixture of the corresponding amino derivative and Et_3N in dichloromethane and refluxed for 8-12 h. Solvent was removed under reduced pressure. Ice-cold water was added to the residue and stirred at room temperature for 2-3 h to precipitate the target compounds (**1a, 2** and **3a**). The crude product was purified by flash chromatography with $CHCl_3$/MeOH mixture solution as eluent to yield desired receptors. The desired receptors **1a, 2** and **3a** were isolated in 95%, 70% and 90% yields respectively.

Nitrate complexes **1b** and **3b** were collected as precipitate after treating suspension of **1a** (and **3a**) in acetonitrile with 25% HNO_3 and stirring the mixture solution at room temperature (for **3b**, mixture was heated at 80 ºC) for 30-45 min.

The suspension of nitrate complexes **1b** and **3b** in ethyl acetate was treated with 20% K_2CO_3 solution and reaction mixture was stirred at room temperature for 1h. The precipitate was filtered and washed twice with cold water followed by diethyl ether to

get free receptor **1** (shiny yellow) and **3** (orange color solid) respectively in 87% and 93% yields.

1a: Gray color solid (yield 95%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 3.12 (t, 6H, J = 5.6 Hz), 3.73 (s, 9H), 4.18 (t, 6H, J = 5.6 Hz), 6.90 (d, 6H, J = 8.8 Hz), 7.03 (d, 6H, J = 8.8 Hz), 7.65 (d, 6H, J = 8.8 Hz), 7.93 (d, 6H, J = 8.8 Hz), 9.96 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 53.5, 55.2, 66.8, 113.7, 114.1, 122.0, 127.0, 129.4, 132.4, 155.4, 161.0, 164.5. HRESIMS m/z 825.3494 (calcd m/z 825.3500 for $[M+H]^+$).

1b: Orange color solid (yield 92%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 3.86 (s, 9H), 3.92 (s, 6H), 4.58 (s, 6H), 7.15 (d, 6H, J = 8.8 Hz), 7.35 (d, 3H, J = 9.2 Hz), 7.52 (s, 3H), 7.64 (d, 3H, J = 9.2 Hz), 7.98 (d, 6H, J = 8.8 Hz) 10.44 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 53.3, 56.1, 62.7, 109.2, 114.6, 120.2, 124.5, 126.6, 128.0, 129.7, 143.9, 156.4, 160.5, 164.4. HRESIMS *m/z* 1021.2855 (calcd *m/z* 1021.2852 for $[M-H]^-$).

Receptor 1: Deep yellow solid (yield 87%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 3.13 (t, 6H, J = 5.2 Hz), 3.85 (s, 9H), 4.20 (t, 6H, J = 5.2 Hz),7.08 (d, 6H, J = 8.8 Hz), 7.33 (d, 3H, J = 9 Hz), 7.51 (s, 3H), 7.65 (d, 3H, J = 8.8 Hz), 7.92 (d, 6H, J = 8.8 Hz), 10.39 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 53.4, 56.0, 66.9, 109.1, 114.3, 120.2, 124.6, 125.7, 127.7, 129.6, 143.6, 156.1, 161.5, 164.6. HRESIMS *m/z* 960.3060 (calcd *m/z* 960.3052 for $[M+H]^+$).

Self-assembled capsule 1.1: ^{1}H NMR ($CDCl_3$, 400 MHz, 20 ºC) δ 3.18 (t, 6H, *J* = 5.2 Hz), 3.83 (s, 9H), 4.16 (t, 6H, *J* = 5.2 Hz), 6.93 (d, 6H, *J* = 8.8 Hz), 7.21 (d, 3H, *J* = 9.2 Hz), 7.64 (s, 3H), 7.86 (d, 6H, *J* = 8.8 Hz), 8.80 (d, 3H, *J* = 9.2 Hz), 10.97 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 20 ºC) δ 54.6, 56.1, 67.5, 108.7, 114.9, 123.7, 123.9, 126.7, 129.5, 129.6, 137.0, 154.9, 162.3, 165.1. HRESIMS *m/z* 1942.5861 (calcd *m/z* 1942.5879 for $[M+Na]^+$).

Receptor 2: Yellow solid (yield 70%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 3.13 (t, 6H, *J* = 5.2 Hz), 4.21 (t, 6H, *J* = 5.2 Hz), 7.10 (d, 6H, *J* = 8.8 Hz), 7.38 (t, 3H, *J* = 7.6 Hz), 7.73 (t, 3H, *J* = 7.6 Hz), 7.84 (d, 3H, *J* = 8.0 Hz), 7.94 (d, 6H, *J* = 8.8 Hz), 8.00 (d, 3H, *J* = 8.0 Hz), 10.63 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 53.4, 66.9, 114.4, 124.9, 125.1, 125.5, 129.7, 132.0, 134.0, 142.3, 161.7, 164.6. HRESIMS *m/z* 870.2739 (calcd *m/z* 870.2735 for $[M+H]^+$).

Self-assembled capsule 2.2: ^{1}H NMR ($CDCl_3$, 400 MHz, 20 ºC) δ 3.28 (s, 6H), 4.24 (s, 6H), 6.96 (d, 6H, *J* = 8.8 Hz), 7.14 (t, 3H, *J* = 8.0 Hz), 7.63 (t, 3H, *J* = 8.0 Hz), 7.89 (d, 6H, *J* = 8.8 Hz), 8.21 (d, 3H, *J* = 8.4 Hz), 8.91 (d, 3H, *J* = 8.4 Hz), 11.23 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 54.5, 67.0, 114.9, 122.2, 123.2, 126.0, 126.7, 129.6, 135.8, 136.3, 136.4, 162.2, 165.2. HRESIMS *m/z* 1739.5383 (calcd *m/z* 1739.5392 for $[M+H]^+$).

3a: White solid (yield 90%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 2.27 (s, 9H), 3.12 (t, 6H, *J* = 5.2 Hz), 4.18 (t, 6H, *J* = 5.2 Hz), 7.04 (d, 6H, *J* = 8.8 Hz), 7.13 (d, 6H, *J* = 8.4 Hz), 7.65 (d, 6H, *J* = 8.4 Hz), 7.95 (d, 6H, *J* = 8.8 Hz), 10.01 (s, 3H). ^{13}C

NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 20.5, 53.5, 66.8, 114.0, 120.4, 127.0, 128.9, 129.5, 132.3, 136.8, 161.1, 164.6. HRESIMS *m/z* 799.3467 (calcd *m/z* 799.3472 for $[M+Na]^+$).

3b: Yellow solid (yield 91%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 2.35 (s, 9H), 3.91 (s, 6H), 4.57 (s, 6H), 7.12 (d, 6H, *J* = 8.8 Hz), 7.52 (d, 3H, *J* = 7.6 Hz), 7.65 (d, 3H, *J* = 8.4 Hz), 7.80 (s, 3H), 7.95 (d, 6H, *J* = 8.4 Hz), 10.57 (s, 3 H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 20.2, 53.5, 62.8, 114.8, 125.0, 126.0, 126.7, 129.5, 129.9, 134.8, 135.6, 142.7, 160.7, 164.8. HRESIMS *m/z* 973.3002 (calcd *m/z* 973.3004 for $[M-H]^-$).

Receptor 3: Orange solid (yield 93%). ^{1}H NMR (DMSO-d_6, 400 MHz, 20 ºC) δ 2.38 (s, 9H), 3.13 (t, 6H, *J* = 5.6 Hz), 4.20 (t, 6H, 5.6 Hz), 7.08 (d, 6H, *J* = 8.8 Hz), 7.53 (s, 3H, J = 8.0 Hz), 7.69 (d, 3 H, *J* = 8.0 Hz), 7.83 (s, 3H), 7.91 (d, 6H, *J* = 8.8 Hz), 10.50 (s, 3 H). ^{13}C NMR (DMSO-d_6, 100 MHz, 20 ºC) δ 20.0, 53.3, 62.7, 114.6, 124.8, 125.8, 126.5, 129.3, 129.7, 134.6, 135.4, 142.5, 160.5, 164.5. HRFABMS *m/z* 912.3196 (calcd *m/z* 912.3204 for $[M+H]^+$).

Self-assembled capsule 3.3: ^{1}H NMR ($CDCl_3$, 400 MHz, 20 ºC) δ 2.37 (s, 9H), 3.20 (s, 6H), 4.17 (s, 6H), 6.95 (s, 6H), 7.46 (s, 3H), 7.89 (s, 6 H), 8.01 (s, 3H), 8.80 (s, 3H), 11.13 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz, 20 ºC) δ 20.8, 54.6, 67.5, 114.9,

122.2, 125.8, 126.7, 129.6, 133.5, 136.4, 137.3, 162.3, 165.2. HRESIMS *m/z* 1846.6067 (calcd *m/z* 1846.6184 for $[M+Na]^+$).

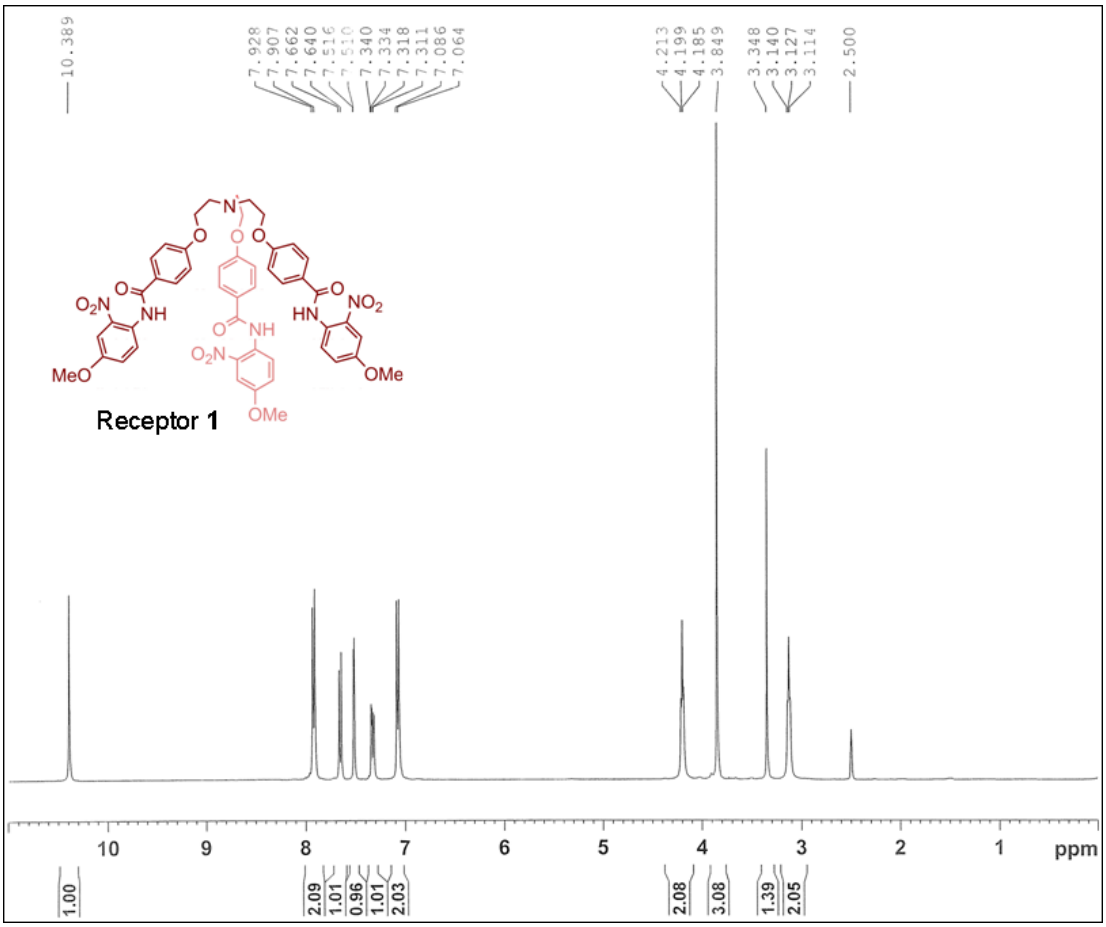


Fig. S1 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **1**.

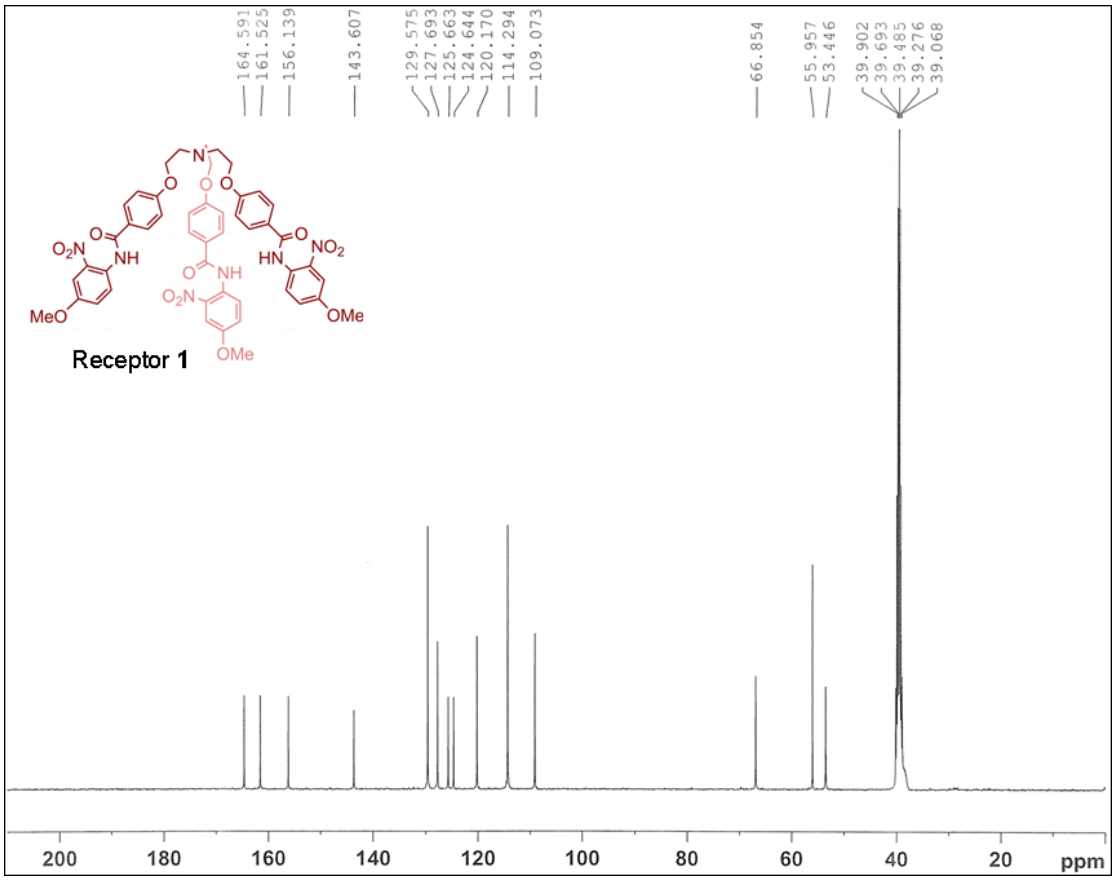


Fig. S2 ^{13}C NMR (100 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **1**.

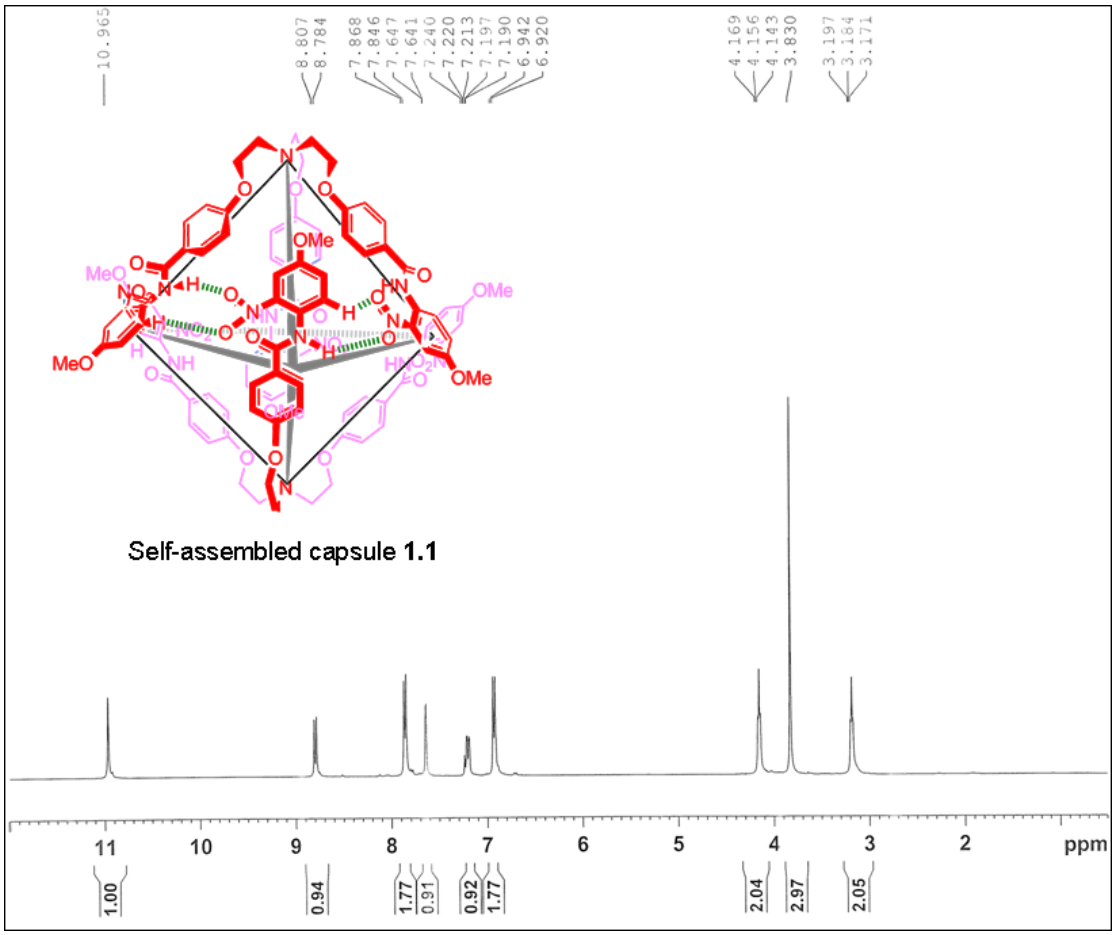


Fig. S3 ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) spectrum of self-assembled capsule **1.1**.

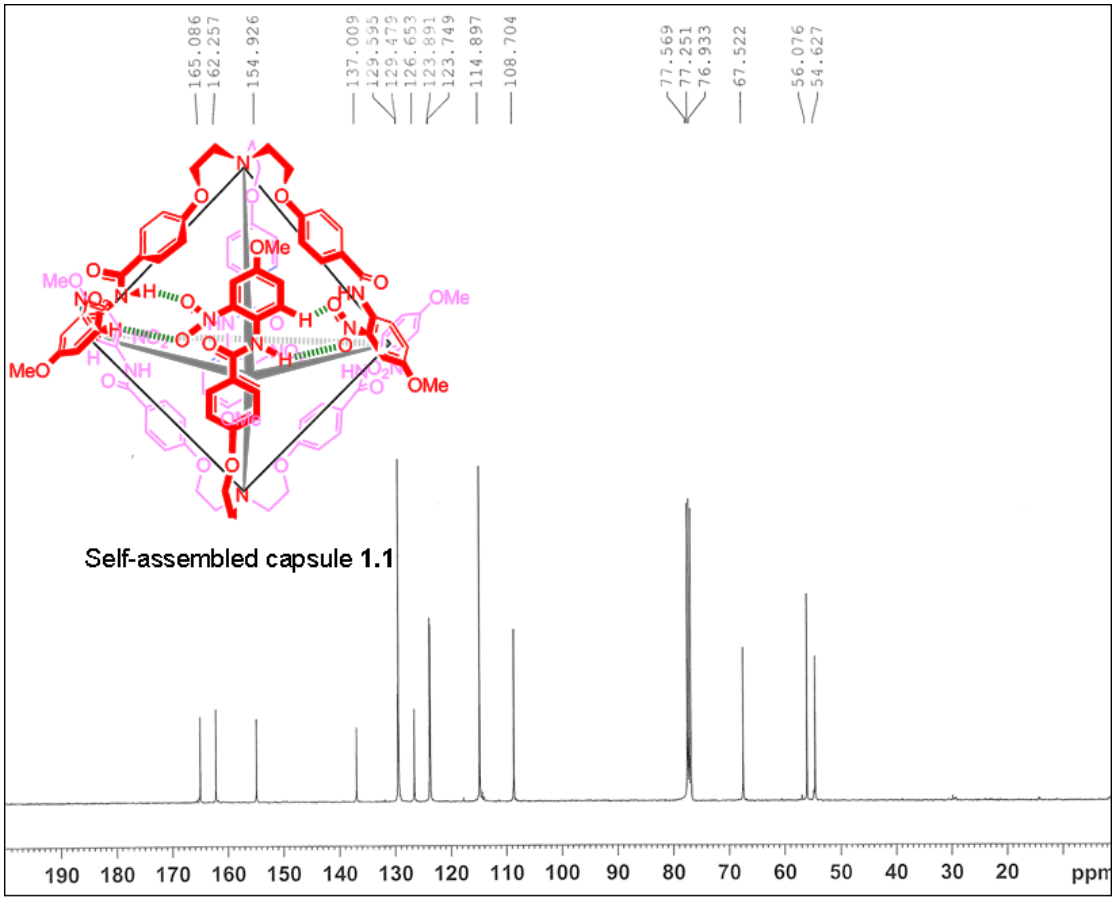


Fig. S4 ^{13}C NMR (100 MHz, $CDCl_3$, 20 ºC) spectrum of self-assembled capsule **1.1**.

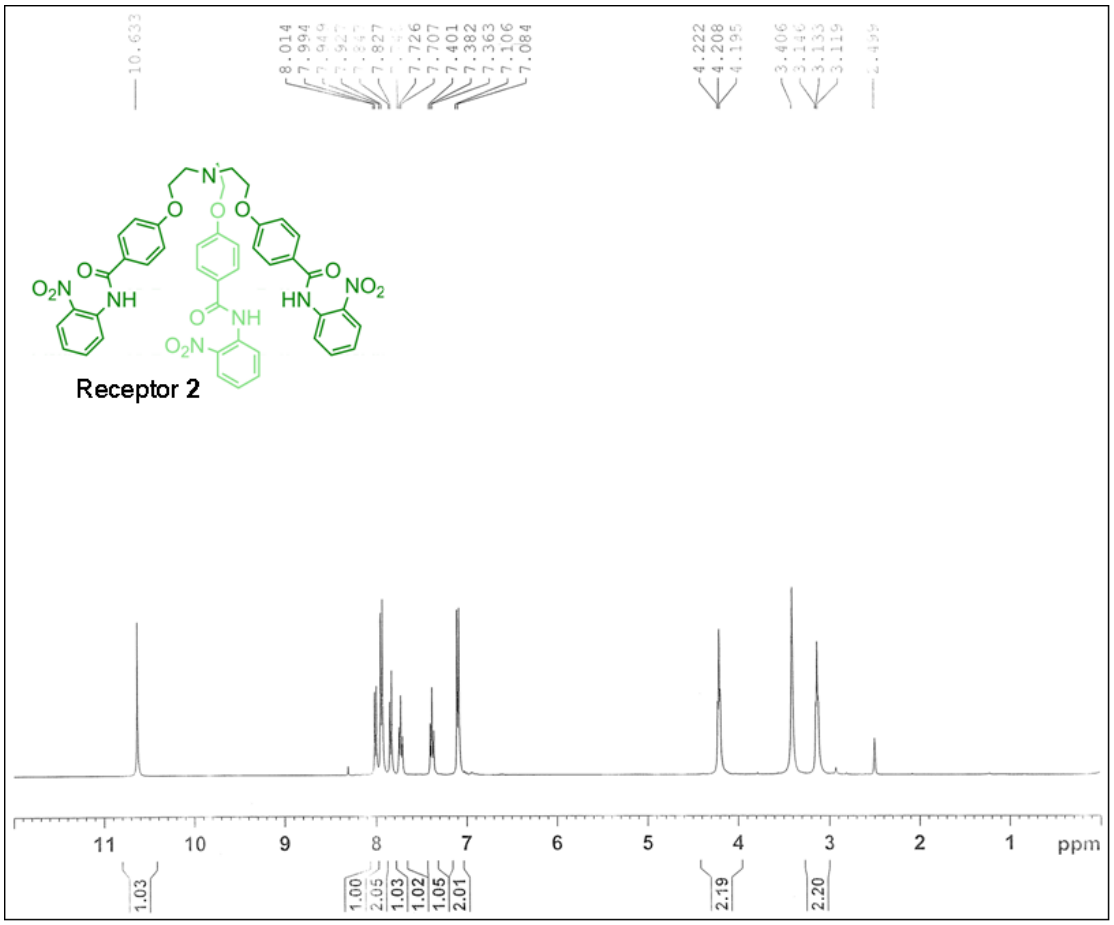


Fig. S5 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **2**.

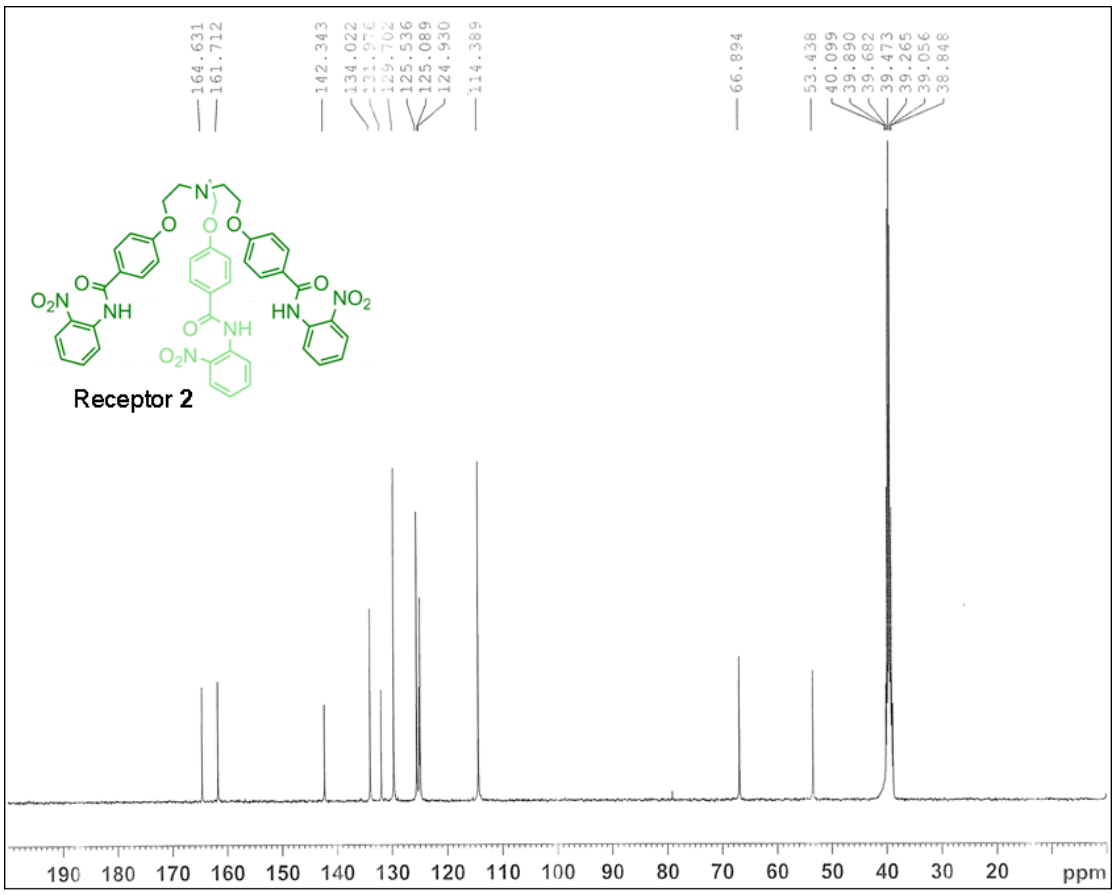


Fig. S6 ^{13}C NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **2**.

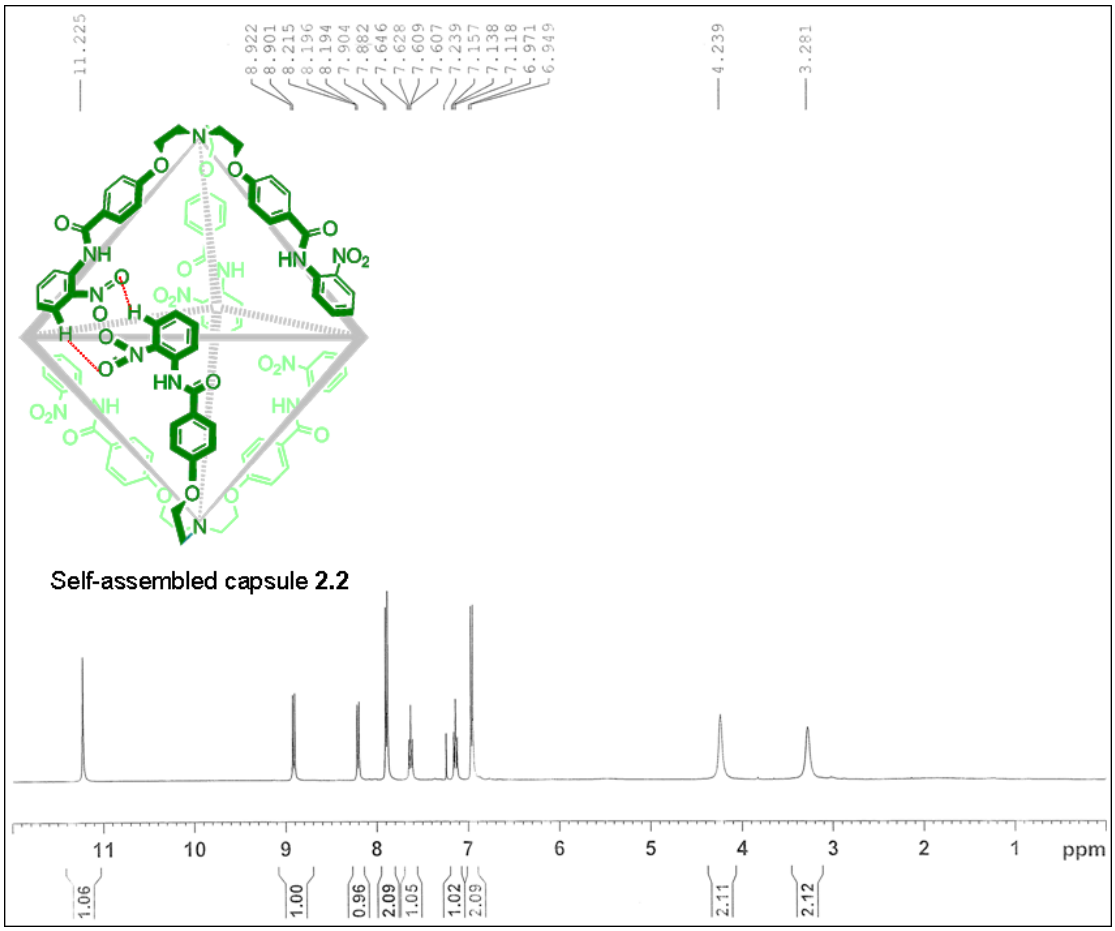


Fig. S7 ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) spectrum of self-assembled capsule **2.2**.

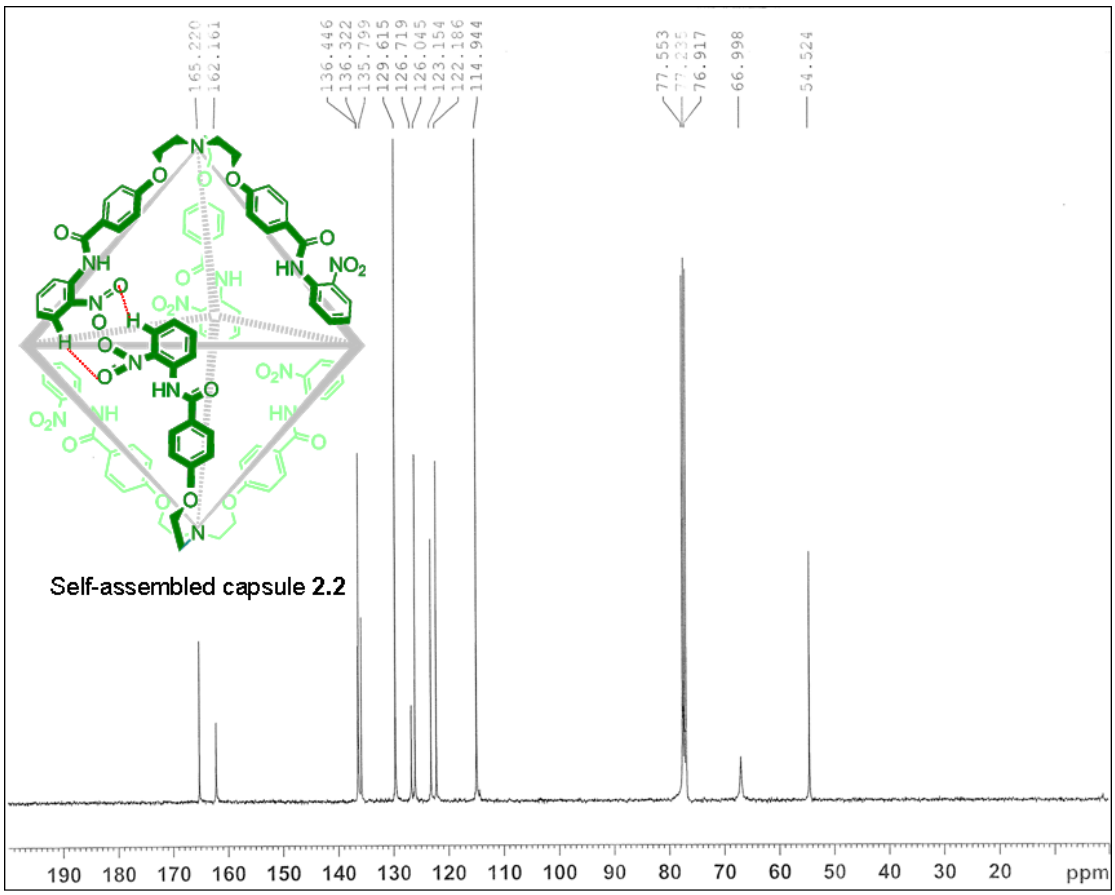


Fig. S8 ^{13}C NMR (400 MHz, $CDCl_3$, 20 ºC) spectrum of self-assembled capsule **2.2**.

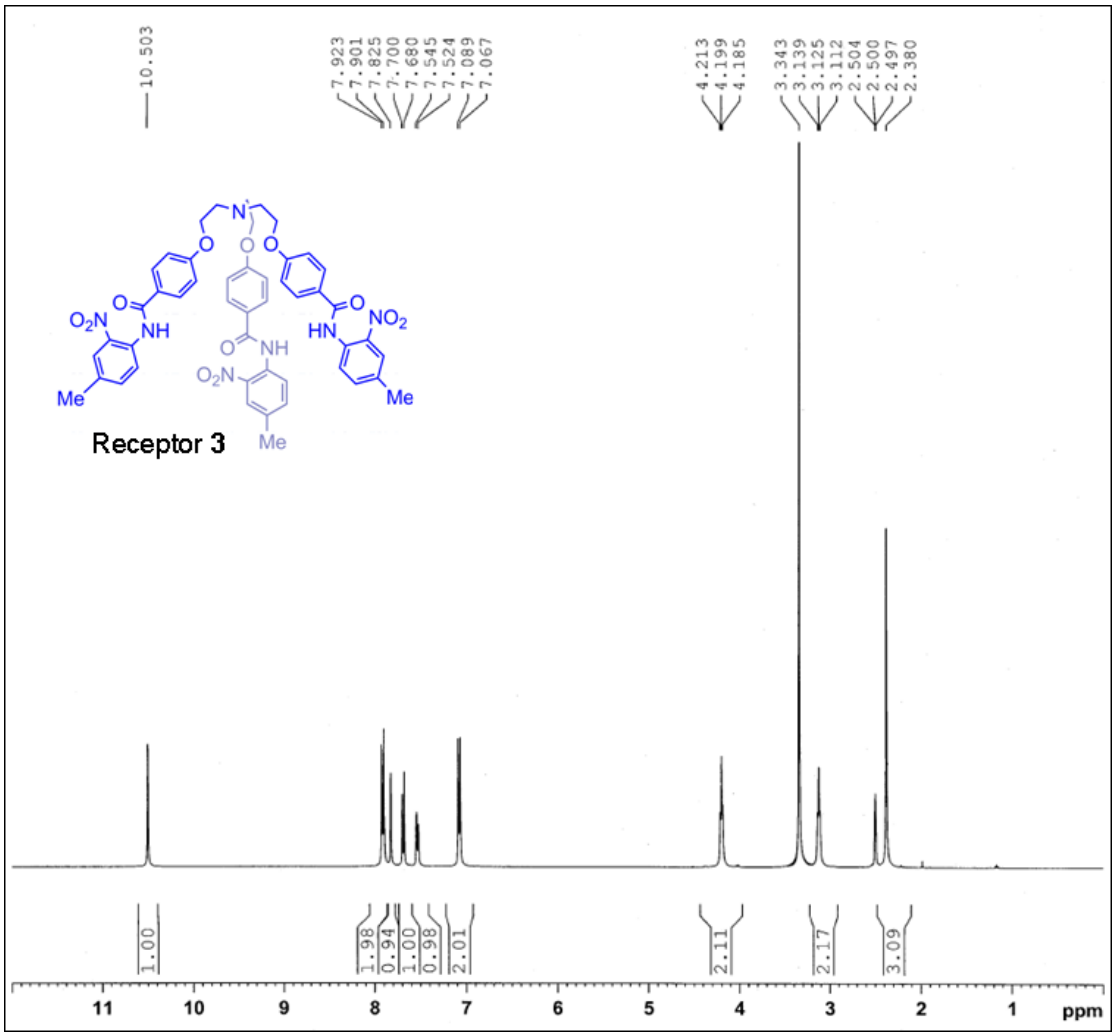


Fig. S9 ^{1}H NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **3**.

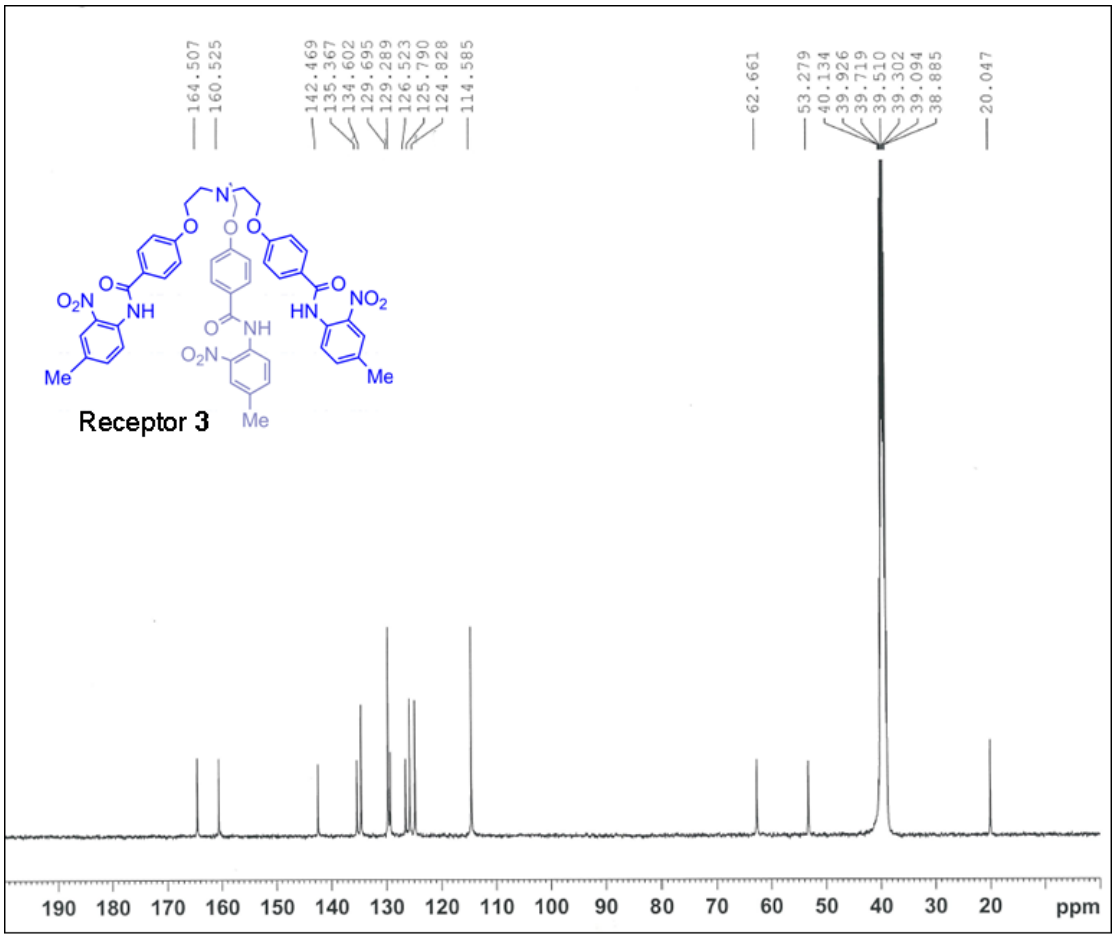


Fig. S10 ^{13}C NMR (400 MHz, DMSO-d_6, 20 ºC) spectrum of receptor **3**.

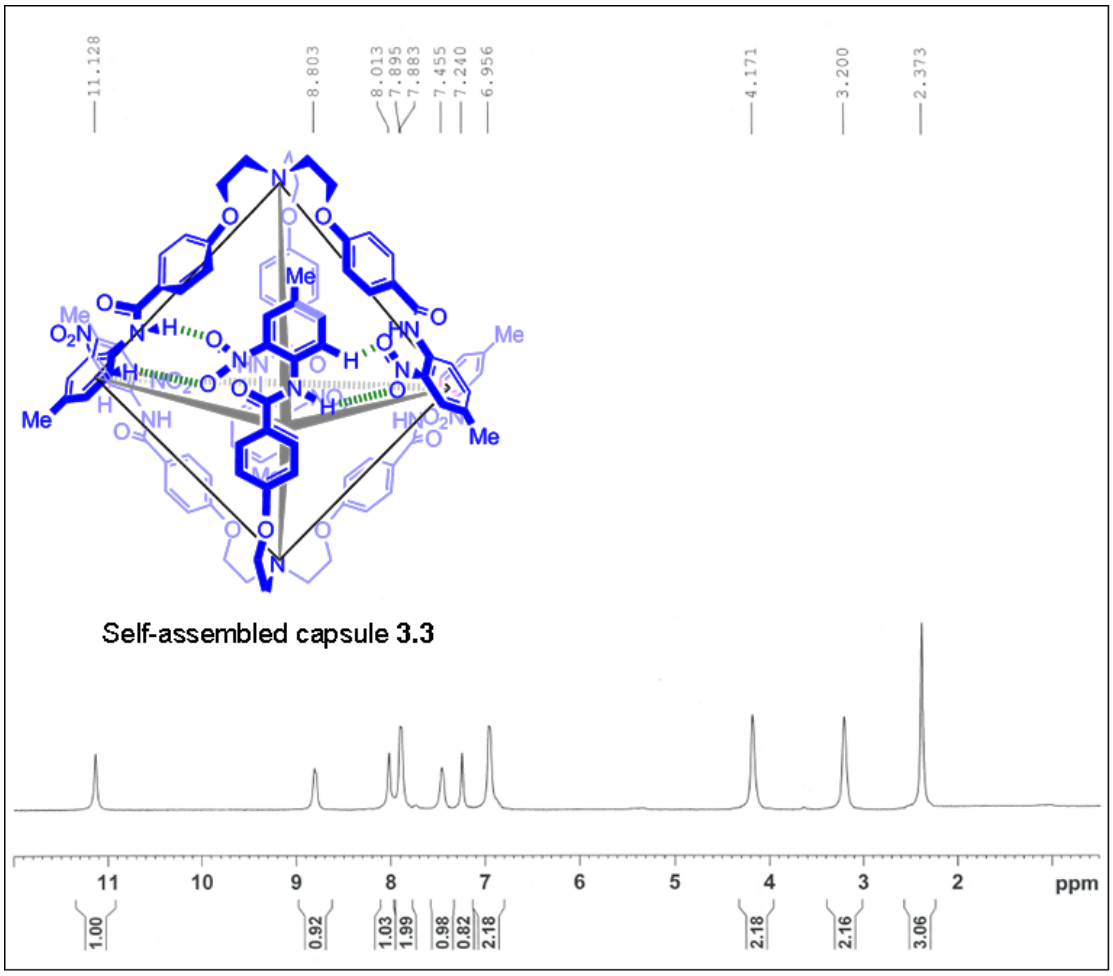


Fig. S11 ^{1}H NMR (400 MHz, $CDCl_3$, 20 ºC) spectrum of self-assembled capsule **3.3**.

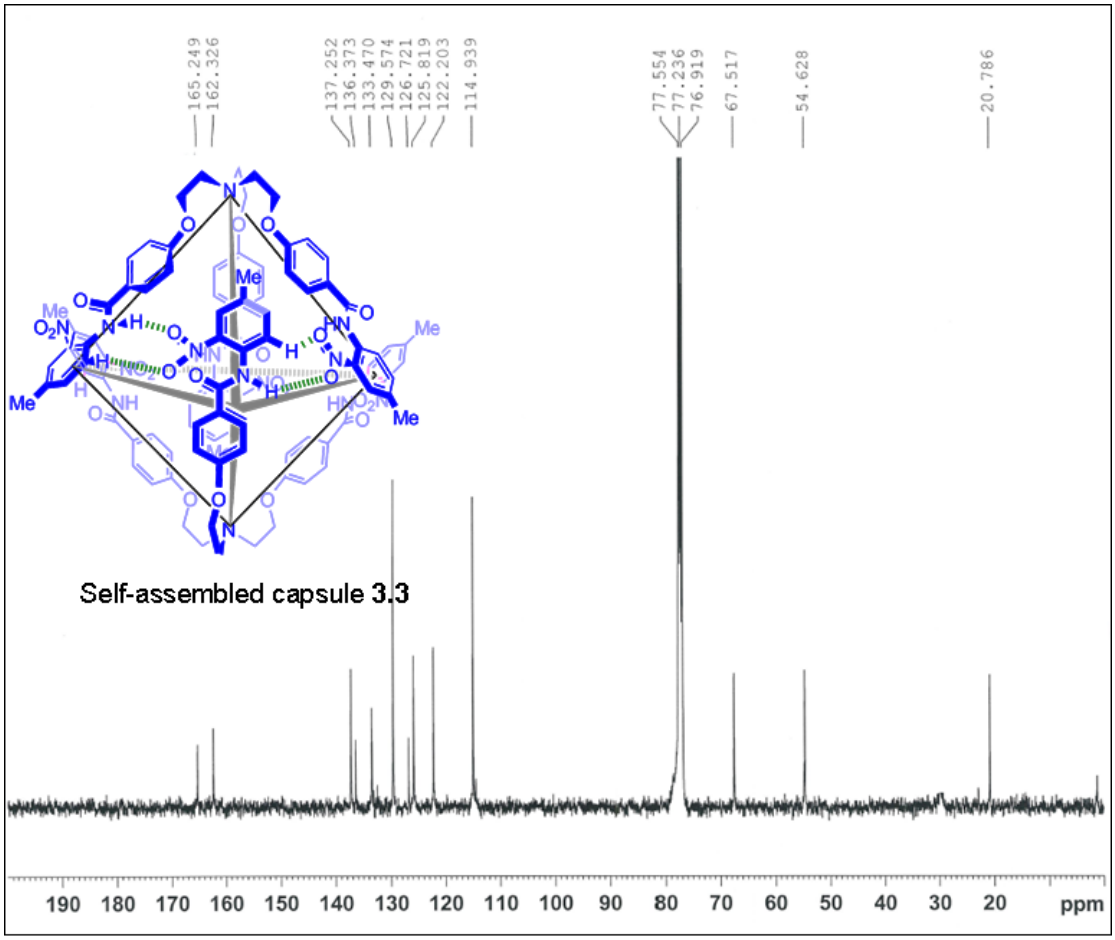


Fig. S12 ^{13}C NMR (400 MHz, $CDCl_3$, 20 ºC) spectrum of self-assembled capsule **3.3**.

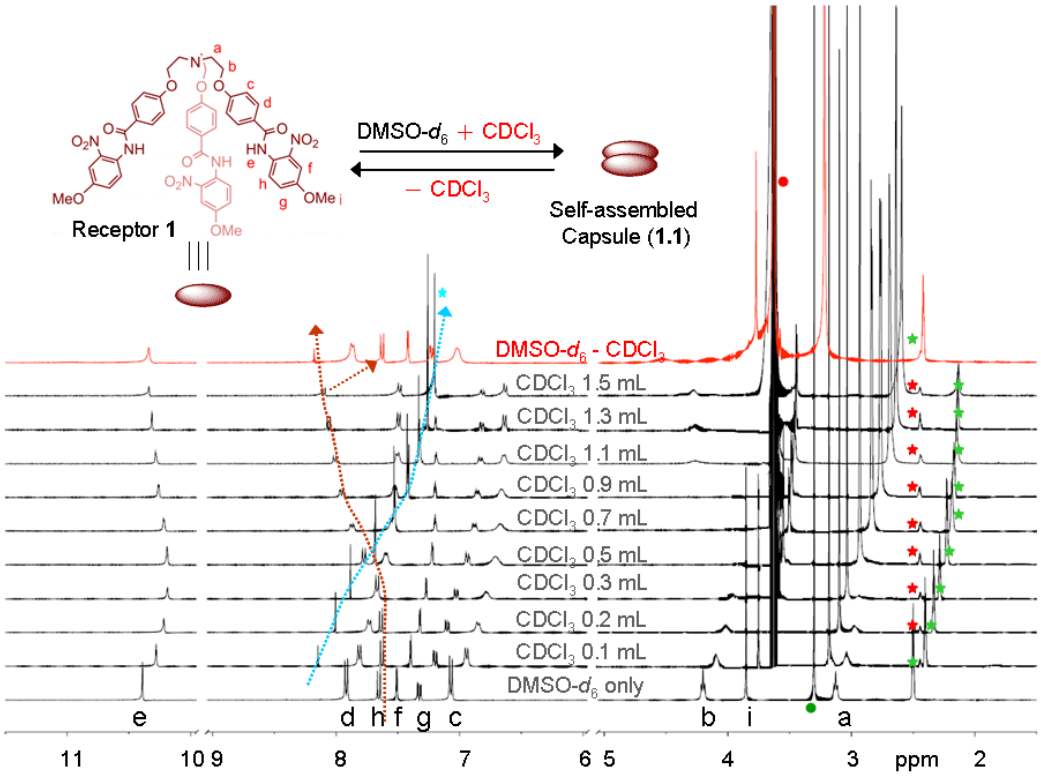


Fig. S13 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **1** (10.3 mM) in a DMSO-d_6 solution with varying amount of $CDCl_3$ with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal 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**.

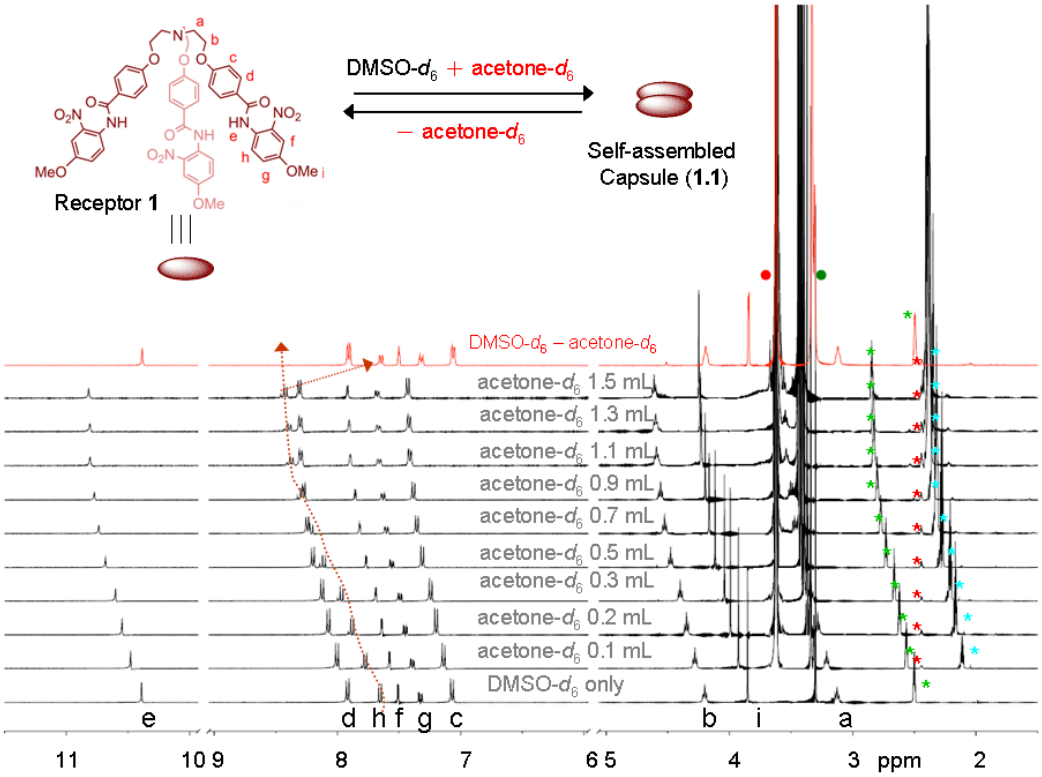


Fig. S14 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **1** (10.3 mM) in a DMSO-d_6 solution with varying amount of acetone-d_6 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the 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**.

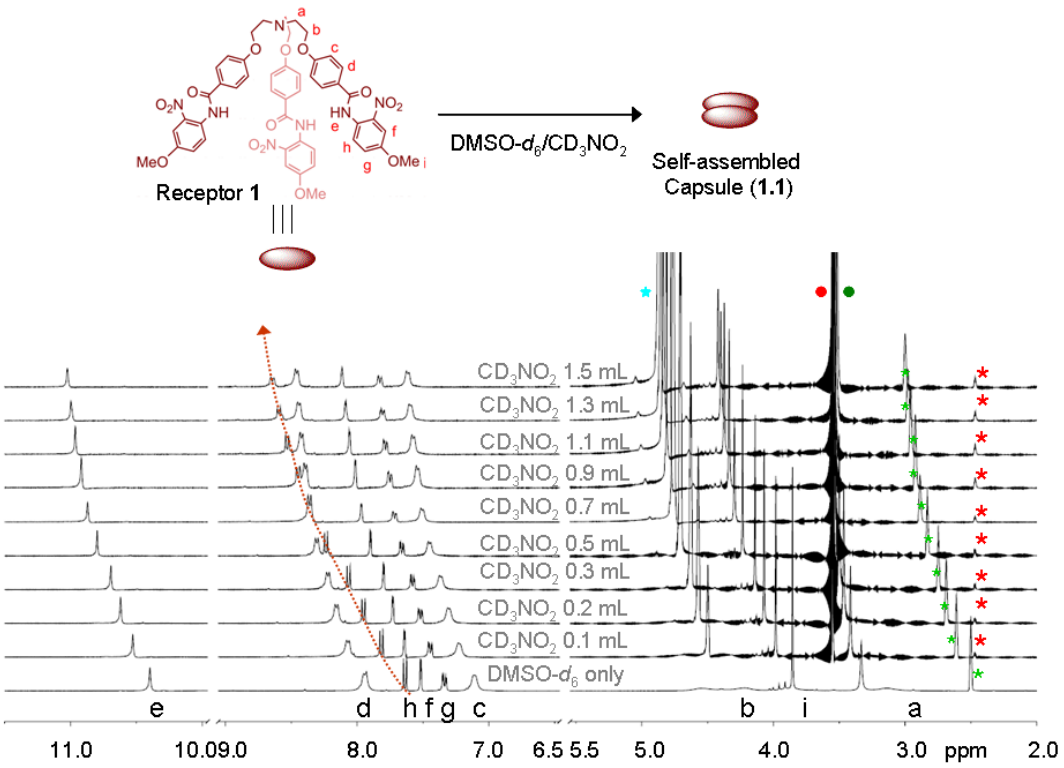


Fig. S15 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **1** (10.3 mM) in a DMSO-d_6 solution with varying amount of CD_3NO_2 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal 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_3NO_2.

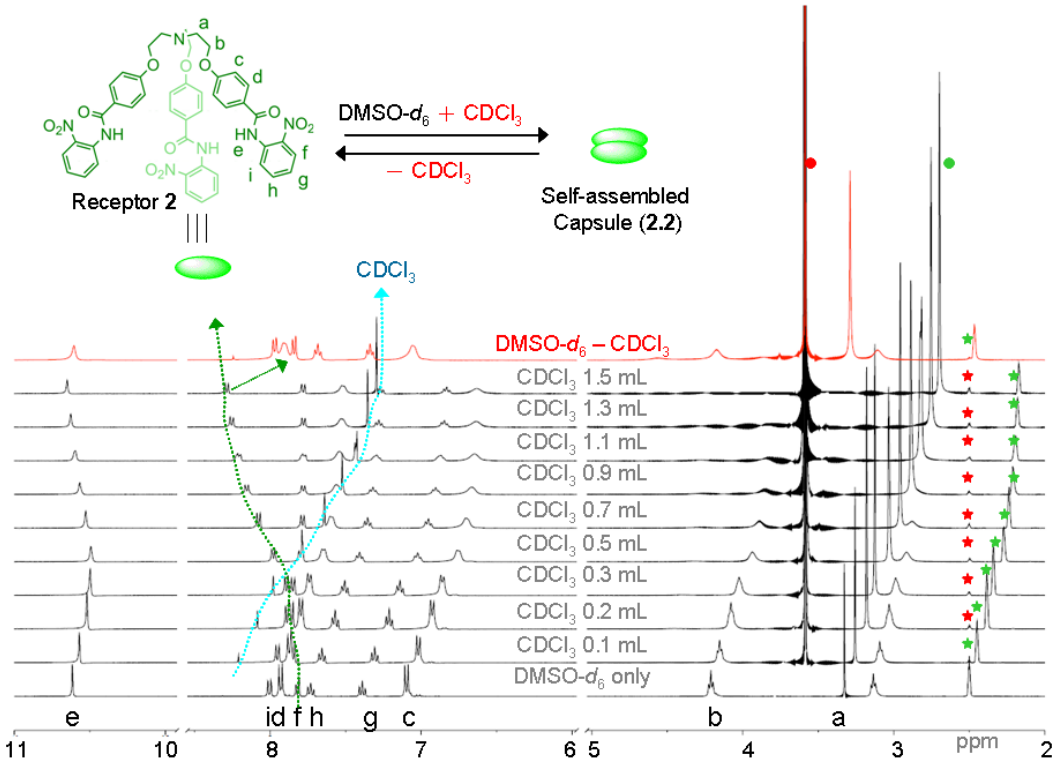


Fig. S16 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **2** (10.3 mM) in a DMSO-d_6 solution with varying amount of $CDCl_3$ with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal reference. Circles in green and red color represent the peaks for water from solvent DMSO-d_6 and from internal reference, respectively. A dash line 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 capsule formation through dynamic self-assembly of receptor **2**.

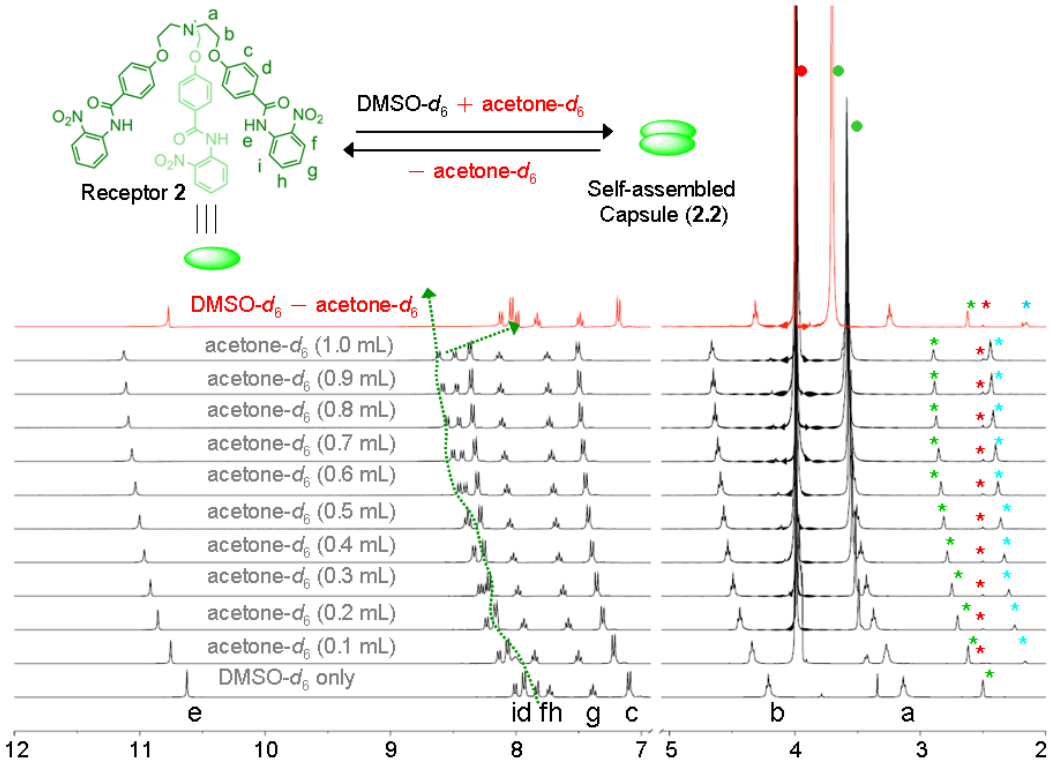


Fig. S17 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **2** (10.3 mM) in a DMSO-d_6 solution with varying amount of acetone-d_6 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the 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 capsule formation through dynamic self-assembly of receptor **2**.

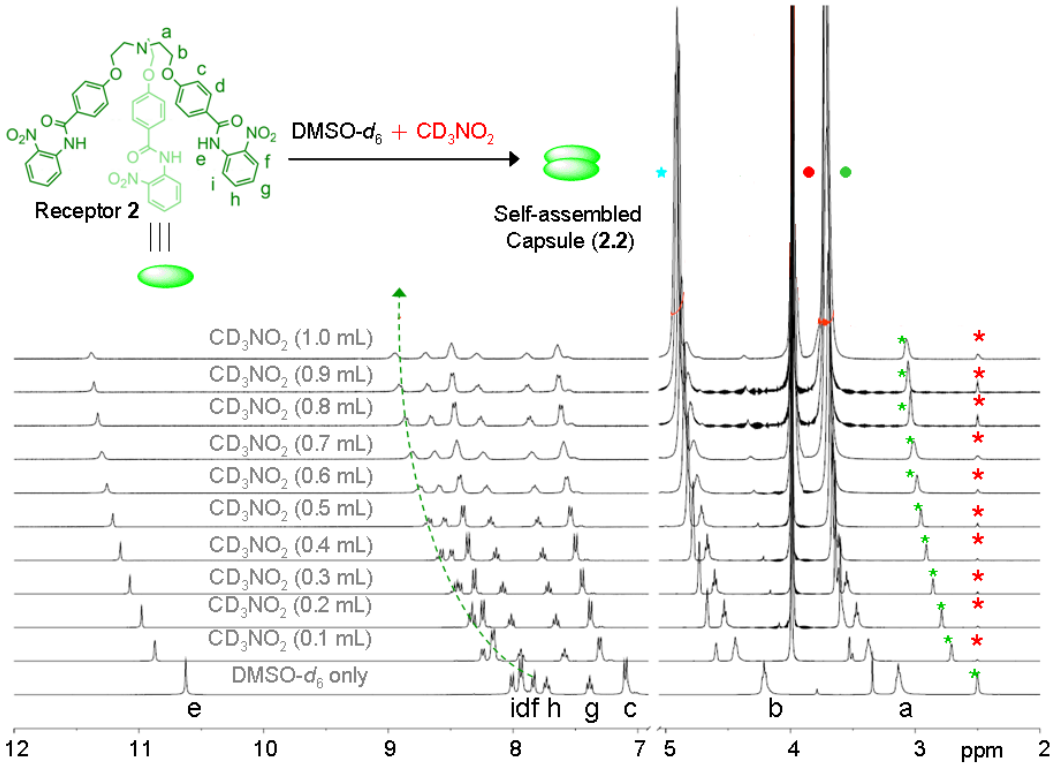


Fig. S18 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **2** (10.3 mM) in a DMSO-d_6 solution with varying amount of CD_3NO_2 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal 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_3NO_2.

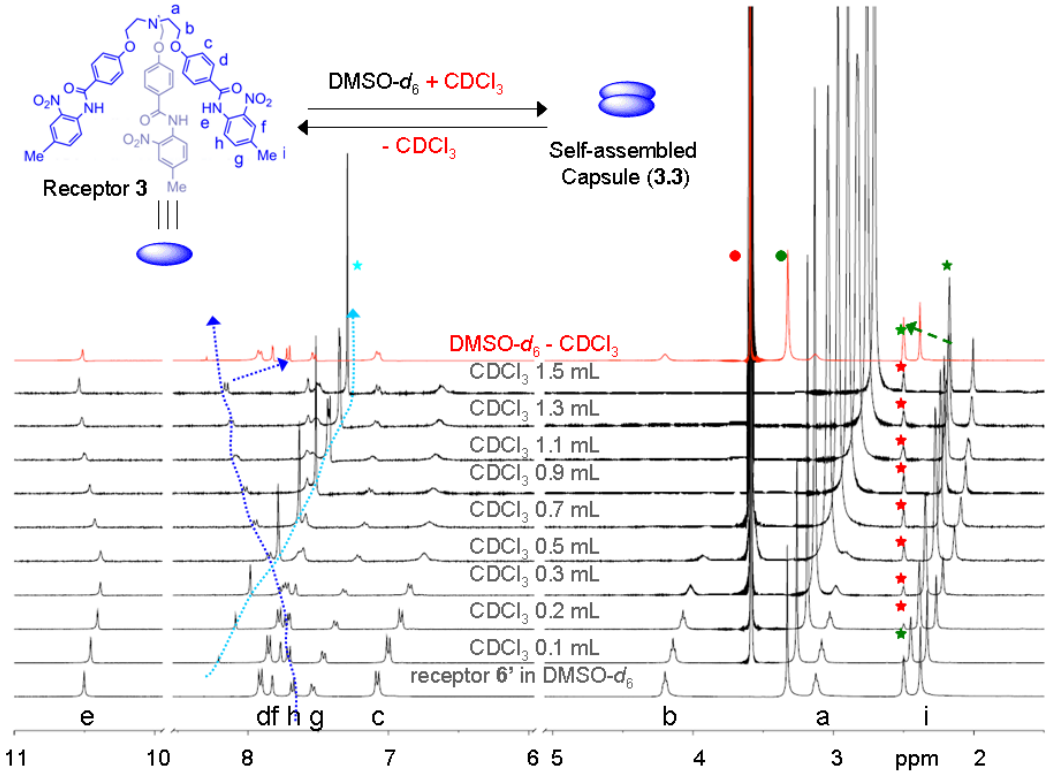


Fig. S19 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **3** (10.3 mM) in a DMSO-d_6 solution with varying amount of $CDCl_3$ with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal 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 **3**.

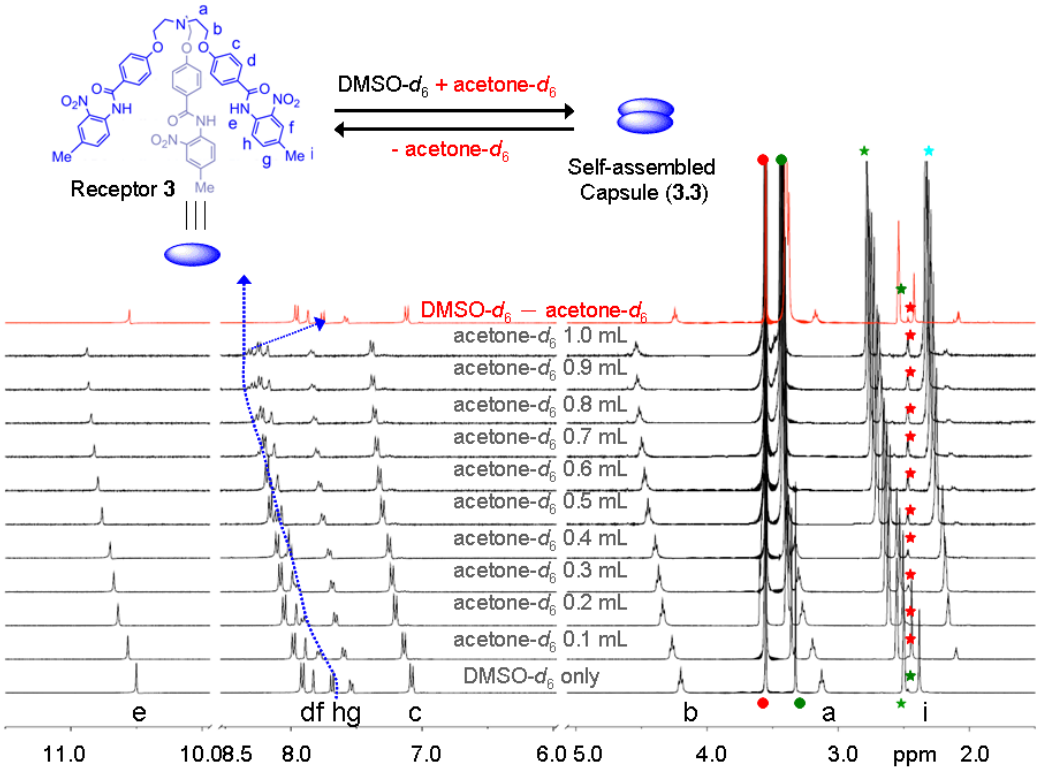


Fig. S20 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **3** (10.3 mM) in a DMSO-d_6 solution with varying amount of acetone-d_6 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the 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 capsule formation through dynamic self-assembly of receptor **3**.

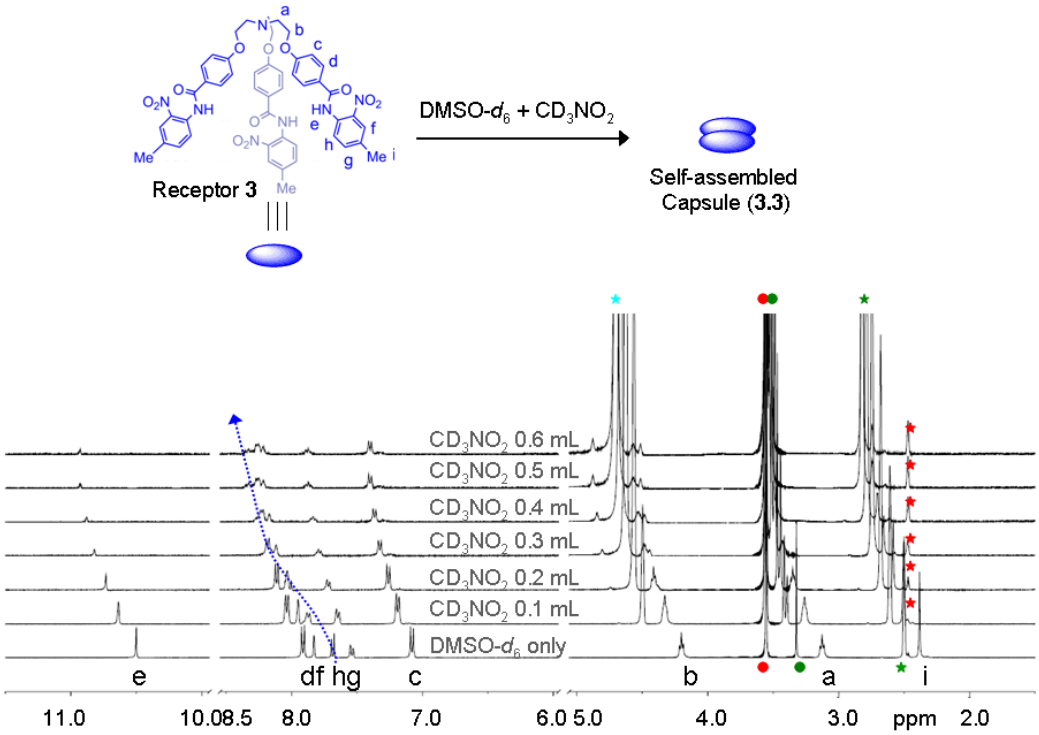


Fig. S21 ^{1}H NMR (400 MHz, 20 °C) titration spectra of receptor **3** (10.3 mM) in a DMSO-d_6 solution with varying amount of CD_3NO_2 with TMS (in DMSO-d_6) as the internal reference. Green stars represent the peaks of DMSO-d_6 used as solvent. Red stars represent the peaks of DMSO-d_6 from the internal 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_3NO_2.

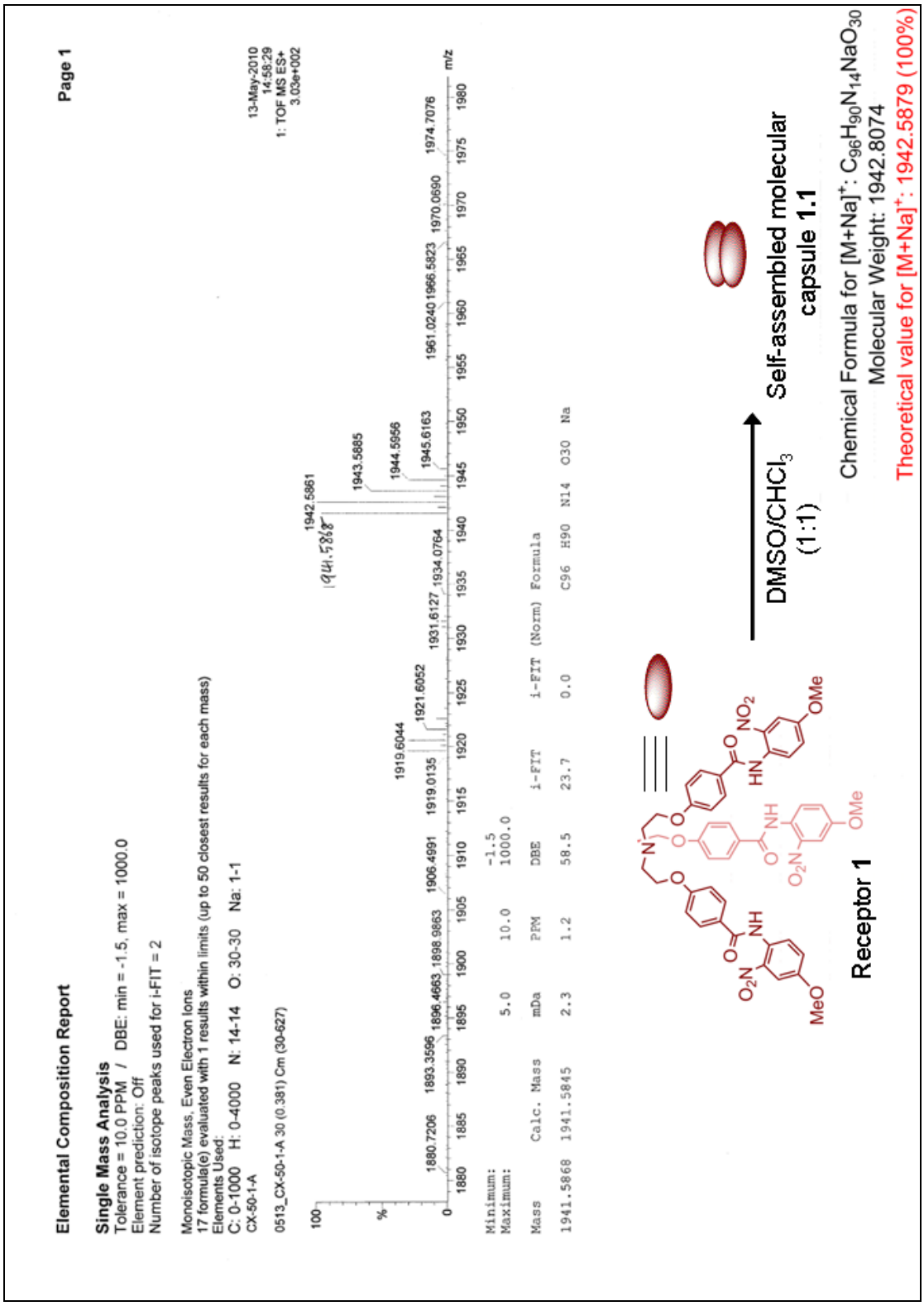


Fig. S22 HRESI mass spectrum of the self-assembled capsule (**1.1**) recorded after dissolving receptor **1** in a mixture solution of DMSO/$CHCl_3$ (1:1).

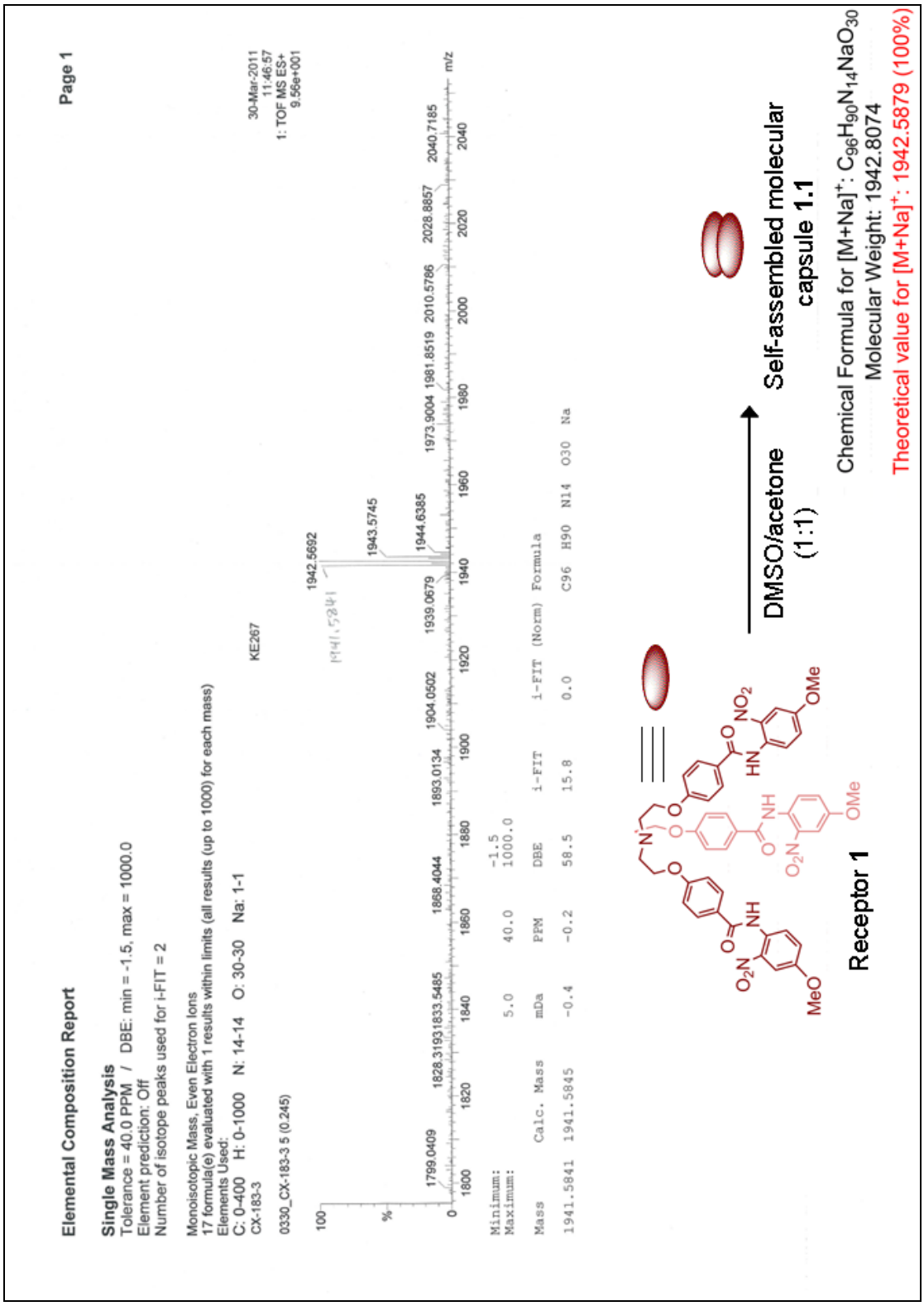


Fig. S23 HRESI mass spectrum of the self-assembled capsule (**1.1**) recorded after dissolving receptor **1** in a mixture solution of DMSO/acetone (1:1).

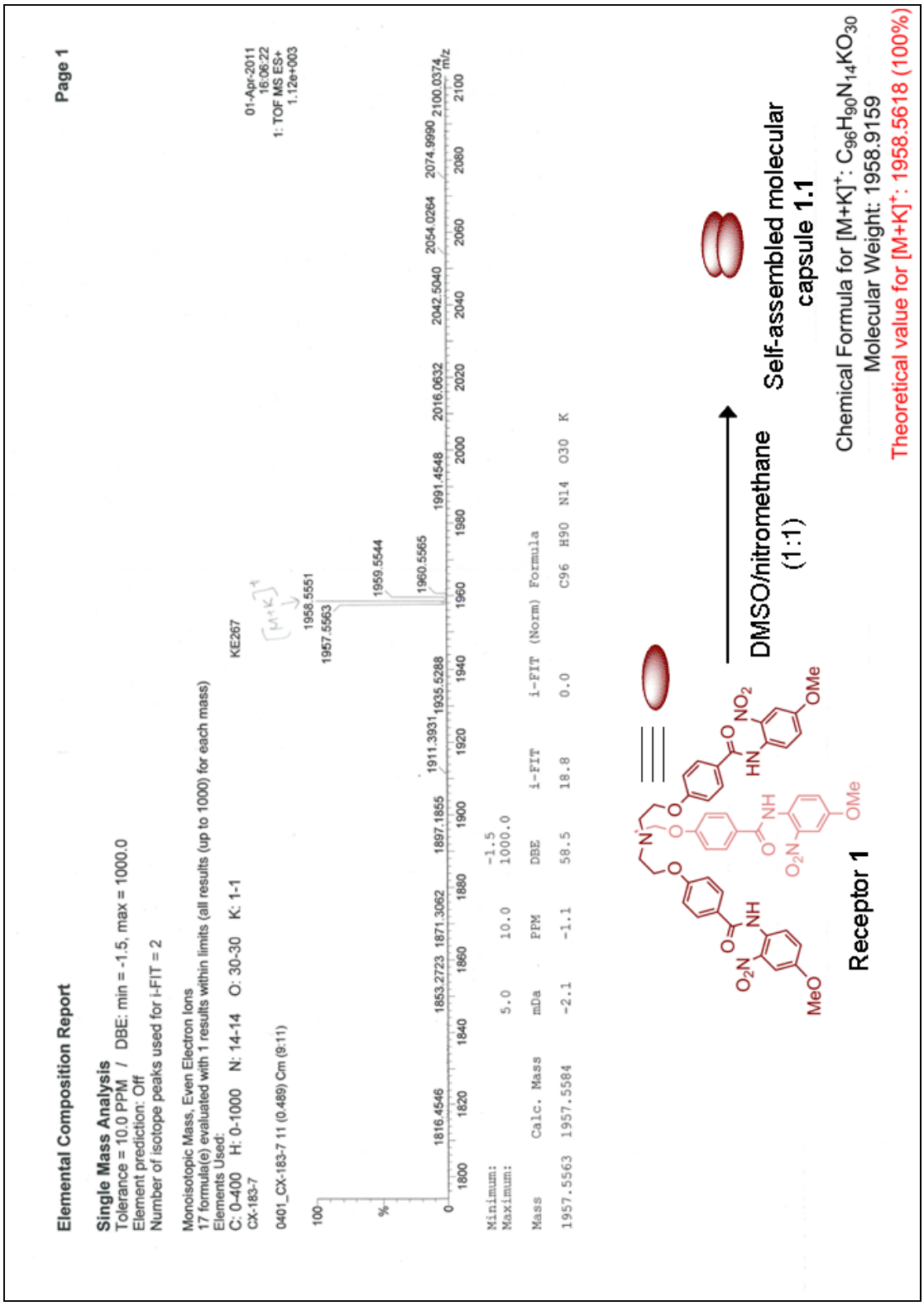


Fig. S24 HRESI mass spectrum of the self-assembled capsule (**1.1**) recorded after dissolving receptor **1** in a mixture solution of DMSO/nitromethane (1:1).

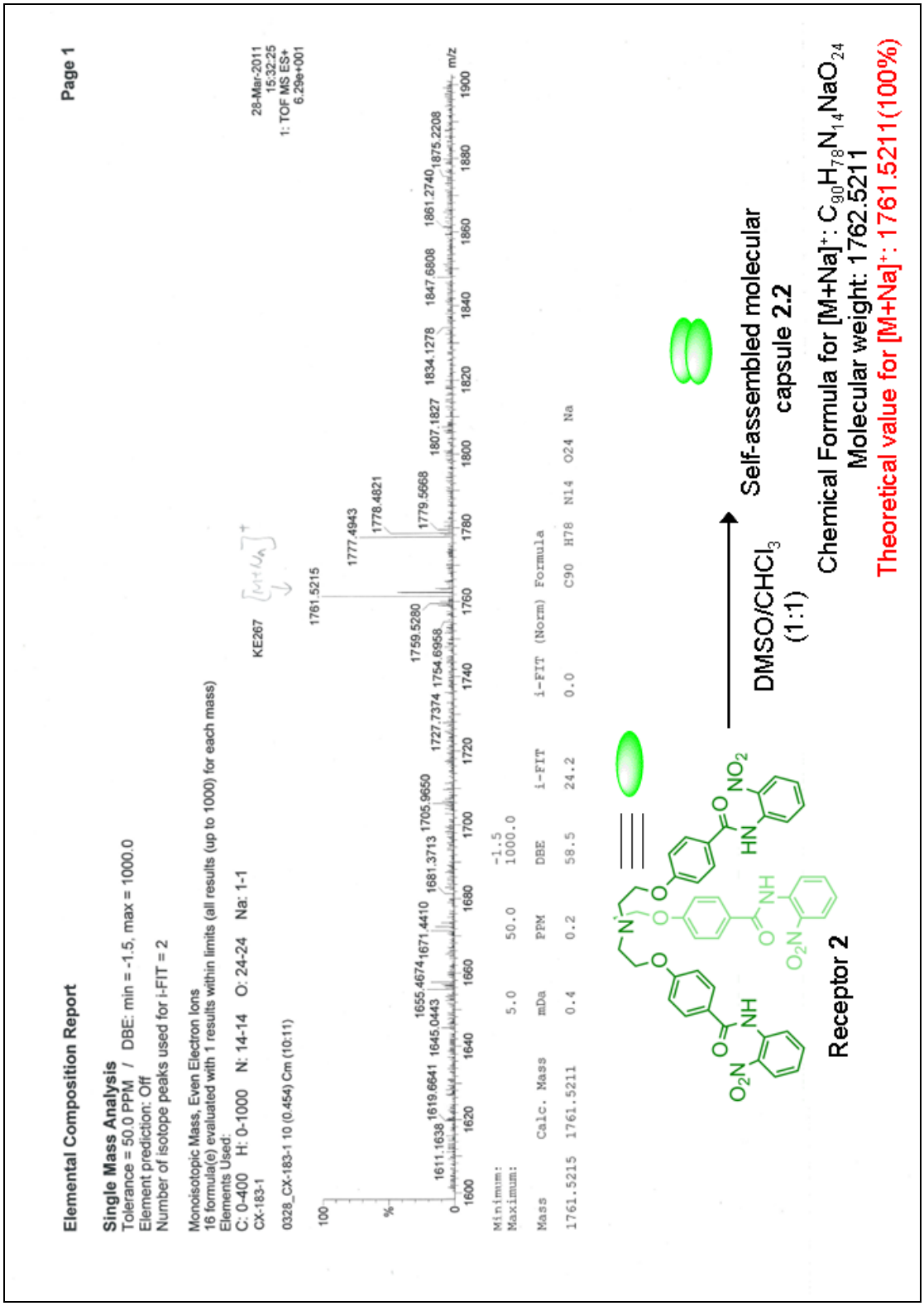


Fig. S25 HRESI mass spectrum of the self-assembled capsule (**2.2**) recorded after dissolving receptor **2** in a mixture solution of DMSO/$CHCl_3$ (1:1).

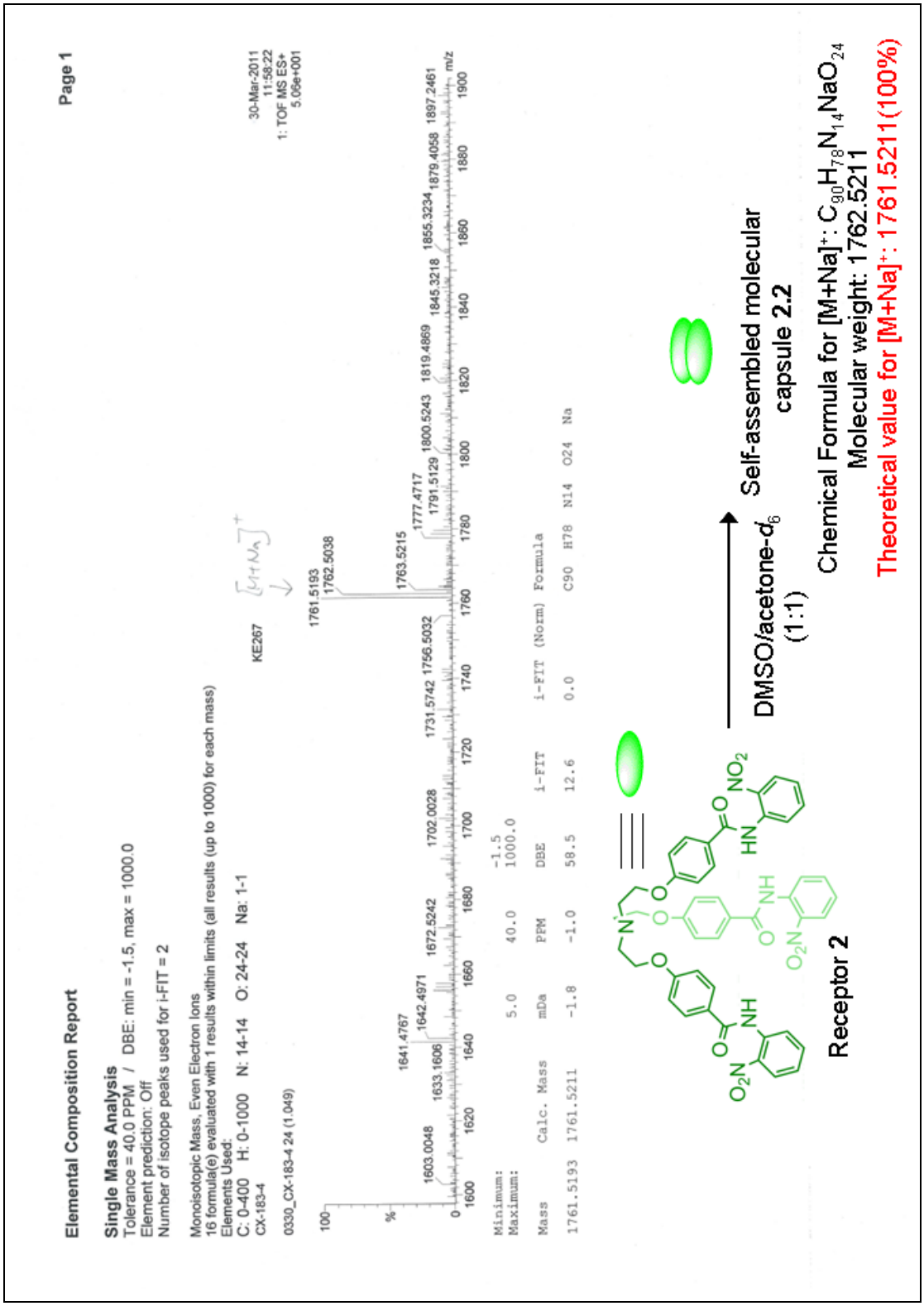


Fig. S26 HRESI mass spectrum of the self-assembled capsule (**2.2**) recorded after dissolving receptor **2** in a mixture solution of DMSO/acetone (1:1).

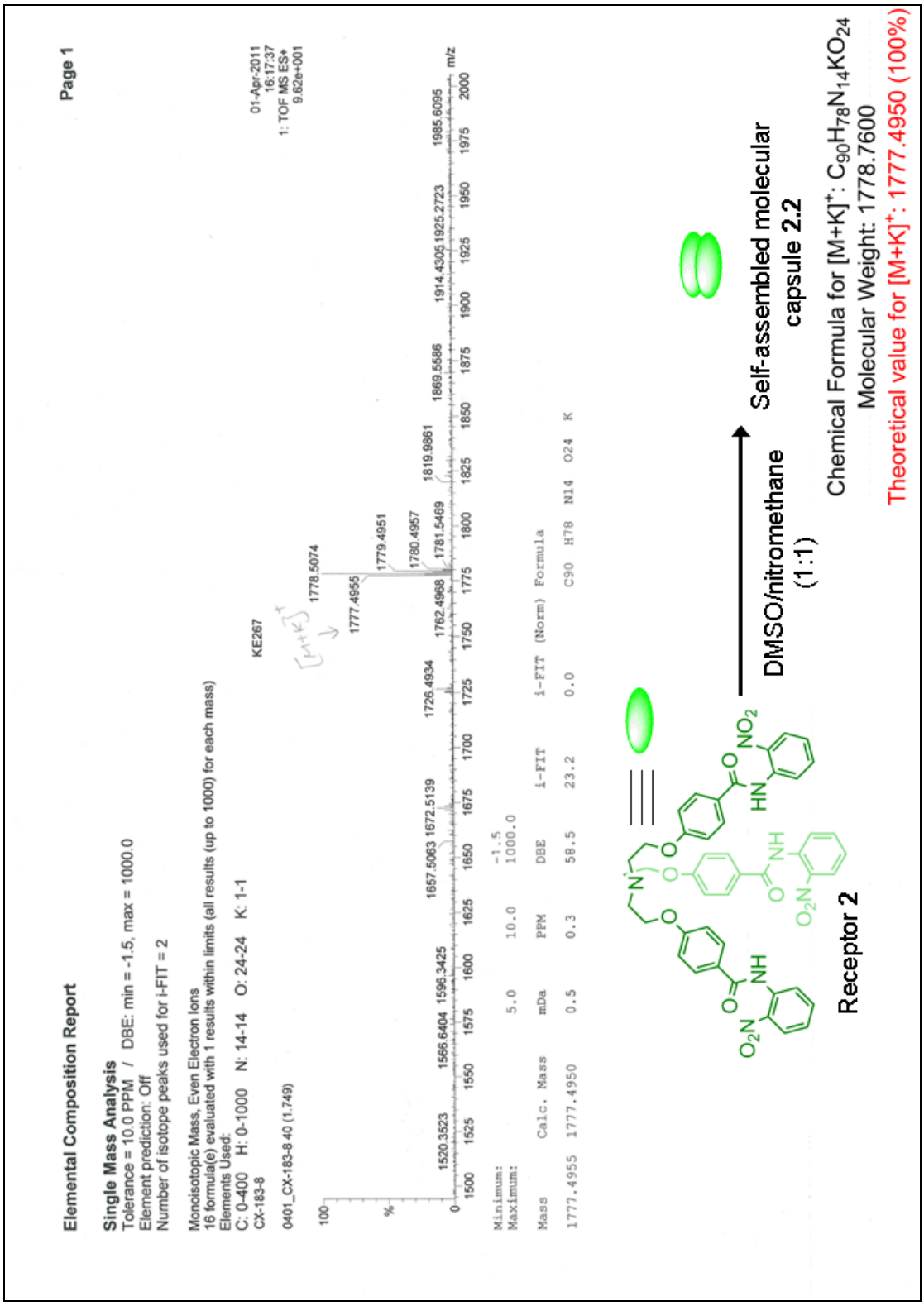


Fig. S27 HRESI mass spectrum of the self-assembled capsule (**2.2**) recorded after dissolving receptor **2** in a mixture solution of DMSO/nitromethane (1:1).

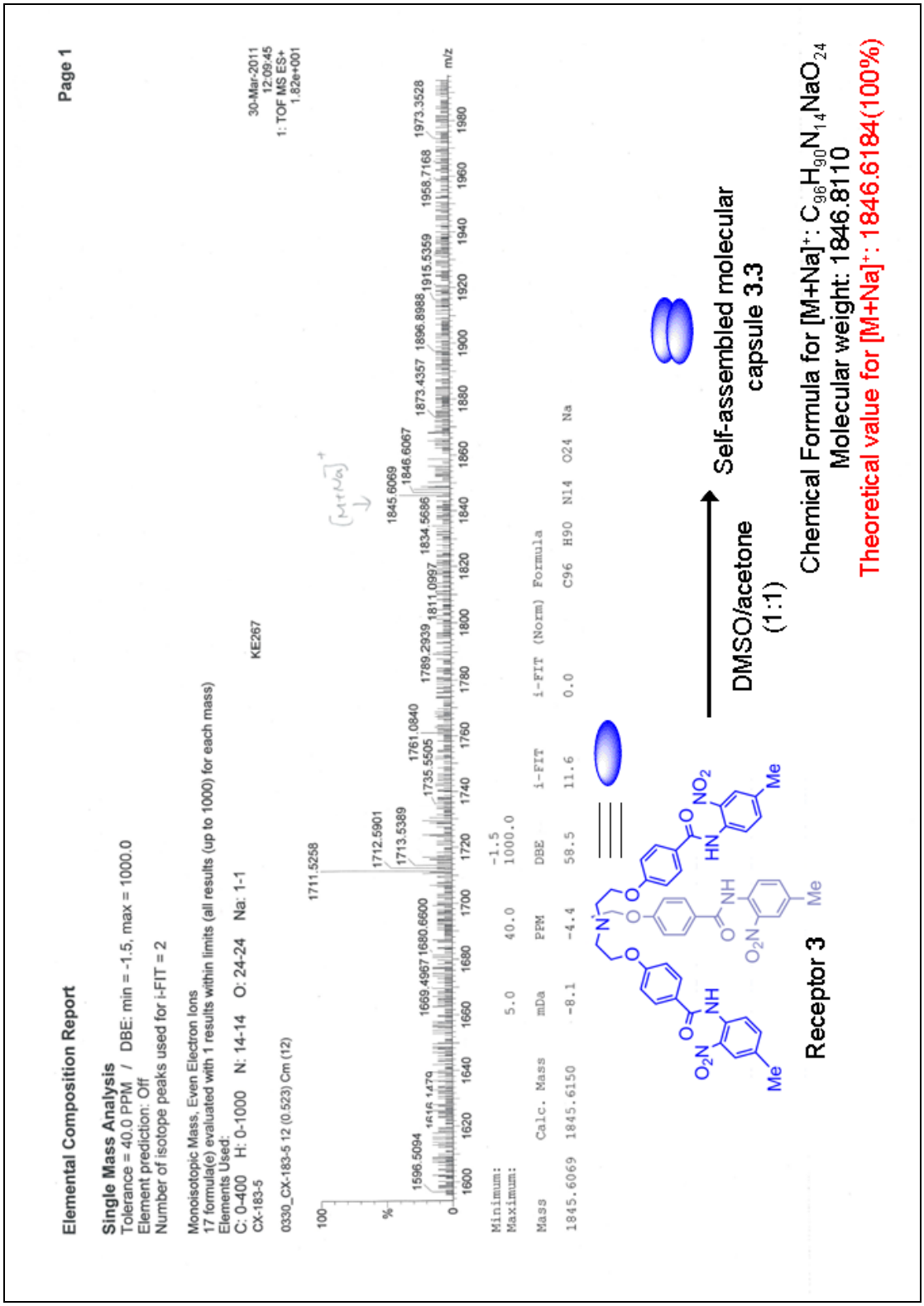


Fig. S28 HRESI mass spectrum of the self-assembled capsule (**3.3**) recorded after dissolving receptor **3** in a mixture solution of DMSO/acetone (1:1).

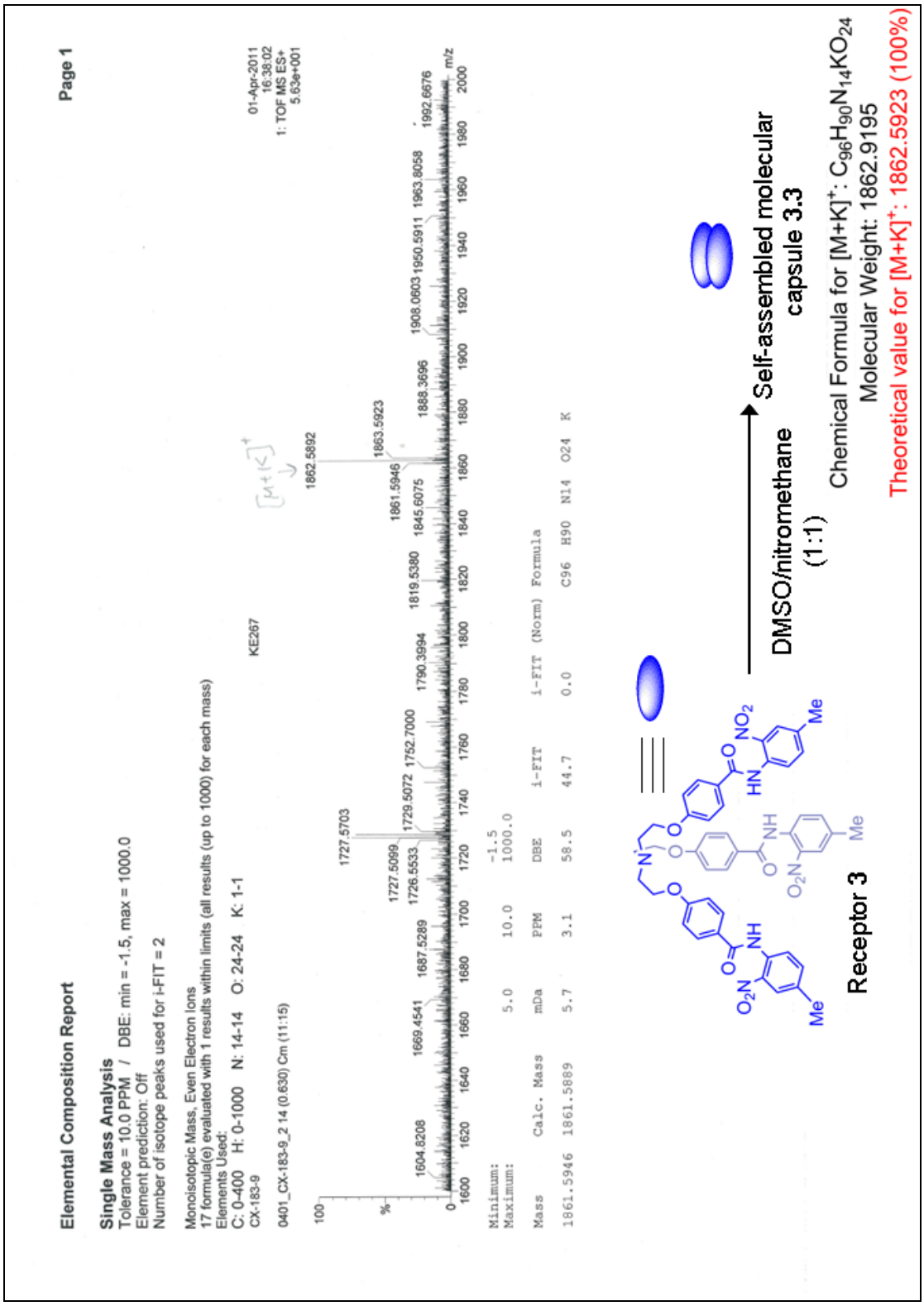


Fig. S29 HRESI mass spectrum of the self-assembled capsule (**3.3**) recorded after dissolving receptor **3** in a mixture solution of DMSO/nitromethane (1:1).

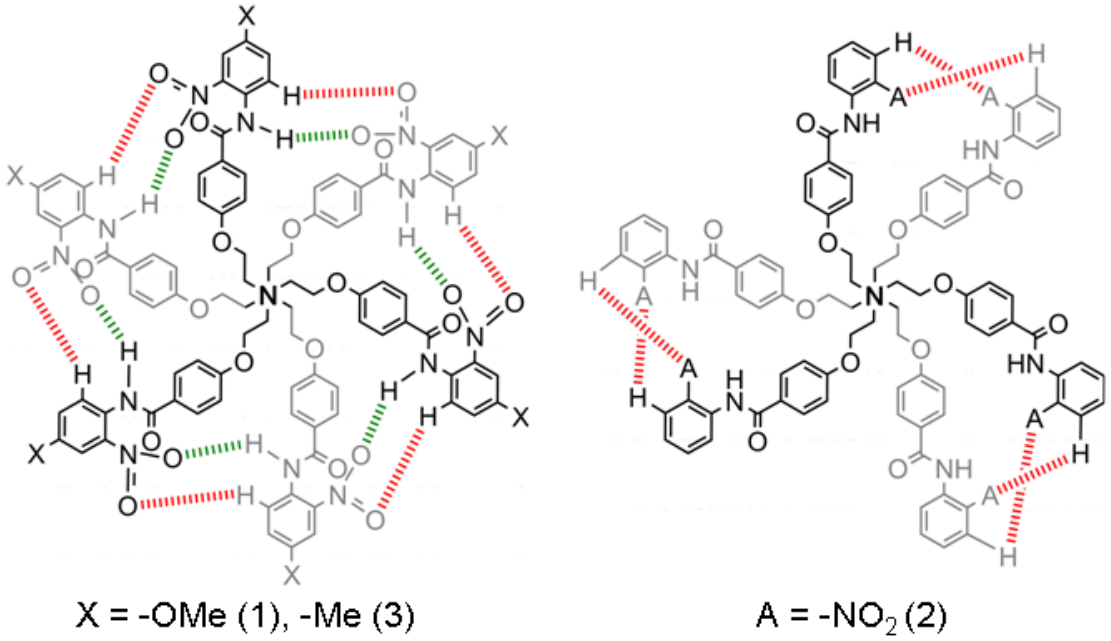


Fig. S30 The binding modes of self-assembled capsules for receptors **1** and **3** (left) and model receptor **2** (right), respectively.

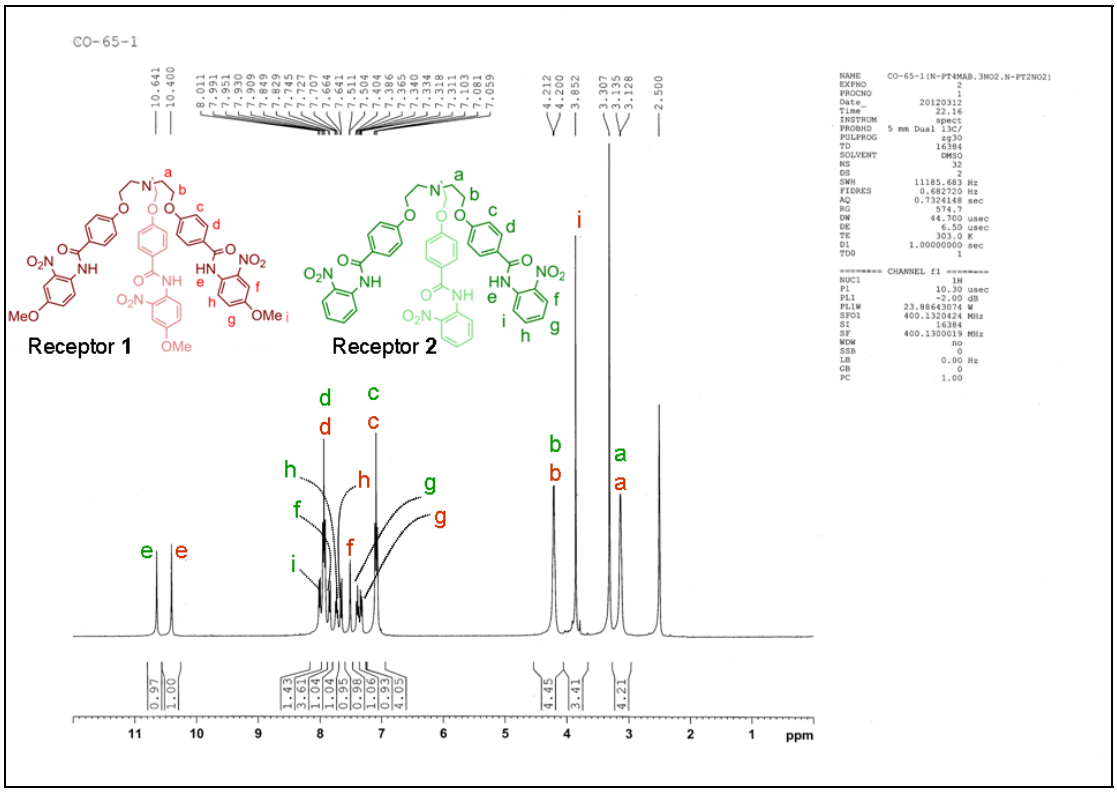


Fig. S31 ^{1}H NMR (400 MHz, DMSO-d_6, 30 ºC) spectrum of the mixture of receptors **1** and **2** (in 1:1 ratio, [c] = 6.25 mM).

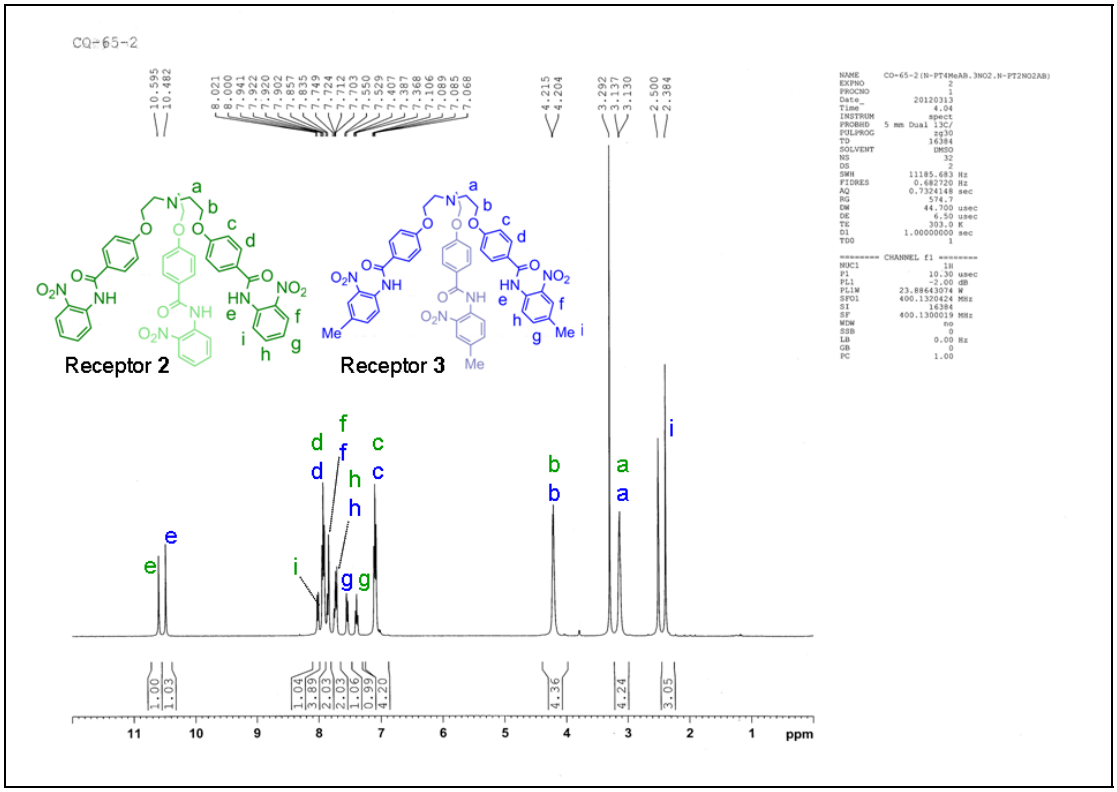


Fig. S32 ^{1}H NMR (400 MHz, DMSO-d_6, 30 ºC) spectrum of the mixture of receptors **2** and **3** (in 1:1 ratio, [c] = 6.25 mM).

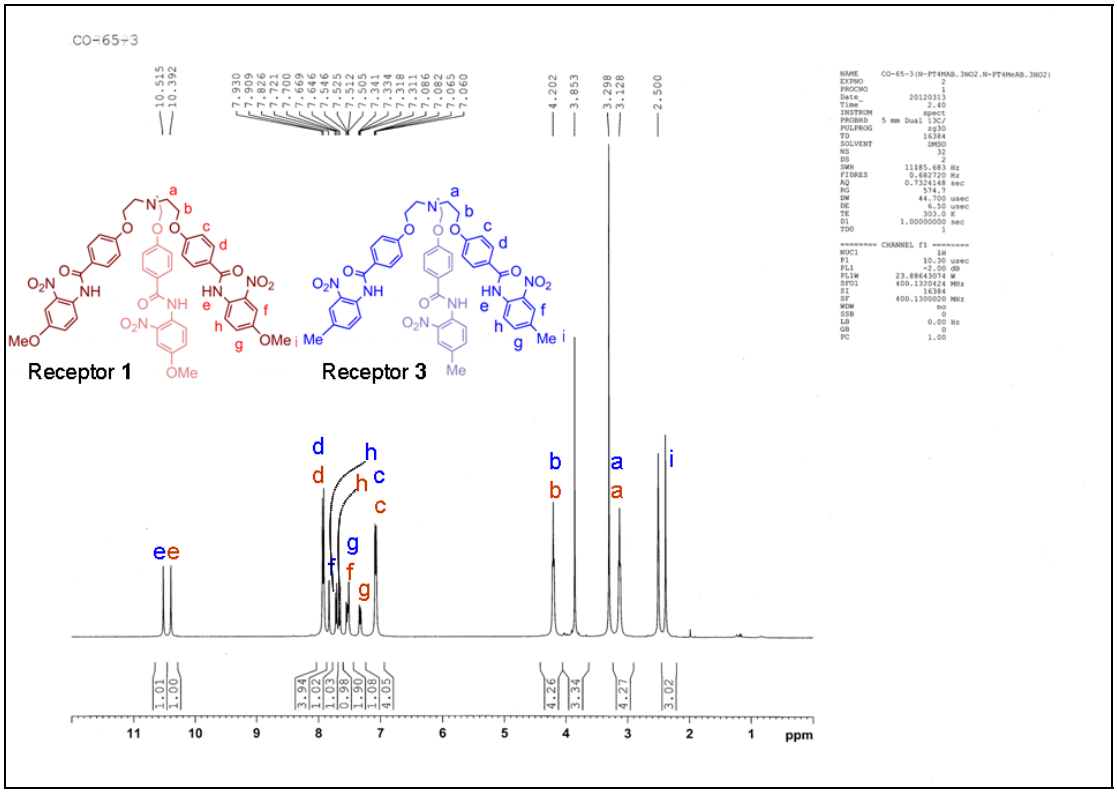


Fig. S33 ^{1}H NMR (400 MHz, DMSO-d_6, 30 ºC) spectrum of the mixture of receptors **1** and **3** (in 1:1 ratio, [c] = 6.25 mM).

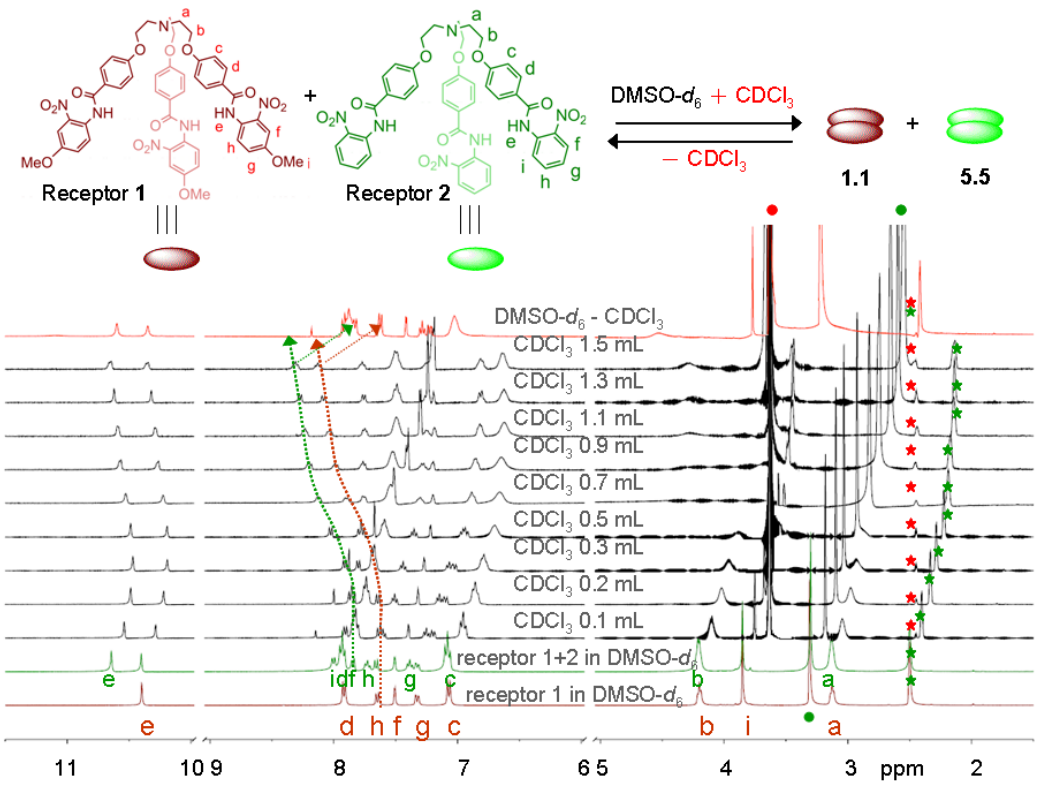


Fig. S34 Two-component self-sorting: ^{1}H NMR (400 MHz, 30 ºC) titration spectra of receptors **1** and **2** in a 1:1 ratio (6.25 mM each) in a DMSO-d_6 solution upon addition of varying amount of $CDCl_3$. After partial evaporation of $CDCl_3$, the resulting spectra (in red color) merged to the original one recorded in DMSO-d_6. Star marks in green and red colors in spectra represent peaks for DMSO-d_6 solvent and from internal reference in TMS, respectively. Circle marks in green and red colors represent the residual water peaks from deuterated solvents.

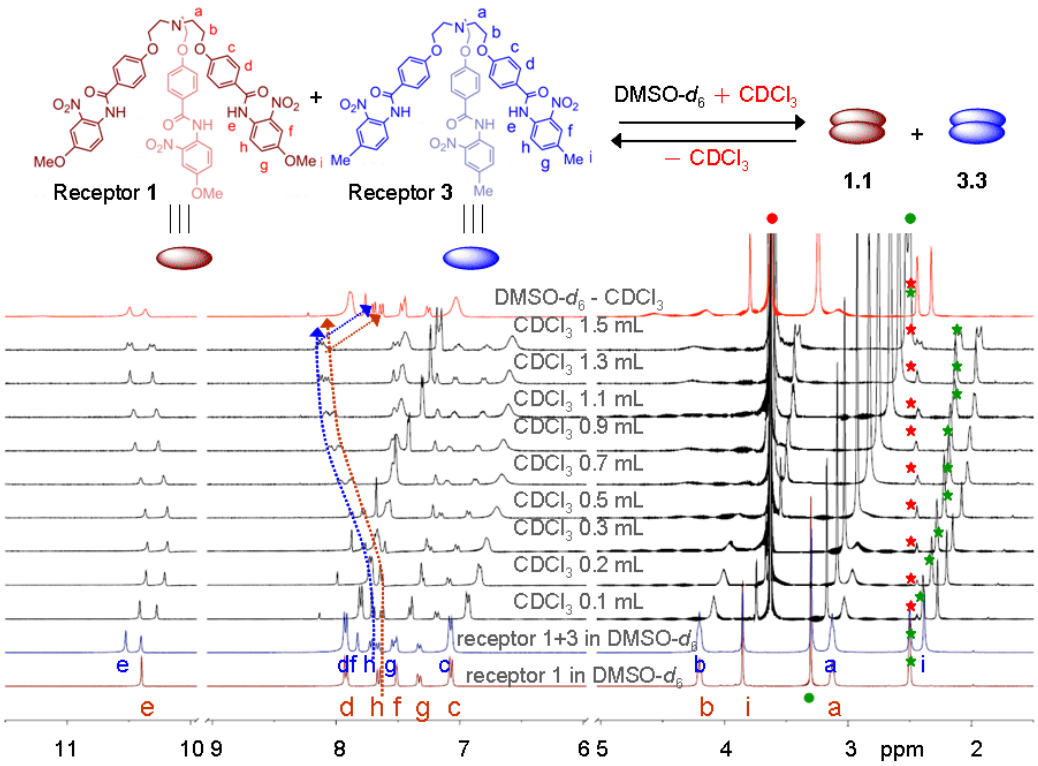


Fig. S35 ^{1}H NMR (400 MHz, 30 ºC) titration spectra of receptors **1** and **3** (in 1:1 ratio, 6.25 mM each) in a DMSO-d_6 solution upon addition of varying amount of $CDCl_3$. After partial evaporation of $CDCl_3$ the resulting spectrum (in red color) merged to the original one recorded in DMSO-d_6. Star marks in green and red colors in all spectra represent peaks for DMSO-d_6 solvent and from internal reference in TMS, respectively. Circle marks in green and red colors represent the residual water peaks from deuterated solvents.

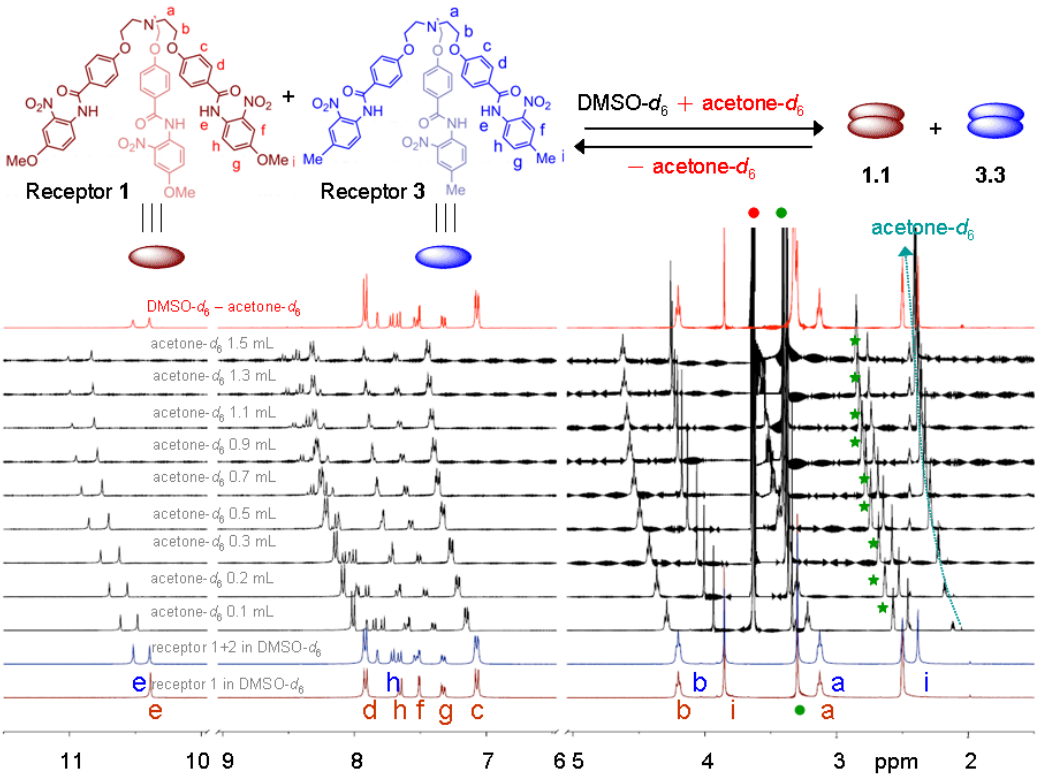


Fig. S36 ^{1}H NMR (400 MHz, 30 ºC) titration spectra of receptors **1** and **3** (in 1:1 ratio, 6.25 mM each) in a DMSO-d_6 solution upon addition of varying amount of acetone-d_6. After partial evaporation of acetone-d_6 the resulting spectrum (in red color) merged to the original one recorded in DMSO-d_6. Star marks in green and red colors in all spectra represent peaks for DMSO-d_6 solvent and from internal reference in TMS, respectively. Circle marks in green and red colors represent the residual water peaks from deuterated solvents.

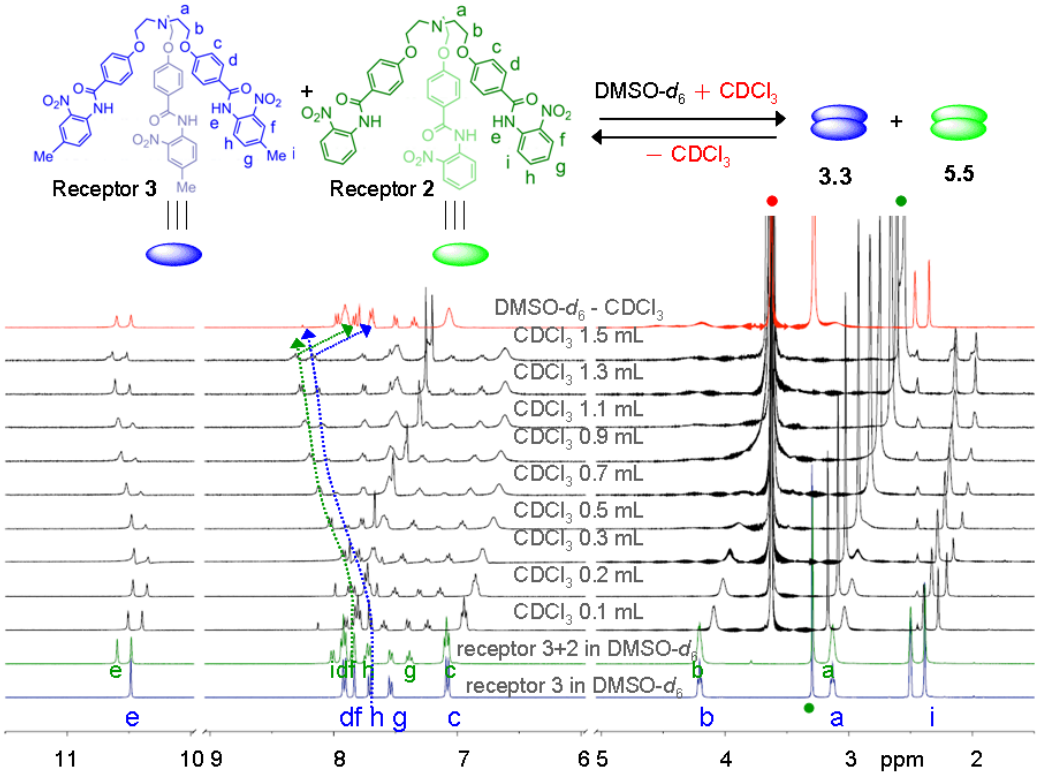


Fig. S37 ^{1}H NMR (400 MHz, 30 ºC) titration spectra of receptors **2** and **3** (in 1:1 ratio, 6.25 mM each) in a DMSO-d_6 solution upon addition of varying amount of $CDCl_3$. After partial evaporation of $CDCl_3$ the resulting spectrum (in red color) merged to the original one recorded in DMSO-d_6. Star marks in green and red colors in all spectra represent peaks for DMSO-d_6 solvent and from internal reference in TMS, respectively. Circle marks in green and red colors represent the residual water peaks from deuterated solvents.

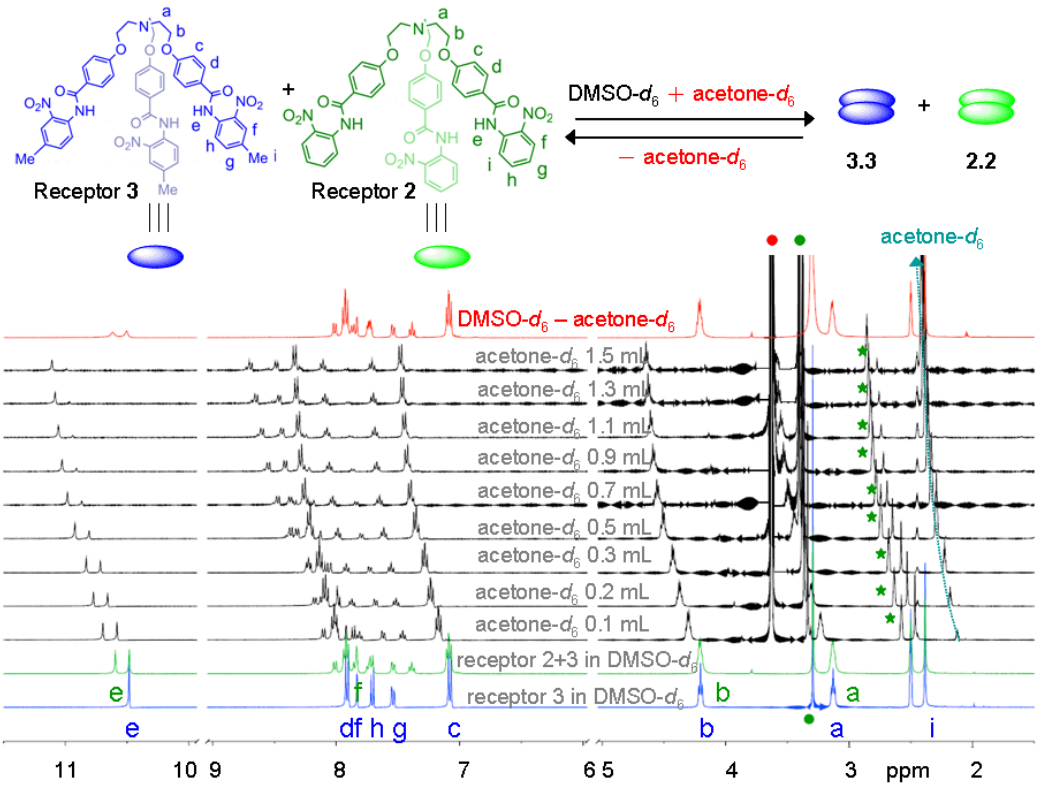


Fig. S38 ^{1}H NMR (400 MHz, 30 ºC) titration spectra of receptors **2** and **3** (in 1:1 ratio, 6.25 mM each) in a DMSO-d_6 solution upon addition of varying amount of acetone-d_6. After partial evaporation of acetone-d_6 the resulting spectrum (in red color) merged to the original one recorded in DMSO-d_6. Star marks in green and red colors in all spectra represent peaks for DMSO-d_6 solvent and from internal reference in TMS, respectively. Circle marks in green and red colors represent the residual water peaks from deuterated solvents.

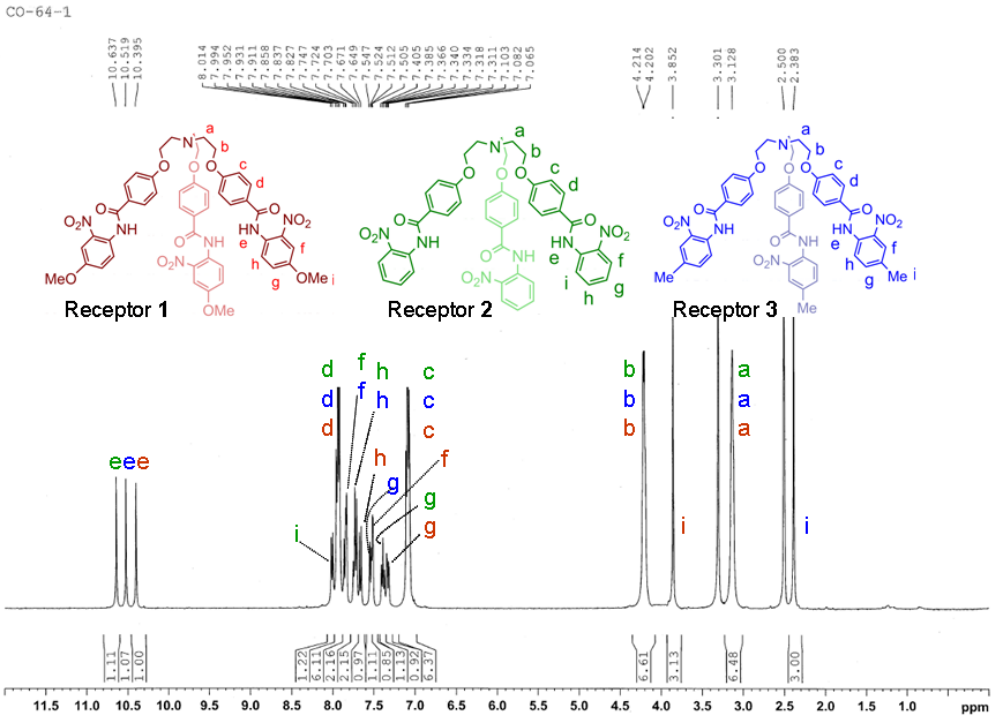


Fig. S39 ^{1}H NMR (DMSO-d_6, 400 MHz, 30 ºC) spectrum of receptors **1, 2** and **3** (in 1:1:1 ratio, 6.25 mM each).

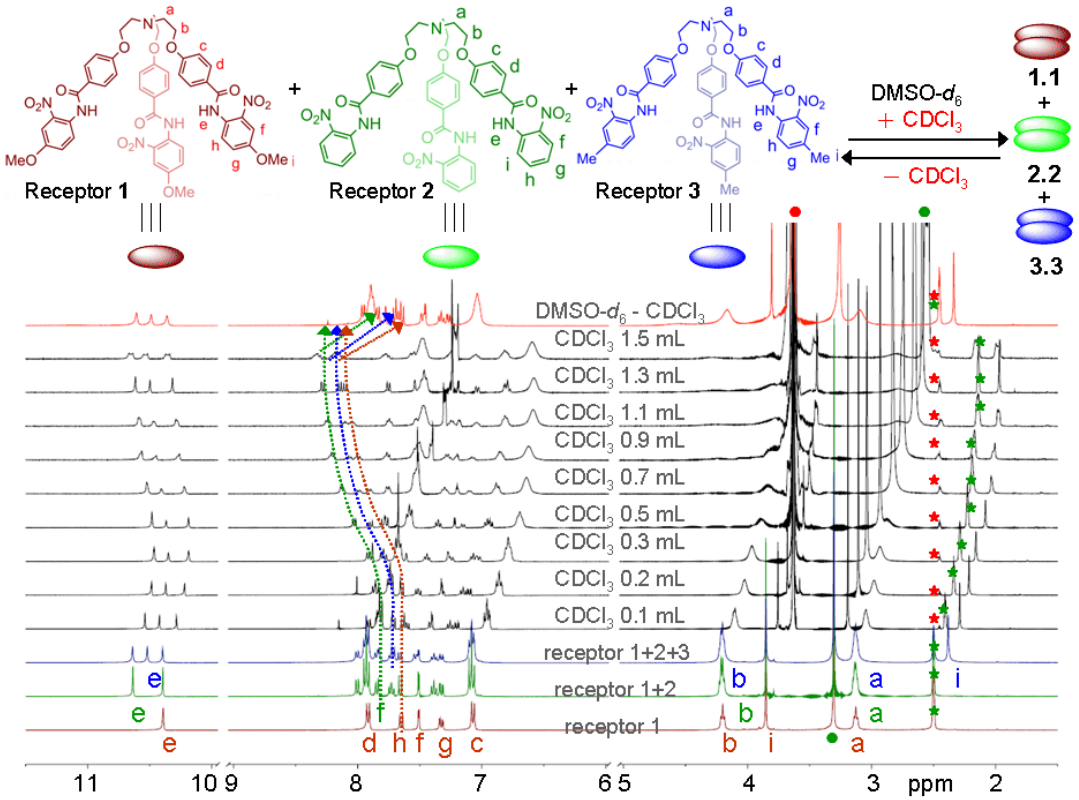


Fig. S40 Three-component self-sorting: ^{1}H NMR (400 MHz, 30 ºC) titration spectra of receptors **1, 2** and **3** (in a 1:1:1 ratio, 6.25 mM each) in a DMSO-d_6 solution upon addition of varying amount of $CDCl_3$. After partial evaporation of $CDCl_3$ the resulting spectra (in red color) merged to the original one recorded in DMSO-d_6. Star marks in green and red colors in spectra represent peaks for DMSO-d_6 solvent and from internal reference in TMS, respectively. Circle marks in green and red colors represent the residual water peaks from deuterated solvents.

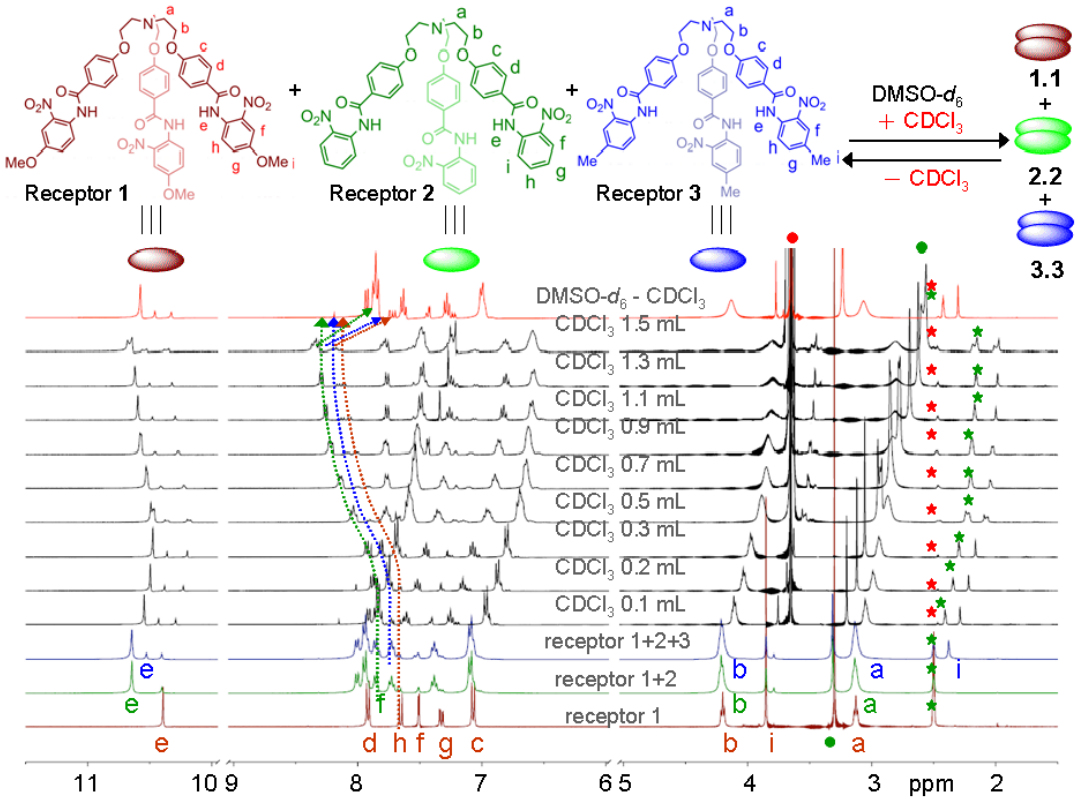


Fig. S41 ^{1}H NMR (400 MHz, 30 ºC) titration spectra of receptors **1, 2** and **3** (in 1:5:1 ratio, 6.25 mM for receptors **1** and **3**) in a DMSO-d_6 solution upon addition of varying amount of $CDCl_3$. After partial evaporation of $CDCl_3$ the resulting spectrum (in red color) merged to the original one recorded in DMSO-d_6. Star marks in green and red colors in all spectra represent peaks for DMSO-d_6 solvent and from internal reference in TMS, respectively. Circle marks in green and red colors represent the residual water peaks from deuterated solvents.

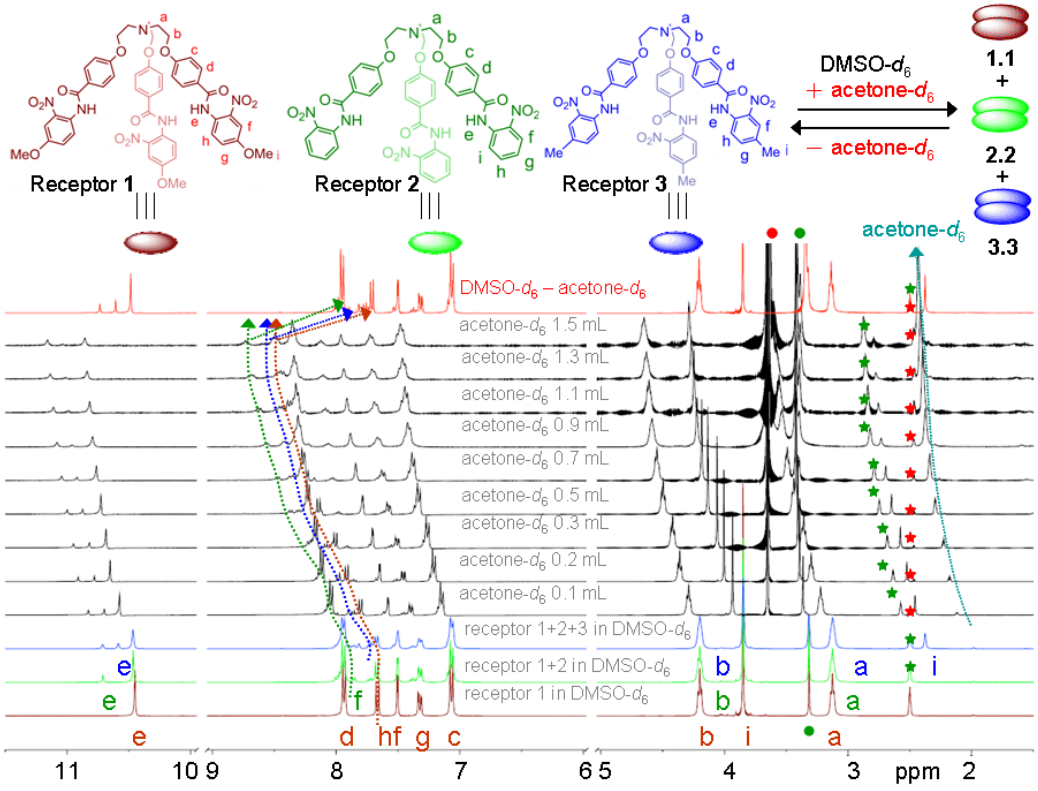


Fig. S42 ^{1}H NMR (400 MHz, 30 ºC) titration spectra of receptors **1, 2** and **3** (in 5:1:1 ratio, 6.25 mM for receptors **2** and **3**) in a DMSO-d_6 solution upon addition of varying amount of acetone-d_6. After partial evaporation of acetone-d_6 the resulting spectrum (in red color) merged to the original one recorded in DMSO-d_6. Star marks in green and red colors in all spectra represent peaks for DMSO-d_6 solvent and from internal reference in TMS, respectively. Circle marks in green and red colors represent the residual water peaks from deuterated solvents.

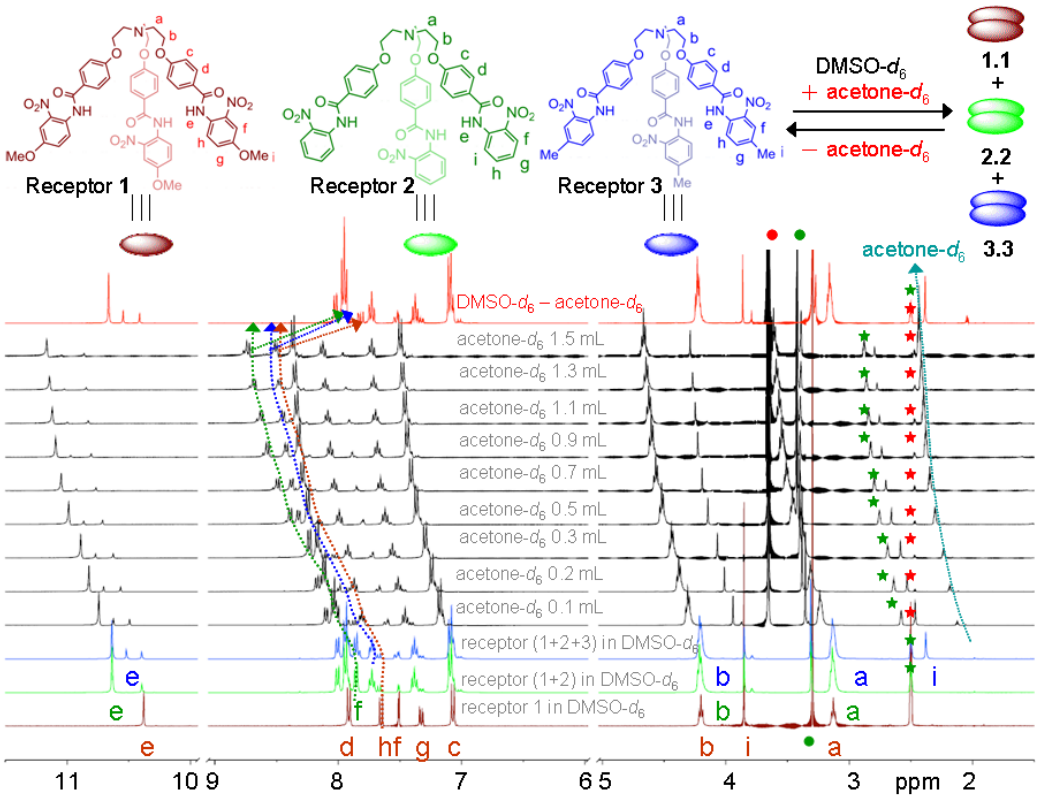


Fig. S43 ^{1}H NMR (400 MHz, 30 ºC) titration spectra of receptor **1, 2** and **3** (in 1:5:1 ratio, 6.25 mM for receptors **1** and **3**) in a DMSO-d_6 solution upon addition of varying amount of acetone-d_6 respectively. After partial evaporation of acetone-d_6 the resulting spectra (in red color) merged to the original one recorded in DMSO-d_6. Star marks in green and red colors in all spectra represent peaks for DMSO-d_6 solvent and from internal reference in TMS, respectively. Circle marks in green and red colors represent the residual water peaks from deuterated solvents.