Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

# Supporting Information



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# Dangling Arms: A Tetrahedral Supramolecular Host with Partially Encapsulated Guests

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## Materials and Methods

### General Considerations

All reagents were obtained from commercial suppliers and used without further purification unless noted otherwise. $H_4L$ ($H_4L$ = 1,5-biscatecholamide naphthalene), $K_{12}[Ga_4L_6]$, and $[Ru(\eta_5\text{-}C_5H_5)(CH_3CN)_3]PF_6$ were synthesized according to literature procedure.[1-3] Molecular mechanics calculations, using the MMFF force fields, were performed with Spartan'02 for Linux.[4] Three-dimensional molecular graphics were rendered using POV-Ray for Windows.[5] Routine mass spectrometry and elemental analysis was performed by the Mass Spectrometry Laboratory and Microanalysis Facility in the College of Chemistry at the University of California, Berkeley. High resolution electrospray mass spectra for host-guest complexes were recorded using a Waters Micromass Q-Tof API-US mass spectrometer at Waters Corporation, Dublin, CA.

## Experimental Procedures

**1-bromo-4-phenylbutane ($C_4Br$).** A stirred solution of 1 g (6.7 mmol) of 4-phenyl-1-butanol and 3 mL of pyridine in 75 mL of $CH_2Cl_2$ was cooled to -10 °C in an ice/salt bath. An addition funnel containing 6 g (20 mmol) of phosphorous tribromide dissolved in 25 mL $CH_2Cl_2$ was affixed to the reaction vessel, and this solution was added dropwise to the stirred solution over a 30 minute period. The reaction mixture was stirred for 15 hours at room temperature, filtered to remove an orange solid, then washed with dilute brine (2 x 300 mL), dilute sulfuric acid (250 mL), 1 M hydrochloric acid (2 x 250 mL), and concentrated brine (250 mL). The organic fraction was collected, dried over $MgSO_4$, and the solvent removed via rotary evaporation, yielding a yellowish oil. Purification via chromatography (basic alumina, $CH_2Cl_2$) and removal of solvent yielded 0.50 g (36%) of a clear oil. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 1.77 (m, 2H), 1.9 (m, 2), 2.65 (t, 2, $J$=7.6 Hz), 3.42 (t, 2, $J$=6.8 Hz), 7.2 (m, 5).

**Sodium(4-phenylbutane-1-sulfonate) ($C_4SO_3Na$).**[6] A solution of 1.0 g (8.0 mmol) of sodium sulfite in 20 mL of $H_2O$ was added to 0.50 g (2.3 mmol) of $C_4Br$. The reaction mixture was heated at reflux for 24 h, cooled to room temperature, and filtered to collect the white crystals, washing once with cold $H_2O$. The volume of the filtrate was reduced, cooled to 4 °C, and the white crystalline solid was collected on a frit and washed with cold $H_2O$, then dried for 24 hours *in vacuo* at 50 °C to yield 570 mg (96%) of white solid. Anal. Calc. (found) for $C_{10}H_{13}NaO_3S$: %C, 50.84 (50.45); H, 5.55 (5.31). MS(FAB+): *m/z* 237 ($\{MNaH\}^+$), 259 ($\{MNa_2\}^+$). $^1$H NMR ($D_2O$, 300 MHz): $\delta$ 1.73 (m, 4H), 2.67 (t, $J$=7.1 Hz, 2H), 2.93 (t, $J$=7.5 Hz, 2H), 7.3 (m, 5H).

**1-bromo-6-phenylhexane ($C_6Br$).** A stirred solution of 2.52 g (14.1 mmol) of 6-phenyl-1-hexanol in 80 mL of $Et_2O$ was cooled to 0 °C in an ice bath. An addition funnel containing 4 g (16 mmol) of phosphorous tribromide in 25 mL of $Et_2O$ was affixed to the reaction vessel, and this solution was added dropwise to the stirred solution over a 30 minute period. The reaction mixture was stirred for 15 hours, allowing the ice bath to gradually return to room temperature. The ether solution was treated with aqueous sodium bicarbonate (2 x 250 mL) followed by brine (100 mL). The organic layer was collected, dried over $MgSO_4$, and the solvent removed via rotary evaporation to yield a cloudy, colorless oil. Purification via chromatography (basic alumina, $CH_2Cl_2$) and removal of solvent yielded 1.16 g (34%) of a clear oil. $^1$H NMR ($CDCl_3$, 400 MHz): δ 1.39 (m, 2H), 1.49 (m, 2H), 1.66 (m, 2H), 1.88 (m, 2H), 2.64 (t, $J$ = 7.6 Hz, 2H), 3.42 (t, $J$ = 6.8 Hz, 2H), 7.21 (m, 3H), 7.31 (m, 2H).

**Sodium(6-phenylhexane-1-sulfonate) ($C_6SO_3Na$).**[6] A solution of 2.1 g (15 mmol) of sodium sulfite in 50 mL of $H_2O$/EtOH (4:1) was added to 1.16 g (4.8 mmol) of $C_6Br$. The reaction mixture was heated at reflux for 24 h, cooled to 4 °C, and filtered to collect the white crystals. The solid was dried for 24 hours *in vacuo* at 50 °C to yield 1.2 g (96%) of white solid. Anal. Calc. (found) for $C_{12}H_{17}NaO_3S\cdot(H_2O)_{0.5}$: %C, 52.73 (52.21); H, 6.64 (6.28). MS(ES-): *m/z* 241.1 ($M^-$), 483.3 ($\{HM_2\}^-$), 505.2 ($\{NaM_2\}^-$). $^1$H NMR (MeOD, 300 MHz): $\delta$ 1.39 (m, 4H), 1.62 (m, 2), 1.77 (m, 2), 2.60 (t, 2, $J$=7.8 Hz), 2.76 (t, 2, $J$=8.1 Hz), 7.17 (m, 5).

**1-bromo-8-phenyloctane ($C_8Br$).** A stirred solution of 2.87 g (13.9 mmol) of 8-phenyl-1-octanol in 75 mL of anhydrous $Et_2O$ was cooled to 0 °C under air in an ice/salt bath. A solution of 3 g (10 mmol) of phosphorous tribromide in 15 mL of $Et_2O$ was added dropwise over 30 minutes, and the reaction mixture was stirred for 90 additional minutes at 0 °C. The reaction mixture was treated with aqueous $NaHCO_3$, the organic layer collected and dried with $MgSO_4$,

and the solvent removed to yield a cloudy colorless oil. Purification via chromatography (basic alumina, $CH_2Cl_2$) and removal of solvent yielded 1.0 g (27%) of a clear, colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 1.38 (br s, 8H), 1.65 (m, 4H), 2.66 (t, 2H, *J*=7.6 Hz), 3.46 (t, 2H, *J*=6.8 Hz), 7.3 (m, 5H).

**Sodium(8-phenyloctane-1-sulfonate) ($C_8SO_3Na$).**[6] To 1 g of $C_8Br$ was added a solution of 1.5 g (12 mmol) of sodium sulfite dissolved in 40 mL of $H_2O$ with 10 mL of ethanol. The reaction mixture was heated at reflux under air for 24 hours, then allowed to cool to room temperature. A white polycrystalline solid formed, which was collected on a frit and washed with cold $H_2O$ (2 x 5 mL and isopropyl alcohol (2 x 20 mL), then dried overnight to yield 0.5 g (46%) of shiny white flakes. Anal. Calc. (found) for $C_{14}H_{21}NaO_3S$: %C, 57.51 (57.15); H, 7.24 (7.41); S, 10.97 (10.90). MS(ES-): *m/z* 269.1 ($M^-$). $^1$H NMR ($D_2O$, 300 MHz): $\delta$ 1.3 (m, 8H), 1.57 (m, 2H), 1.67 (m, 2H), 2.59 (t, *J*=7.8 Hz, 2H), 2.84 (t, *J*=8.0 Hz, 2H), 7.3 (m, 5H).

**1-bromo-10-phenyldecane ($C_{10}Br$).** A stirred solution of 2.56 g (10.9 mmol) of 10-phenyl-1-decanol in 75 mL of anhydrous $Et_2O$ was cooled to 0 °C under air in an ice bath. An addition funnel containing 3 g (10 mmol) of phosphorous tribromide in 25 mL of $Et_2O$ was affixed to the reaction vessel, and this solution was added dropwise to the stirred solution over a 30 minute period. The reaction mixture was stirred for 90 minutes, then treated with aqueous sodium bicarbonate (250 mL). The organic layer was collected, dried over $MgSO_4$, and its solvent removed to yield a cloudy, colorless oil. Purification via chromatography (silica, $CH_2Cl_2$) yielded 0.85 g (25%) of a colorless oil. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ 1.30 (br s, 10 H), 1.43 (m, 2H), 1.62 (m, 2H), 1.86 (m, 2H), 2.615 (t, 2H, *J*=7.6 Hz), 3.421 (t, 2H, *J*=6.8 Hz), 7.24 (m, 5H).

**Sodium(10-phenyldecane-1-sulfonate) ($C_{10}SO_3Na$).**[6] To 0.84 g (2.8 mmol) of $C_{10}Br$ was added a solution of 1.2 g (8.4 mmol) of sodium sulfite dissolved in 35 mL of $H_2O$ with 10 mL of ethanol. The reaction mixture was heated at reflux under air for 24 hours, then allowed to cool to room temperature. A white polycrystalline solid formed, which was collected on a frit and washed with 10 mL of cold $H_2O$, then for two days at 60 °C in a vacuum oven to yield 0.76 g (84%) of shiny white flakes. Anal. Calcd. (found) for $C_{16}H_{25}NaO_3S$: C, 59.97 (60.16); H, 7.86 (7.73). MS(ES-): *m/z* 297.2 ($M^-$). $^1$H NMR (MeOD, 400 MHz): 1.35 (m, 12H), 1.60 (m, 2H), 1.78 (m, 2H), 2.59 (t, *J*=7.6 Hz, 2H), 2.78 (t, *J*=8.0 Hz, 2H), 7.2 (m, 5H).

**[Ru($\eta_5$-$C_5H_5$)($\eta_6$-$C_6H_5(CH_2)_{10}SO_3$)]·$NaPF_6$ ($RuC_{10}$·$NaPF_6$).**[7] This reaction was performed under argon using standard Schlenk techniques. To 156 mg (0.49 mmol) of $C_{10}SO_3Na$ and 200 mg (0.46 mmol) of [Ru($\eta_5$-$C_5H_5$)($CH_3CN)_3$]$PF_6$ was added 100 mL of anhydrous $CHCl_3$. The reaction mixture was heated at reflux for 24 hours, during which time a brown solid appeared on the walls of the flask. The solvent was removed, and the light brown residue was dissolved in methanol, filtered, and precipitated with ether to yield 150 mg (52%) of beige solid. Anal. Calc. (found) for $C_{21}H_{30}F_6NaO_3PRuS$: %C, 39.94 (39.05); H, 4.79 (4.73); S, 5.08 (4.82). MS(ES+): *m/z* 465.1 ($\{MH\}^+$), 487.1 ($\{MNa\}^+$). $^1$H NMR (MeOD, 500 MHz): $\delta$ 1.34 (s, 6H), 1.40 (m, 6H), 1.63 (m, 2H), 1.78 (m, 2H), 2.53 (t, *J*=8.0 Hz, 2H), 2.78 (t, *J*=8.0 Hz, 2H), 5.41 (s, 5H), 6.13 (m, 1H), 6.17 (m, 2H), 6.23 (d, *J*=6.0 Hz, 2H). $^1$H NMR ($D_2O$, 300 MHz): δ 1.32 (m, 12H), 1.58 (m, 2H), 1.71 (m, 2H), 2.48 (t, *J*=7.8 Hz, 2H), 2.87 (t, *J*=8.0 Hz, 2H), 5.33 (s, 5H), 6.07 (m, 3H), 6.14 (m, 2H). $^{19}$F NMR (MeOD, 376 MHz): δ -74.0 ppm vs. $CFCl_3$ (d, *J*=709 Hz).

**Ru($\eta_5$-$C_5H_5$)($\eta_6$-$C_6H_5(CH_2)_4SO_3$)]·$NaPF_6$ ($RuC_4$·$NaPF_6$).** A procedure similar to the synthesis of $RuC_{10}$·$NaPF_6$ was used, with 127 mg (0.278 mmol) of [Ru($\eta_5$-$C_5H_5$)($CH_3CN$)$_3$]$PF_6$ and 71 mg (0.28 mmol) of $C_4SO_3Na$ in place of $C_{10}SO_3Na$. Recrystallization from methanol/ether yielded 60 mg (40%) of beige powder. Anal. Calc. (found) for $C_{15}H_{18}F_6NaO_3PRuS$: %C, 32.91 (32.35); H, 3.31 (3.55); S, 5.86 (5.50). MS(ES+): *m*/z 381.1 ({MH}$^+$), 403.1 ({MNa}$^+$). $^1$H NMR ($D_2O$, 500 MHz): $\delta$ 1.74 (m, 2H), 1.81 (m, 2H), 2.55 (t, *J*=7.7 Hz, 2H), 2.94 (t, *J*=7.5 Hz, 2H), 5.35 (s, 5H), 6.08 (m, 3H), 6.18 (d, *J*=5.5 Hz, 2H).

**Ru($\eta_5$-$C_5H_5$)($\eta_6$-$C_6H_5(CH_2)_6SO_3$)]·$NaPF_6$ ($RuC_6$·$NaPF_6$).** A procedure similar to the synthesis of $RuC_{10}$·$NaPF_6$ was used, with 215 mg (0.50 mmol) of [Ru($\eta_5$-$C_5H_5$)($CH_3CN$)$_3$]$PF_6$ and 140 mg (0.50 mmol) of $C_6SO_3Na$ in place of $C_{10}SO_3Na$. Recrystallization from methanol/ether yielded 150 mg (53%) of beige powder. Anal. Calc. (found) for $C_{17}H_{22}F_6NaO_3PRuS$: C, 35.48 (35.30); H, 3.85 (4.15); S, 5.57 (5.29). MS(ES+): *m*/z 409.1 ({MH}$^+$), 431.1 ({MNa}$^+$). $^1$H NMR ($D_2O$, 400 MHz): $\delta$ 1.43 (m, 4H), 1.61 (m, 2H), 1.72 (m, 2H), 2.50 (t, *J*=7.8 Hz, 2H), 2.89 (t, *J*=8.0 Hz, 2H), 5.34 (s, 5H), 6.06 (m, 3H), 6.16 (d, *J*= 5.6 Hz, 2H).

**Ru($\eta_5$-$C_5H_5$)($\eta_6$-$C_6H_5(CH_2)_8SO_3$)]·$NaPF_6$ ($RuC_8$·$NaPF_6$).** A procedure similar to the synthesis of $RuC_{10}$·$NaPF_6$ was used, with 185 mg (0.425 mmol) of [Ru($\eta_5$-$C_5H_5$)($CH_3CN$)$_3$]$PF_6$ and 125 mg (0.425 mmol) of $C_8SO_3Na$ in place of $C_{10}SO_3Na$. Recrystallization from methanol/ether yielded 170 mg (66%) of beige powder. Anal. Calc. (found) for $C_{19}H_{26}F_6NaO_3PRuS$: C, 37.81 (37.13); H, 4.34 (4.56); S, 5.31 (5.28). MS(ES+): *m/z* 437.1 ({MH}$^+$), 459.1 ({MNa}$^+$). $^1$H NMR ($D_2O$, 400 MHz): $\delta$ 1.38 (m, 8H), 1.60 (m, 2H), 1.71 (m, 2H), 2.49 (t, *J*=7.8 Hz, 2H), 2.88 (t, *J*=8.0 Hz, 2H), 5.34 (s, 5H), 6.07 (m, 3H), 6.16 (d, *J*=5.6 Hz, 2H). $^{19}$F NMR (MeOD, 376 MHz): $\delta$ -71.3 ppm vs. $CFCl_3$ (d, *J*=709 Hz).

**$K_{12}[RuC_{10} \subset Ga_4L_6]$.**[8] This reaction was performed under argon using standard Schlenk techniques. A suspension of 102 mg (0.24 mmol) of $H_4L^T$, 58 mg (0.16 mmol) of $Ga(acac)_3$, and 25 mg (0.040 mmol) of $RuC_{10}\cdot NaPF_6$ in 75 mL of MeOH was heated at reflux for 12 hours. The solvent was removed to leave a light tan residue. After drying this residue *in vacuo* for three hours, 50 mL of MeOH was added. Addition of 0.95 mL (0.47 mmol) of methanolic KOH (0.5 M) caused the off-white suspension to become a yellow solution. The reaction mixture was re-degassed with three pump/fill cycles immediately after the addition of base, then stirred at room temperature for 2 hours. Undissolved solid was removed by cannula filtration. The volume was reduced to 5 mL, and 150 mL of acetone was added to precipitate a pale yellow/brown solid. This solid was collected on a frit under a stream of nitrogen, washed with acetone (4 x 10 mL), and dried *in vacuo* overnight to yield 120 mg (80%) of yellow-beige powder. Anal. Calc. (found) for $C_{165}H_{114}Ga_4K_{12}N_{12}O_{39}RuS\cdot Me_2CO\cdot 7H_2O$: C, 51.03 (51.01); H, 3.42 (3.29); N, 4.25 (4.13). MS(ES-): (see text). $^1$H NMR ($D_2O$, 500 MHz): $\delta$ -1.20 (m, 1H), -1.13 (br m, 1H), -1.02 (br m, 1H), -0.91 (br m, 1H), -0.25 (m, 2H), 0.29 (m, 1H), 0.52 (m, 1H), 0.66 (m, 1H), 0.80 (m, 1H), 1.18 (m, 2H), 1.36 (m, 2H), 1.49 (m, 2H), 1.87 (m, 2H), 2.29 (s, 5H), 3.05 (m, 3H), 3.14 (d, *J*=6.0 Hz, 1H), 3.20 (d, *J*=5.9 Hz, 1H), 3.28 (t, *J*=5.8 Hz, 1H), 4.35 (t, *J*=5.6 Hz, 1H), 6.49 (t, *J*=7.8 Hz, 3H), 6.58 (t, *J*=7.8 Hz, 3H), 6.64 (m, 9H), 6.74 (d, *J*=7.3 Hz, 3H), 6.79 (m, 6H), 6.82 (t, *J*=8.2 Hz, 3H), 6.90 (t, *J*=8.0 Hz, 3H), 7.17 (m, 6H), 7.23 (d, *J*=8.3 Hz, 3H), 7.27 (t, *J*=8.3 Hz, 3H), 7.36 (d, *J*=8.3 Hz, 3H), 7.39 (d, *J*=8.3 Hz, 3H), 7.47 (d, *J*=7.6 Hz, 3H), 7.76 (d, *J*=8.6 Hz, 3H), 7.79 (d, *J*=8.6 Hz, 3H), 7.80 (d, *J*=8.6 Hz, 3H), 7.87 (d, *J*=7.8 Hz, 3H), 8.08 (d, *J*=8.7 Hz, 3H), 8.11 (d, *J*=7.8 Hz, 3H), 8.37 (d, *J*=7.8 Hz, 3H). $^{19}$F NMR ($D_2O$, 376 MHz): No signal observed.

**General procedure for NMR encapsulation reactions**

$K_{12}[Ga_4L_6]\cdot Me_2CO$ (10.0 mg, 2.97 $\mu$mol) and $RuC_n\cdot NaPF_6$ (3 $\mu$mol) were combined in a vial and dissolved in 0.6 mL of $D_2O$ at room temperature. The solution was filtered through a glass fiber plug and transferred to an NMR tube, and the spectrum recorded 10 minutes after dissolution. Solutions were discarded within 24 hours due to slow oxidation of the ligands in the cluster.

**Mass spectrometry**

Samples for ESI-MS were prepared in a manner similar to NMR samples using methanol or $H_2O$/methanol, except for $[RuC_{10} \subset Ga_4L_6]^{12-}$ which was prepared as described in the preceding section.

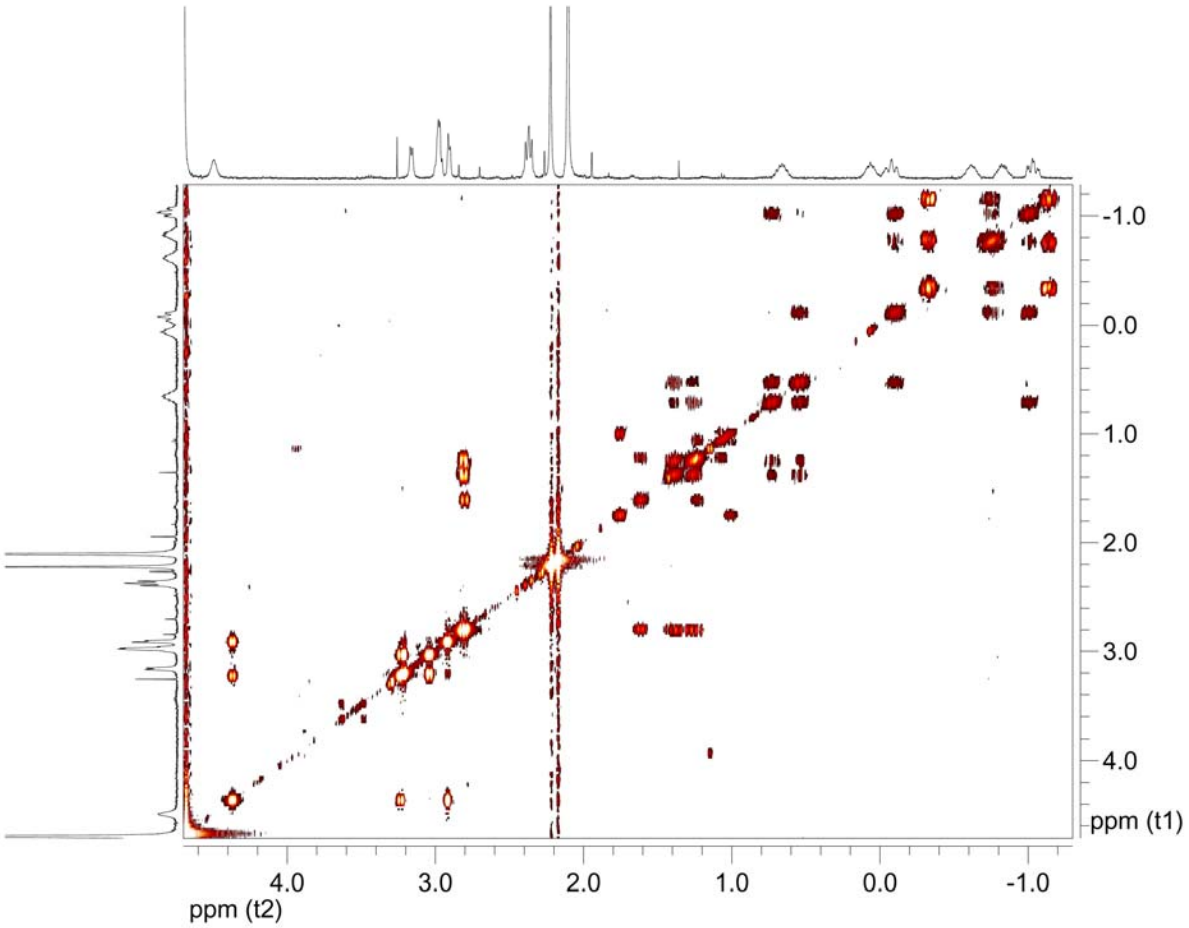


**Figure S1.** Portion of the 2D TOCSY $^{1}$H NMR spectrum ($D_2O$, 400 MHz) of $[RuC_4 \subset Ga_4L_6]^{12-}$, showing the cross peaks between encapsulated $RuC_4$ resonances.

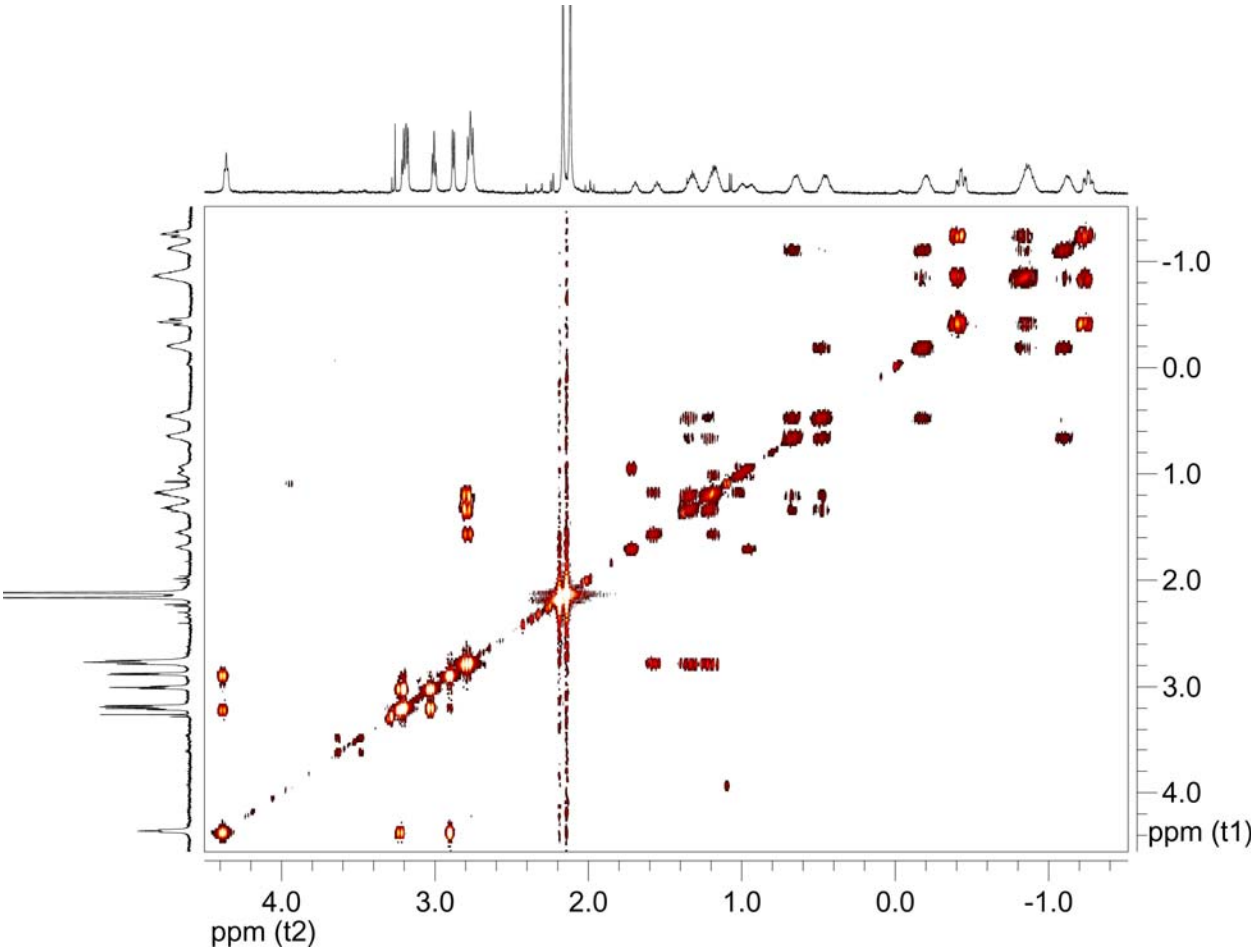


**Figure S2.** Portion of the 2D COSY $^{1}$H NMR spectrum (500 MHz) of $[RuC_6 \subset Ga_4L_6]^{12-}$, showing the cross peaks between encapsulated $RuC_6$ resonances.

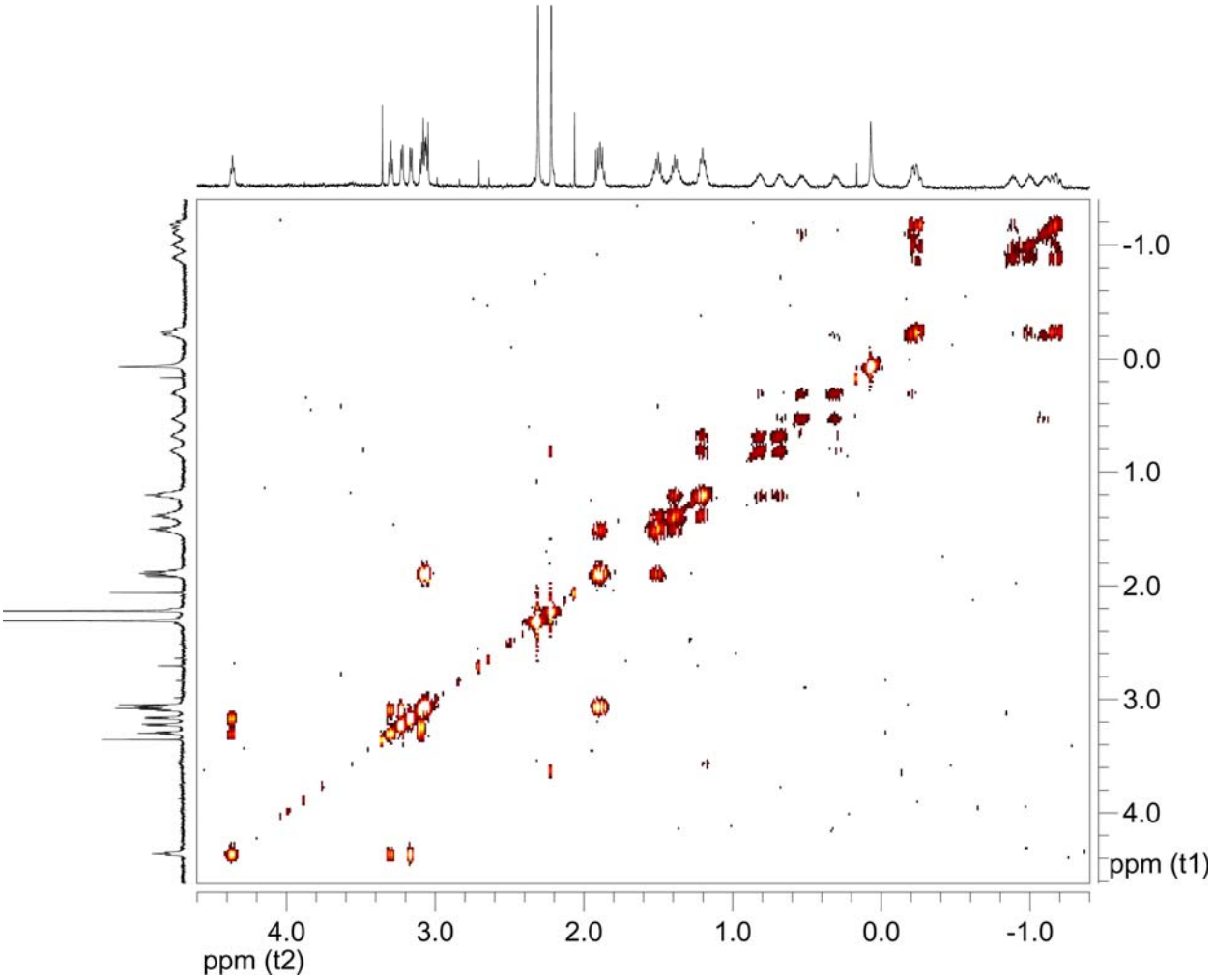


**Figure S3.** Portion of the 2D COSY $^{1}$H NMR spectrum (500 MHz) of $[RuC_{10} \subset Ga_4L_6]^{12-}$, showing the cross peaks between encapsulated $RuC_{10}$ resonances.

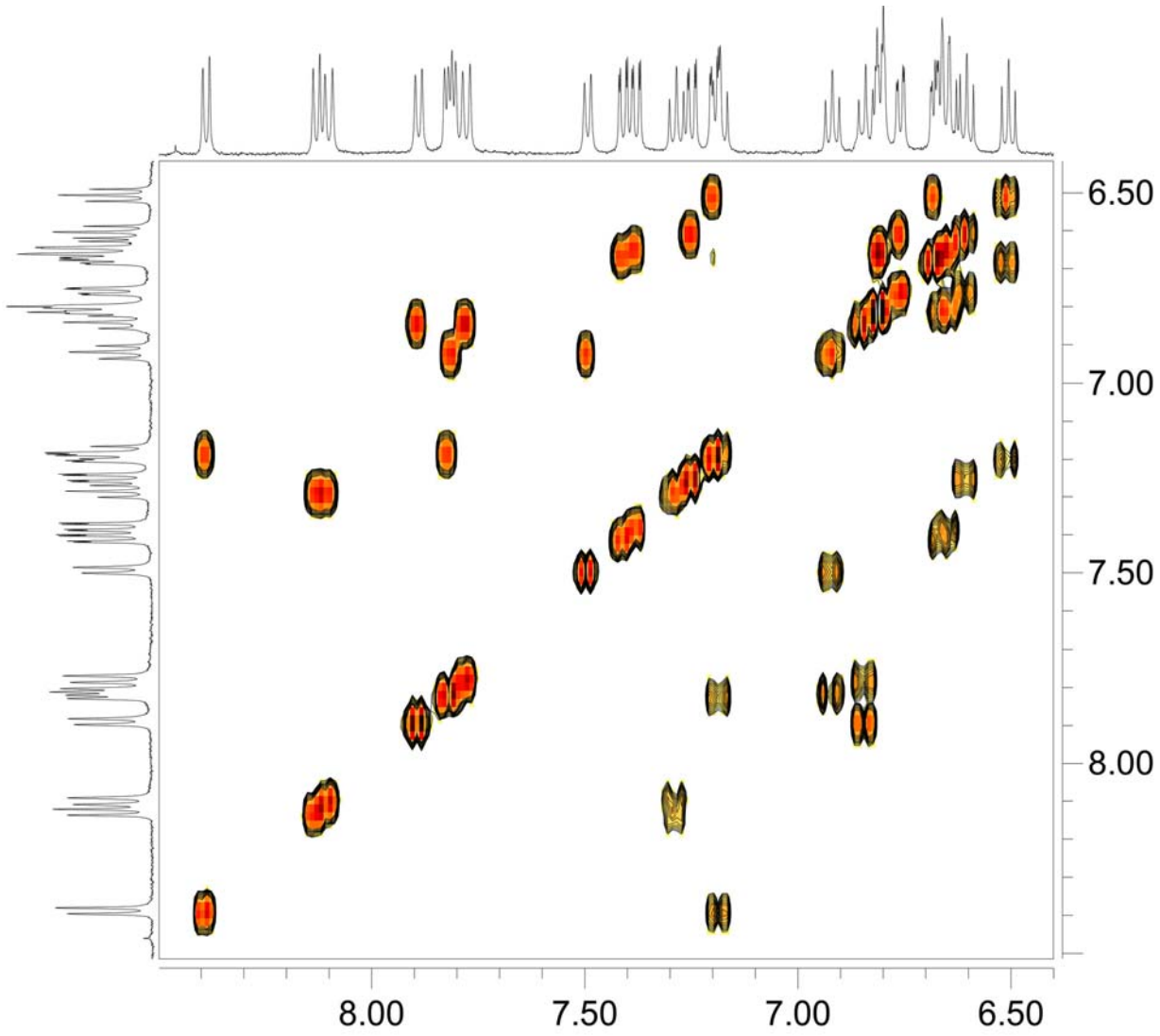


**Figure S4.** Portion of the 2D COSY $^{1}$H NMR spectrum ($D_2O$, 500 MHz) for $[RuC_{10} \subset Ga_4L_6]^{12-}$, showing the coupling between host protons.

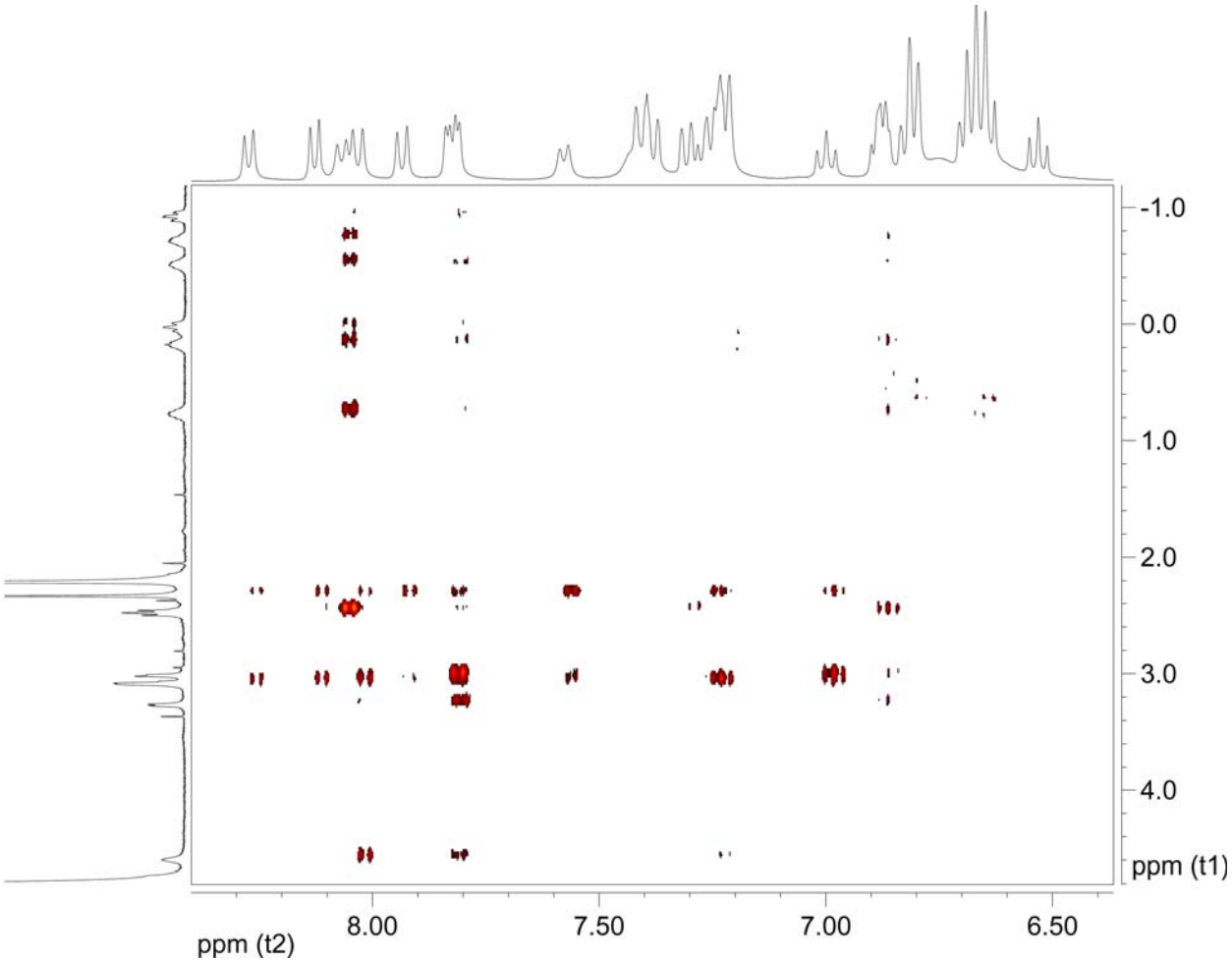


**Figure S5.** Portion of the 2D NOESY $^{1}$H NMR spectrum ($D_2O$, 400 MHz) of $[RuC_4 \subset Ga_4L_6]^{12-}$, showing the cross peaks between host and guest signals.

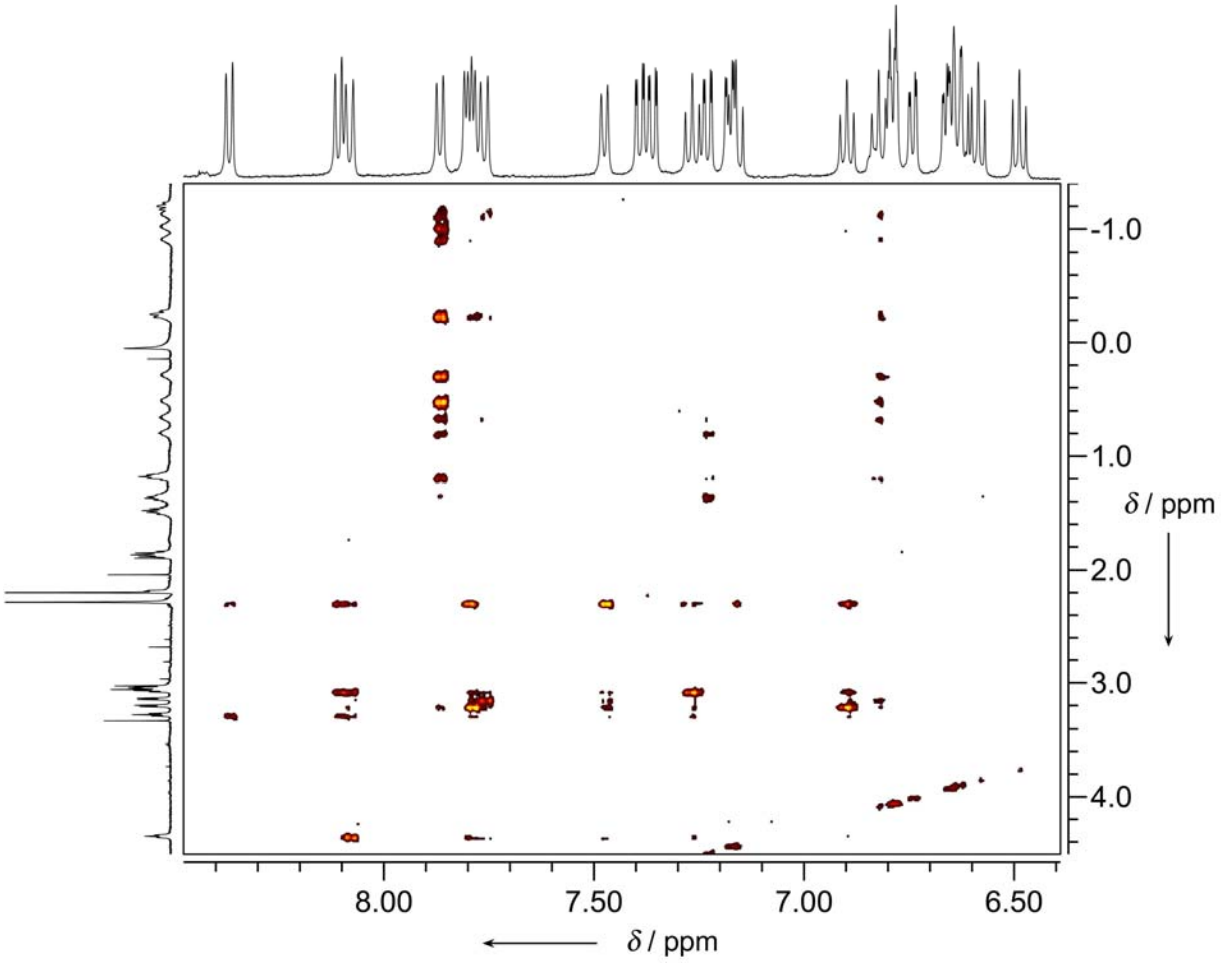


**Figure S6.** Portion of the 2D NOESY $^{1}$H NMR spectrum ($D_2O$, 400 MHz) of $[RuC_{10} \subset Ga_4L_6]^{12-}$, showing the cross peaks between host and guest signals.

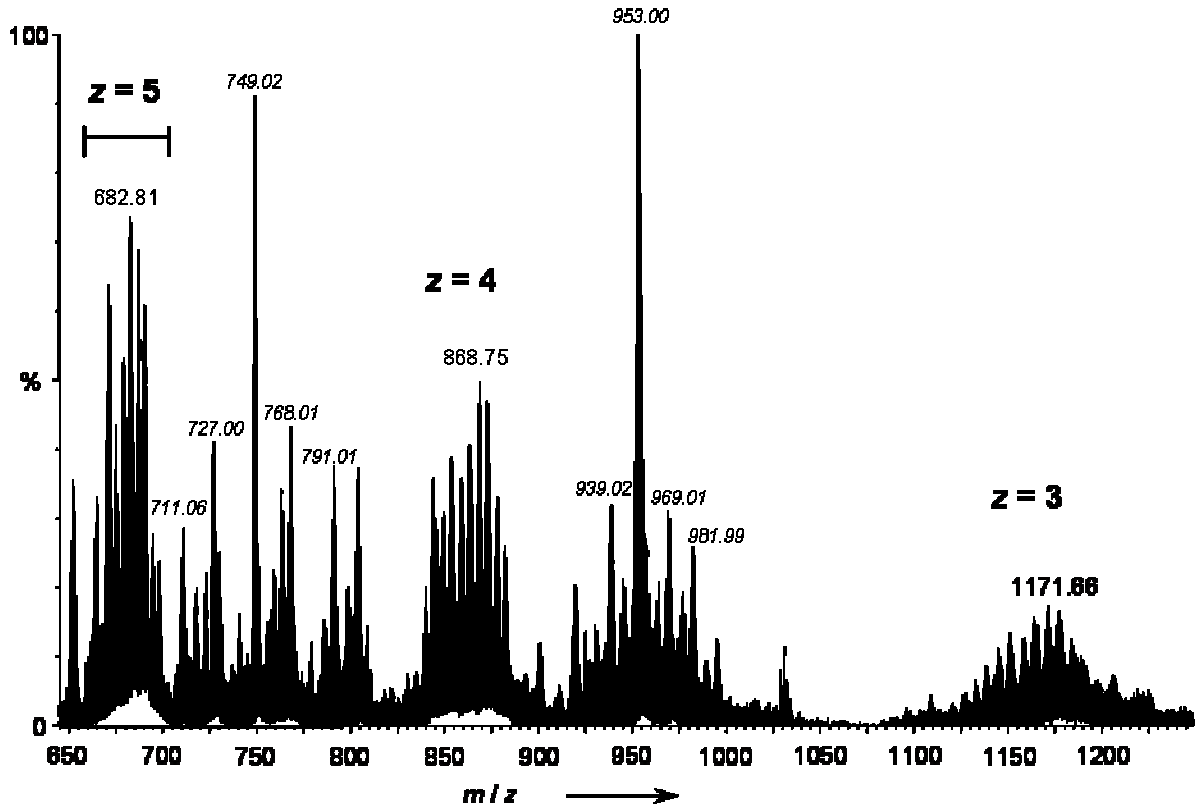


**Figure S7.** Portion of the ESI- mass spectrum of $[RuC_4 \subset Ga_4L_6]^{12-}$ in 75% $H_2O$ with 25% methanol. Peaks from fragments containing the host-guest complex in -3,-4, and -5 charge states are shown here.

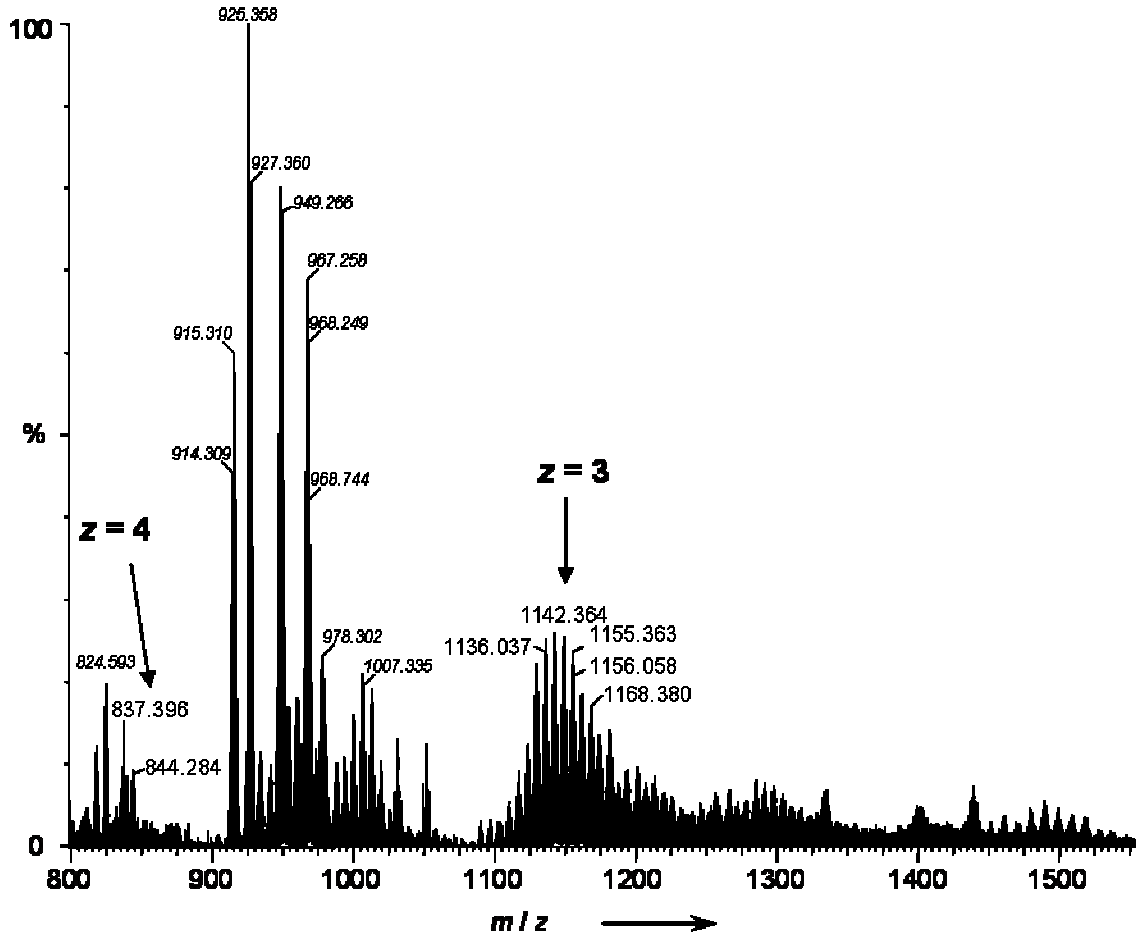


**Figure S8.** Portion of the ESI- mass spectrum of $[RuC_6 \subset Ga_4L_6]^{12-}$ in methanol. Peaks from fragments containing the host-guest complex in -3 and -4 charge states are shown here.

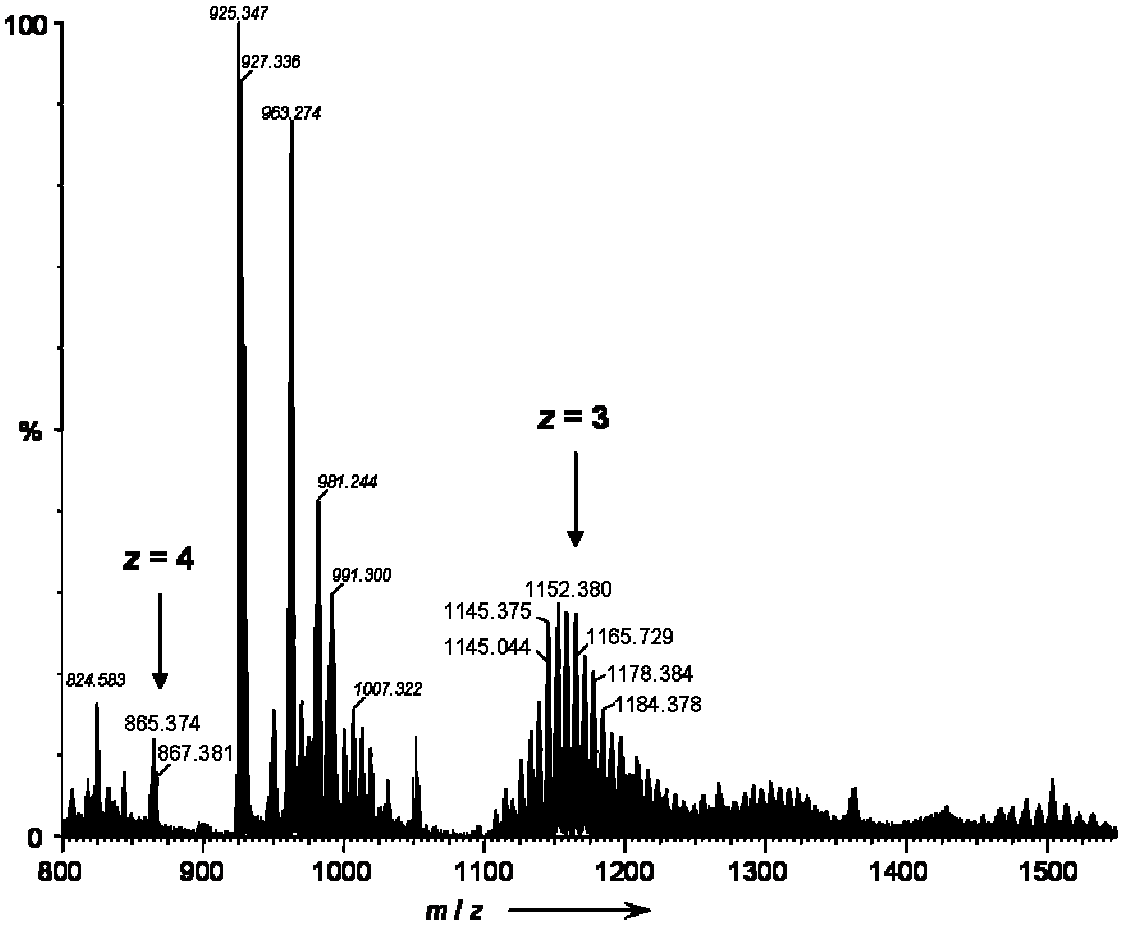


**Figure S9.** Portion of the ESI- mass spectrum of $[RuC_8 \subset Ga_4L_6]^{12-}$ in methanol. Peaks from fragments containing the host-guest complex in -3 and -4 charge states are shown here.

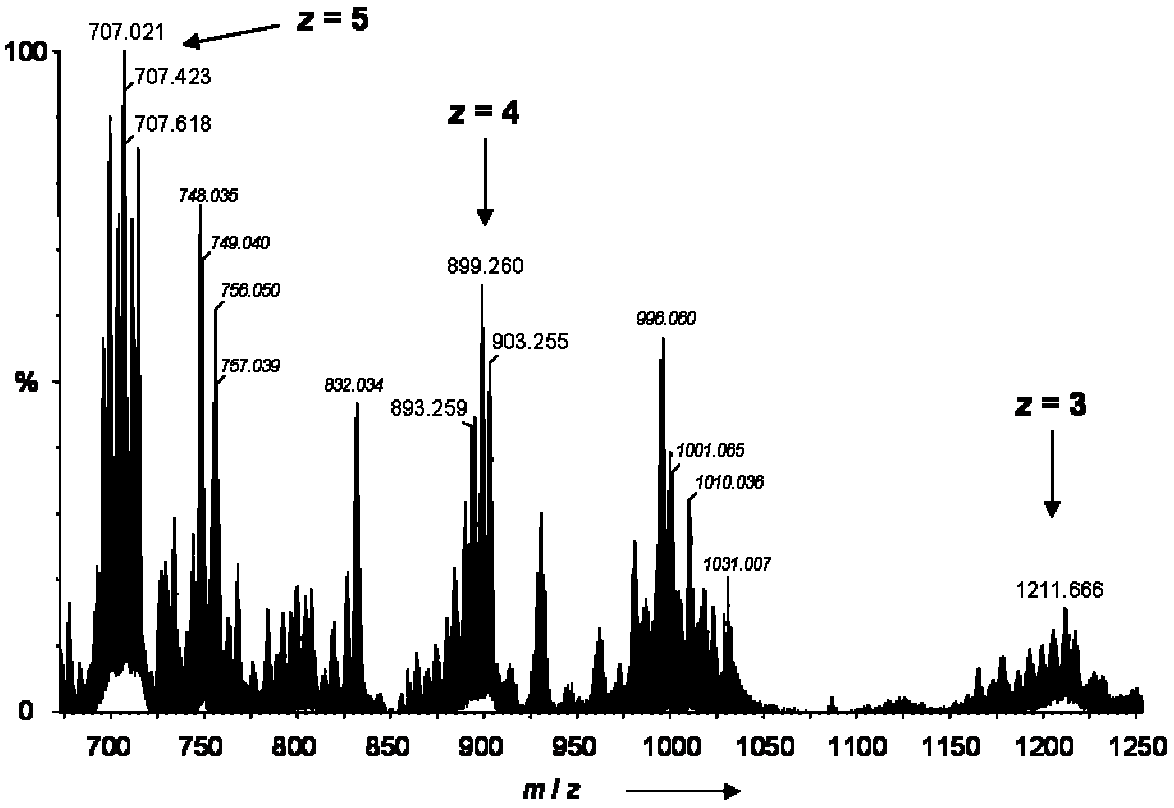


**Figure S10.** Portion of the ESI- mass spectrum of $[RuC_{10} \subset Ga_4L_6]^{12-}$ in methanol. Peaks from fragments containing the host-guest complex in -3, -4, and -5 charge states are shown here.

## References


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