Electronic Supplementary Material (ESI) for Chemical Communications

Cation-responsive silver-selective organogel – exploiting silver-alkene interactions in the gel-phase

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SUPPLEMENTARY INFORMATION

Contents

1. Experimental Methods

General Information

All solvents and reagents were used as supplied. Silica gel column chromatography was carried out on silica gel provided by Fluka (60 Å, 35-70 µL). Thin layer chromatography was carried out on commercially available Merck aluminium backed TLC plates (60, F_{254}). ^{13}C NMR titration and Job plot experiments were carried out on a Bruker AMX 300 spectrometer in undeuterated ethyl acetate (^{1}H 300 MHz, ^{13}C 75 MHz) and the spectra were referenced to TMS. For compound characterisation a Jeol ECX spectrometer (^{1}H 400 MHz, ^{13}C 100 MHz) and reference to residual solvent were used. All chemical shifts (δ) are quoted to ppm. Coupling constant values (*J*) are reported in Hz. ATR-FTIR was carried out using a Jasco FT/IR 4100instrument fitted with a Pike MIRacle ATR sampling accessory. Positive ion electrospray mass spectra were recorded on a Finnigan LCQ mass spectrometer. Melting points were measured on a Stuart SMP3 apparatus. Optical rotation was measured on a Jasco DIP-370digital polarimeter.

Gel Formation and Treatment with Metal Salts

An amount of gelator was weighed into a glass vial with a 2 mL volume and a 10 mm diameter. Solvent (0.5 mL) was added and the vial sonicated for 30 minutes. The sample was then heated to just below the solvent boiling temperature to form a clear homogenous solution. This was then left to stand overnight during which time a gel was formed. When adding metal salts, an amount of salt was weighed out and dissolved in 0.5 mL solvent, this was then gently pipetted onto the gel and left so that the ions could diffuse into the gel. Care was taken to ensure light was excluded from the samples containing silver salts.

2. Synthesis and Characterisation

Gelator **G1-ene** was synthesized using previously reported methodology (Fig. S1) and characterization data for all compounds were in agreement with those previously published.[1]

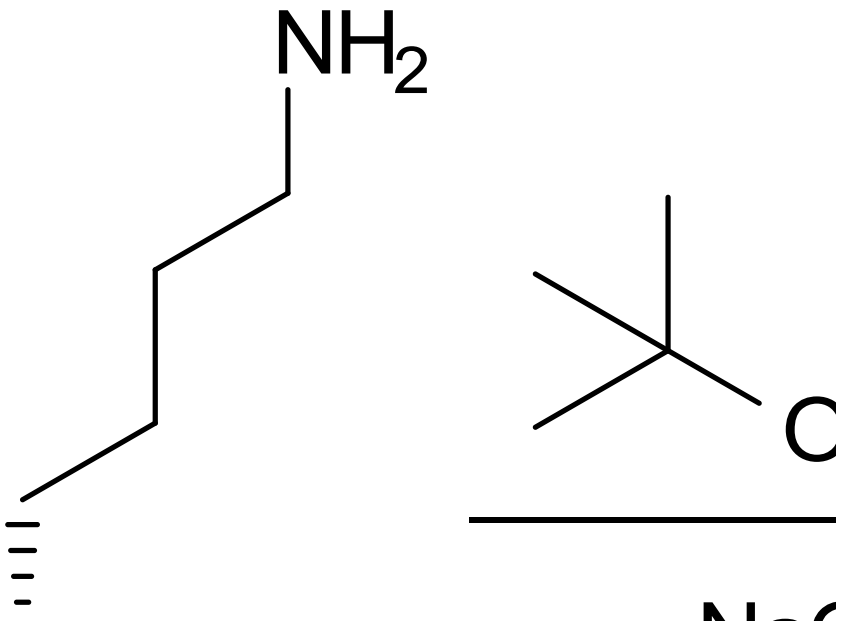

Fig. S1 Synthetic scheme of **G1-ene**.

Gelator **G1-ane** was synthesized using the same methodology but with a novel saturated active ester producing the novel alkene-less gelator. Synthetic methodology and characterization data for these compounds is shown below.

Undecanoyl Active Ester

p-Nitrophenol (3.37 g, 24.2 mmol) was dissolved in toluene (20 mL) and pyridine (1.80 mL, 22.3 mmol). Undecanoyl chloride (4.31 mL, 20.0 mmol) was added and the reaction was refluxed at 120 ^{o}C for 5 hours. After being allowed to cool the reaction was neutralized with sat. $NaHCO_3$. The aqueous layer was removed and the organic layer washed with water, 5% NaOH and 0.1 M HCl. The organic phase was then dried over $MgSO_4$, filtered and volatiles

removed under vacuum to leave an off-white solid. Yield 4.85 g (15.8 mmol, 79%). R_f = 0.88 (9:1 DCM/MeOH, CeMo stain). M.p. = 35.3-36.1°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (2H, d, *J*=9.2, O_2NCCH), 7.26 (2H, d, *J*=9.2, $OCCH$), 2.59 (2H, t, *J*=7.6 Hz, $COCH_2$), 1.75 (2H, qn, *J*=7.6 Hz, $COCH_2CH_2$), 1.45-1.18 (14H, m, CH_2), 0.87 (3H, t, *J*=6.8 CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.43 (C=O), 155.61 (ArCO), 145.32 ($ArCNO_2$), 125.28 (NO_2CCH), 122.53 ($OCCH$), 34.43 ($COCH_2$), 31.98, 29.63, 29.52, 29.39, 29.31, 29.14, 24.83, 22.77 (all CH_2), 14.21 (CH_3). ν_{max} 2916*m* (C-H), 2849*s* (C-H), 1755*s* (C=O), 1522*s* (NO_2), 1346*m* (NO_2), 1212*m* (C-O), 1139*s* (C-O), 1104*m*, 926*m*, 853*m*, 717*m*. ESI MS $C_{17}H_{25}NO_2$ *m/z* calculated 308.1856, found 309.1849 ($[M+H]^+$, 100%), 330.1664 ($[M+Na]^+$, 59%).

Gelator G1-ane

$(Boc)_2$-L-Lys-C_{12}-L-Lys-$(Boc)_2$ (1.00 g, 1.17 mmol) was dissolved in methanol (25 mL) and $HCl_{(g)}$ bubbled through solution for roughly 10 seconds and left stirring until all starting material had reacted (monitored by TLC). Solvent was removed under vacuum and the solid redissolved in DCM (150 mL). Triethylamine (1.30 mL, 9.34 mmol) was added and the undecanoyl active ester (2.15 g, 5.81 mmol), dissolved in dichloromethane (10 mL), was added dropwise to stirring mixture. The reaction was refluxed at 50°C for 7 days. The product was removed by filtration and washed with 1 M NaOH, 1 M HCl and water then

recrystallized from methanol to leave a white solid which was dried for 24 hours in a vacuum oven. Yield 0.80 g (0.71 mmol, 60%). R_f = 0.33 (9:1 DCM/MeOH, CeMo). M.p. 178.2-180.6°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.42 (2H, t, *J*=5.6 N*H*C(O)CH), 6.34 (2H, d, *J*=7.6, C(O)N*H*CH), 5.71 (2H, t, *J*=5.6 CH_2N*H*C(O)CH_2), 4.34 (2H, m, NHC(CH_2)*H*C(O)), 3.22 (8H, m, NHC*H*$_2$), 2.16 (8H, m, C*H*$_2$C(O)), 1.87-1.18 (92H, m, C*H*$_2$), 0.87 (3H, t, *J*=6.8, CH_3). ^{13}C NMR (100MHz, $CDCl_3$) δ 173.59 (*C*=O), 173.43 (*C*=O), 171.72 (*C*=O), 52.95 (NH*C*(CH_2)HC(O)), 39.63 (*C*H_2NH), 38.73 (*C*H_2NH), 36.90 (*C*H_2CO), 36.65 (*C*H_2CO), 31.92, 31.74, 29.61, 28.55, 29.42, 29.39, 29.37, 29.32, 29.26, 29.17, 29.15, 29.00, 26.76, 25.86, 25.76, 22.76, 22.60 (all *C*H_2), 14.04 (CH_3). ν_{max} 3305*m* (N-H), 2917*m* (C-H), 2849*m* (C-H), 1635*s* (C=O), 1561*m* (N-H), 1462*w*, 1274*w*, 1214*w*, 717*m*. ESI MS $C_{68}H_{132}N_6O_6$ *m/z* calculated $[M+H]^+$ 1130.0281, found 1130.0272 (47%), 1152.0057 ($[M+Na]^+$, 41%).

Compounds **1-ene**[2] and **1-ane**[3] have previously been reported but without synthetic methodology or full characterization data. This is reported below.

Unsaturated Small Molecule Analogue 1-ene

Butylamine (1.35 mL, 13.67 mmol) was added to triethylamine (2.10 mL, 15.04 mmol) in dichloromethane (50 mL). The reaction was cooled to 0^{o}C and whilst stirring 10-undecenoyl chloride (3.23 mL, 15.04 mmol) was added dropwise. The reaction was allowed to warm to room temperature and left stirring overnight. The reaction mixture was washed with sat. $NaHCO_3$, brine, 1.33 M $NaHSO_4$ and water. The organic phase was dried over $MgSO_4$, filtered and the volatiles removed under vacuum to leave the crude product which was further

purified by flash chromatography (silica, 7:3 cyclohexane/EtOAc) to produce a white solid. Yield 2.8 g (11.70 mmol, 78%). R_f = 0.55 (9:1 DCM/MeOH, CeMo). M.p. = 34.8-35.6°C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (1H, ddt (overlapped), *J*=17.2, 10.4, 6.4 Hz, CH_2=C*H*), 5.40 (1H, br s, NH), 4.98 (1H, ddt (overlapped), *J*=17.2, 2.0, 1.2 Hz, CH=C*H*H *cis*), 4.92 (1H, ddt (overlapped), *J*=10.4, 2.0, 1.2 Hz, CH=C*H*H *trans*), 3.23 (2H, dt, *J*=7.2, 5.6 Hz, CH_2NH), 2.14 (2H, t, *J*=7.2 Hz, CH_2C=O), 2.02 (2H, m, CH_2CH=CH_2), 1.61 (2H, m, CH_2CH_2CH=CH_2), 1.47 (2H, m, CH_2CH_2NH), 1.39-1.23 (12H, m, CH_2), 0.91 (3H, t, *J*=7.2, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.07 (C=O), 139.11 (=CH), 114.07 (=CH_2), 39.26 (CH_2NH), 36.98 (*C*H_2CO), 33.86 (*C*H_2CH=CH_2), 31.83 (NHCH_2CH_2), 29.39, 29.14, 28.96, 25.92, 20.15 (all CH_2), 13.84 (CH_3). ν_{max} 3291*m* (N-H), 3077*w* (=C-H), 2917*m* (C-H), 2850*m* (C-H), 1635*s* (C=O), 1549*s* (N-H), 1436*w*, 1367*w*, 991*w*, 913*m*. ESI MS $C_{15}H_{29}NO$ *m/z* calculated $[M+H]^+$ 240.2322, found 240.2328 (100%).

Saturated Small Molecule Analogue 1-ane

Butylamine (1.35 mL, 13.67 mmol) was added to triethylamine (2.10 mL, 15.04 mmol) in dichloromethane (50 mL). The reaction was cooled to 0^{o}C and whilst stirring undecanoyl chloride (3.31 mL, 15.04 mmol) was added dropwise. The reaction was allowed to warm to room temperature and left stirring overnight. The reaction mixture was washed with sat. $NaHCO_3$, brine, 1.33 M $NaHSO_4$ and brine. The organic phase was dried over $MgSO_4$, filtered and the volatiles removed under vacuum to leave the crude product which was further purified by flash chromatography (silica, 3:7 cyclohexane/EtOAc) to produce a white solid. Yield 2.9 g (12.0 mmol, 88%). R_f = 0.67 (9:1 DCM/MeOH, CeMo stain). M.p. 46.2-46.9°C. ^{1}H

NMR (400 MHz, $CDCl_3$) δ 5.37 (1H, br s, N*H*), 3.27 (2H, dt, *J*=6, 7.2 Hz, CH_2NH), 2.14 (2H, t, *J*=7.6 Hz, CH_2CO), 1.61 (2H, m, $COCH_2CH_2$), 1.47 (2H, m, $NHCH_2CH_2$), 1.39-1.18 (16H, m, CH_2), 0.92 (3H, t, CH_3), 0.87 (3H, t, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.15 (*C*=O), 39.27 ($NHCH_2$), 37.04 ($COCH_2$), 31.97 ($NHCH_2CH_2$), 31.85 (CH_2), 29.64, 29.58, 29.44, 29.39, 25.93, 22.76, 20.15 (all CH_2), 14.19, 13.84 (both CH_3). ν_{max} 3316*m* (N-H), 2914*s* (C-H), 2848*m* (C-H), 1633*s* (C=O), 1543*s* (N-H), 1469*m*, 1425*w*, 1224*w*, 714*w*, 666*w*. ESI MS $C_{15}H_{31}NO$ *m/z* calculated $[M+H]^+$ 242.2478, found 242.2476 (100%), 264.2293 ($[M+Na]^+$, 46%).

3. Infra Red Spectra of Gels in the Absence and Presence of Metal Salts

Gels were made and treated as described above. They were then dried under high vacuum (in the absence of light for silver salt). The remaining solid was then analysed by ATR-FTIR.

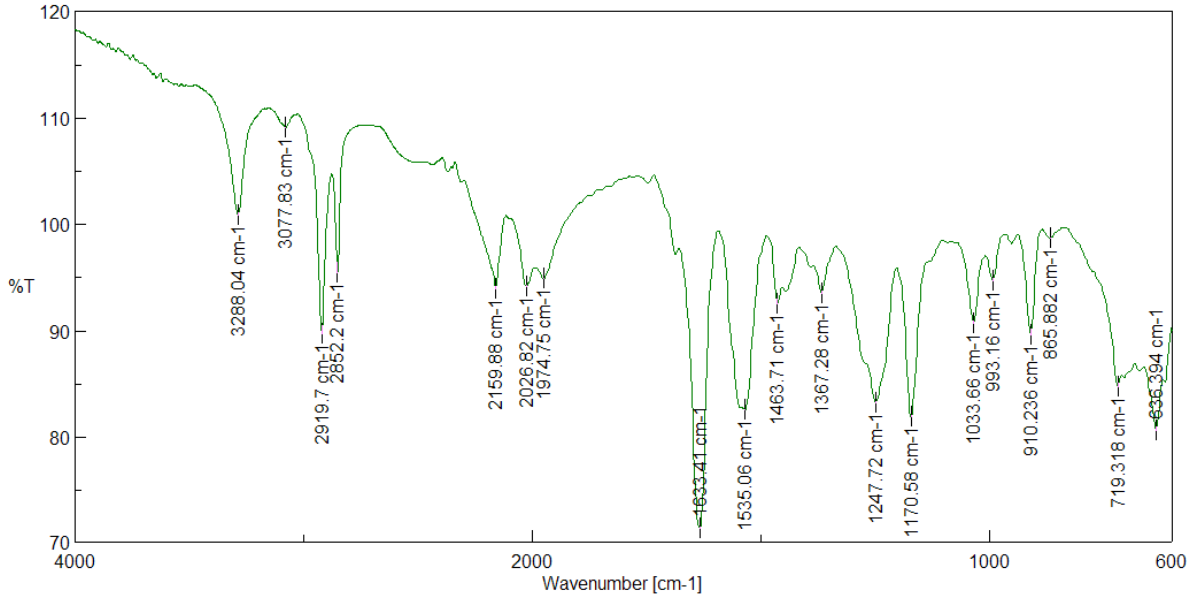

Fig. S2 IR spectrum of xerogel formed by drying gel of compound **G1-ene** formed in ethyl acetate.

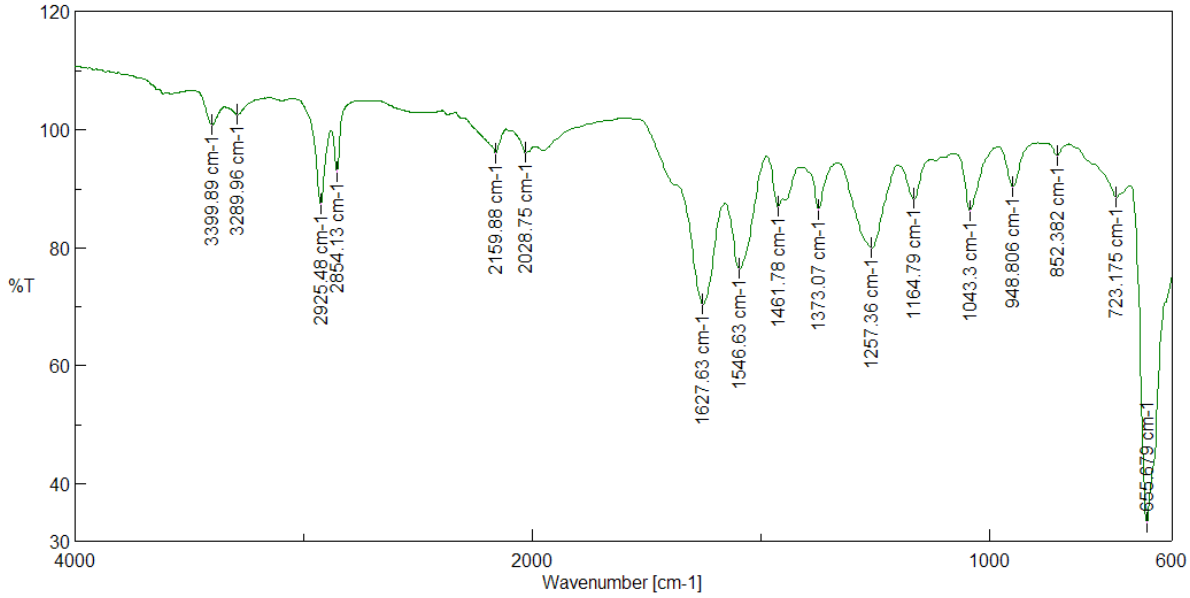

Fig. S3 IR spectrum of dried **G1-ene** gel after addition of $AgSbF_6$.

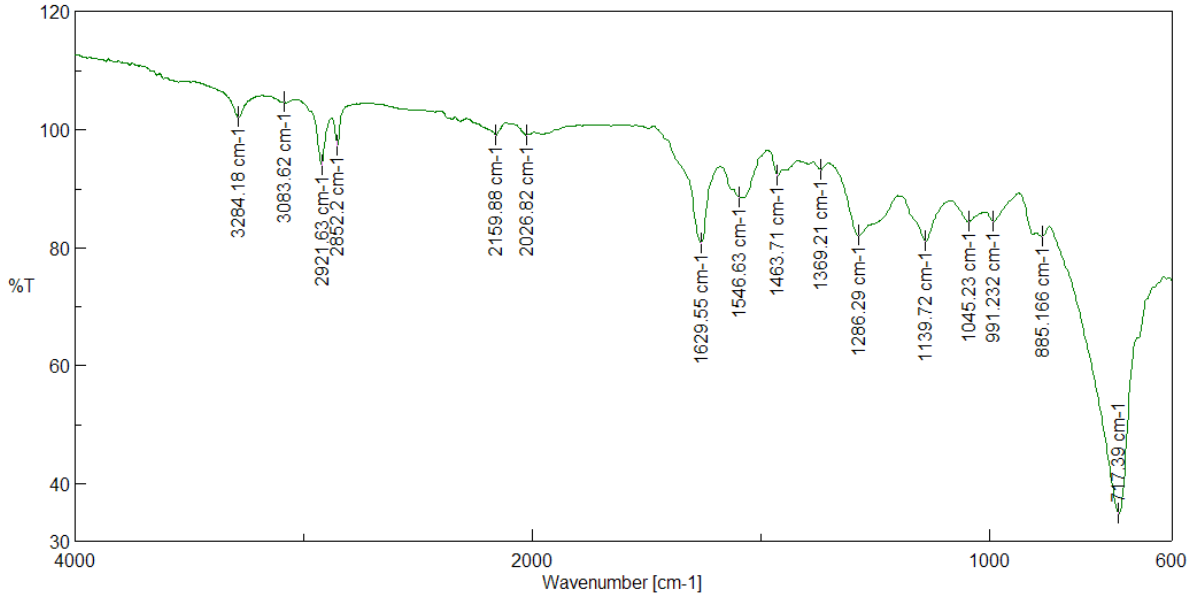

Fig. S4 IR spectrum of dried **G1-ene** gel after addition of $LiPF_6$.

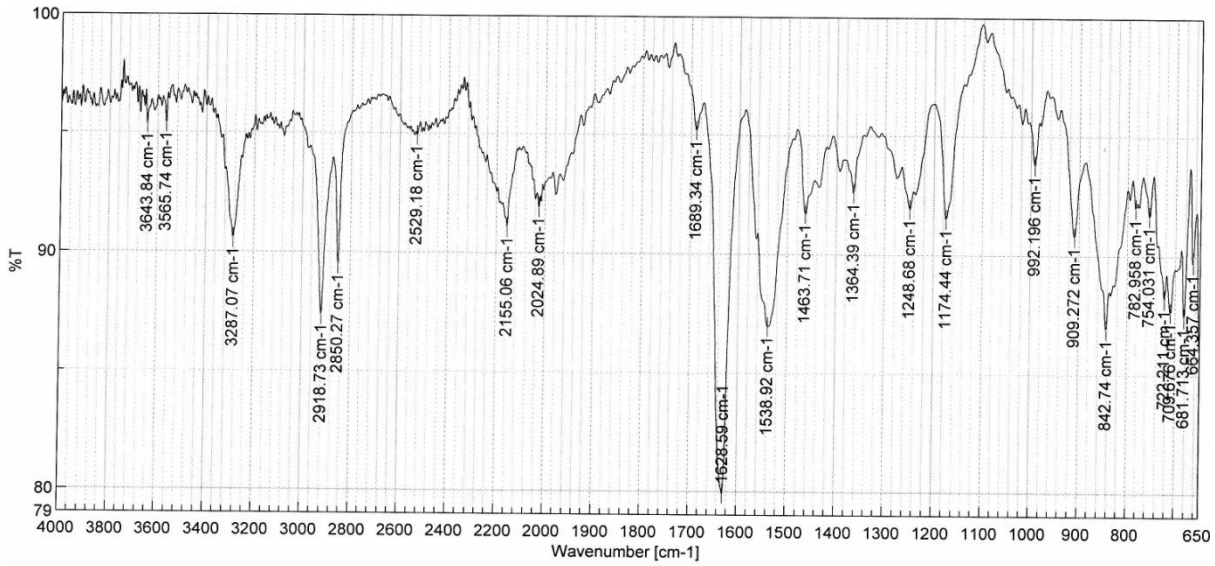

Fig. S5 IR spectrum of dried **G1-ene** gel after addition of $NaPF_6$.

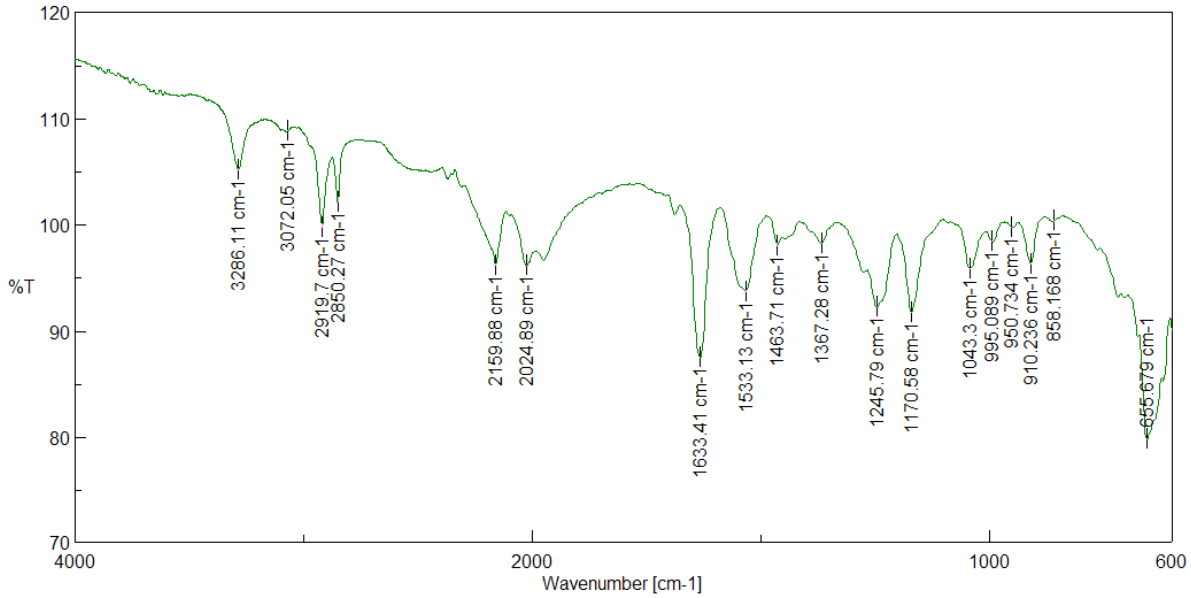

Fig. S6 IR spectrum of dried **G1-ene** gel after addition of $KSbF_6$.

4. NMR Experiments and Data

All ^{13}C NMR experiments were run unlocked, carried out using non-deuterated ethyl acetate (0.75 mL) as the solvent and referenced to TMS which was added to every sample.

Job Plot Analysis

Job plot analyses were carried out with a constant overall concentration of 0.56 M. The proportion of $AgSbF_6$ was varied from 0-100 %. The change in chemical shift of a carbon × [host] was plotted against [host] / ([host] + [guest]). The optimum binding ratio was taken as the apex of the curve produced.

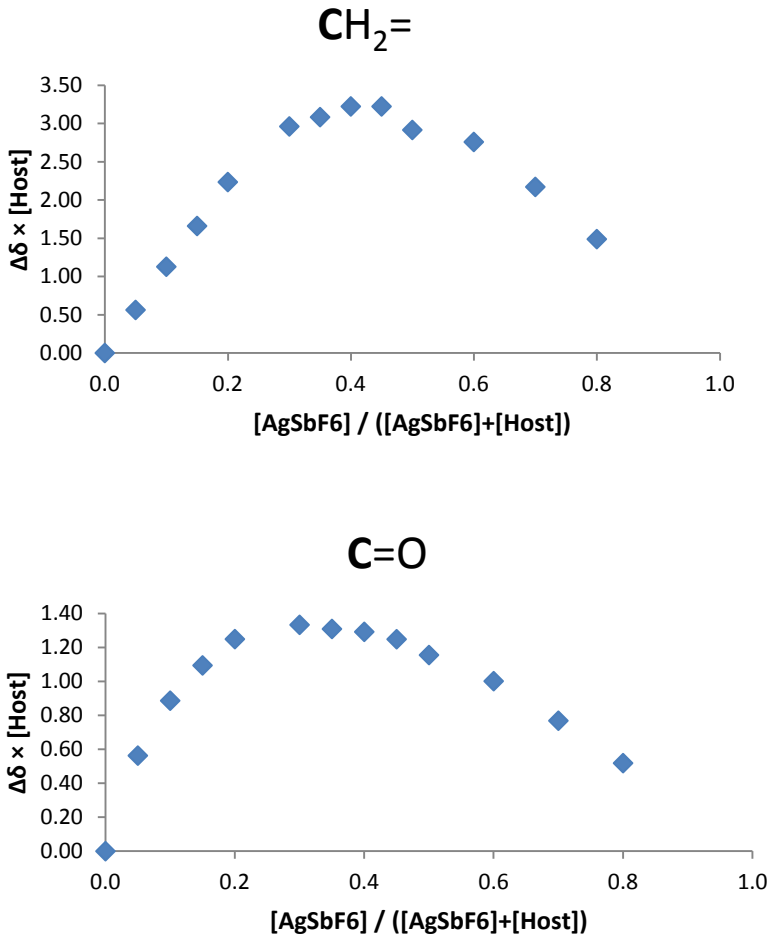

Fig. S7 Job plots of CH_2= and C=O carbons on compound **1-ene** with $AgSbF_6$.

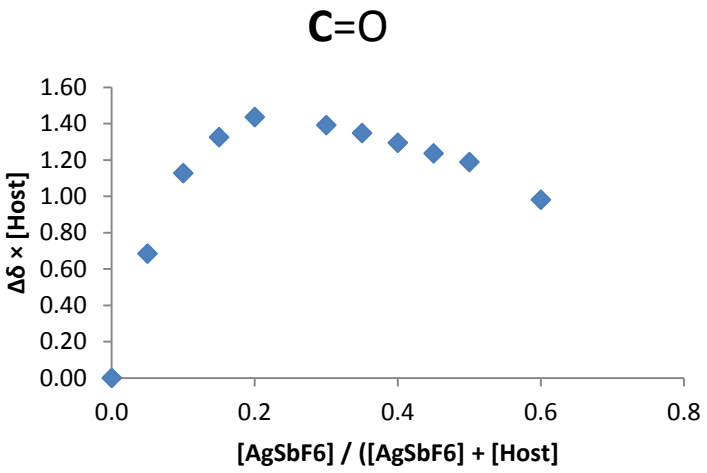

Fig. S8 Job plot of C=O carbon of compound **1-ane** with $AgSbF_6$.

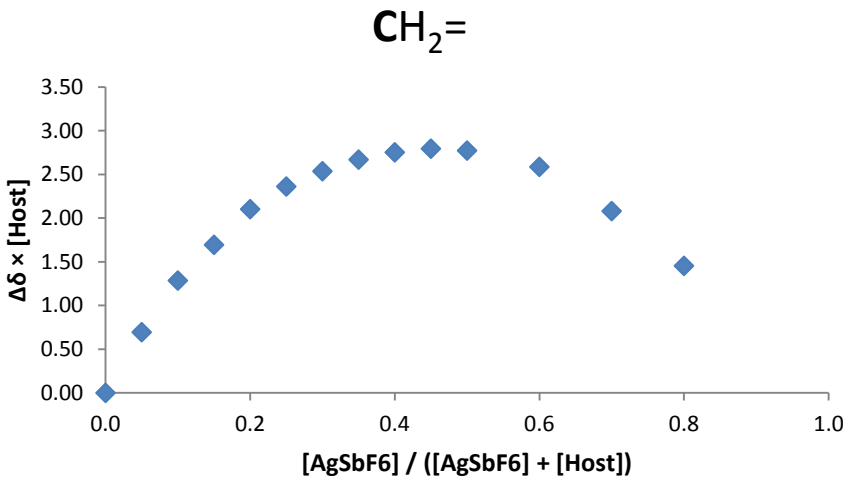

Fig. S9 Job plot analysis of **Octene** with $AgSbF_6$.

NMR Titrations

^{13}C NMR titrations were carried out using a 0.56 M concentration of host. Increasing numbers of equivalents of $AgSbF_6$ salt were added to each sample. Each concentration was made up in a separate tube as the $AgSbF_6$ salt was light sensitive and would degrade over time. This also ensured a constant solvent depth which was essential for well shimmed spectra given the use of non-deuterated ethyl acetate. The change in chemical shift with increasing $AgSbF_6$ concentration for each compound is plotted below.

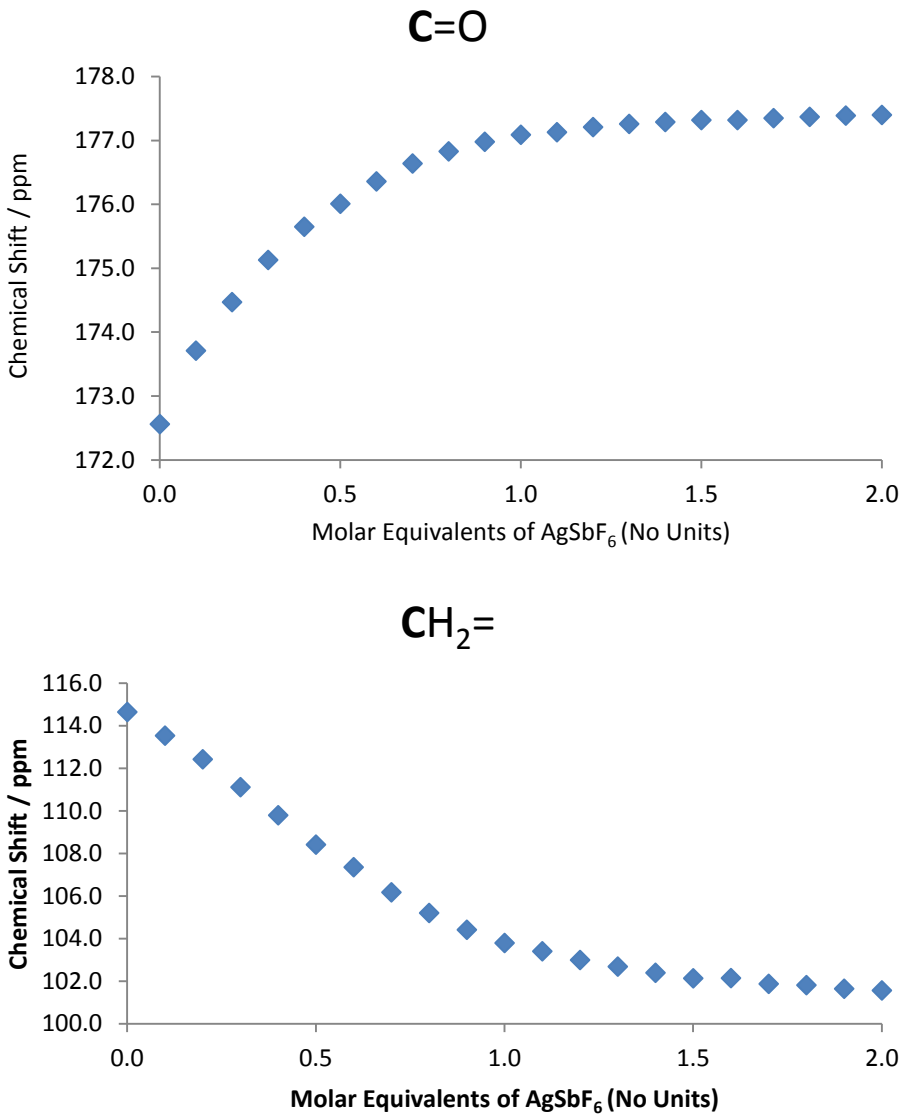

Fig. S10 Plots of chemical shift changing on the C=O and CH_2= carbons of compound **1-ene** with increasing amounts of $AgSbF_6$.

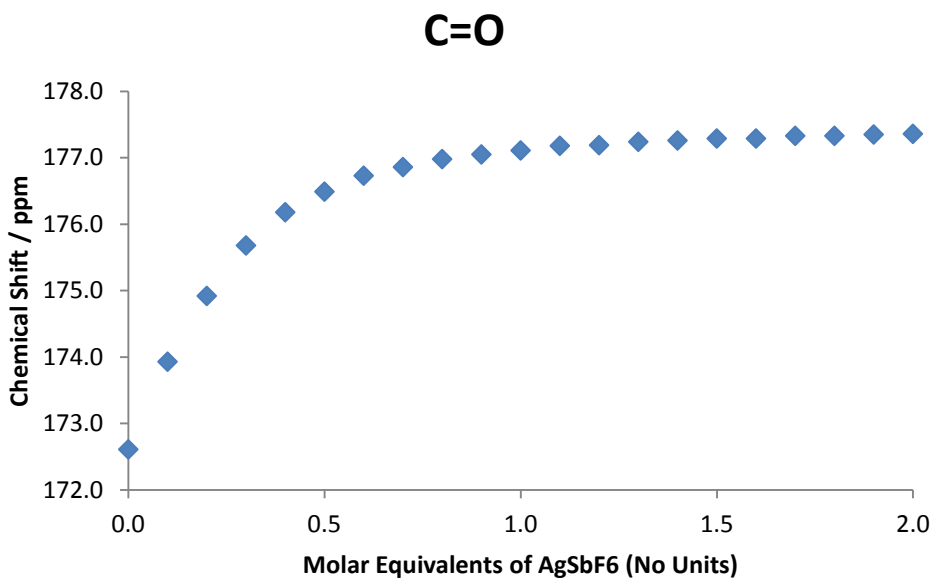

Fig. S11 Plot of chemical shift changing on the C=O carbon of compound **1-ane** with increasing amounts of $AgSbF_6$

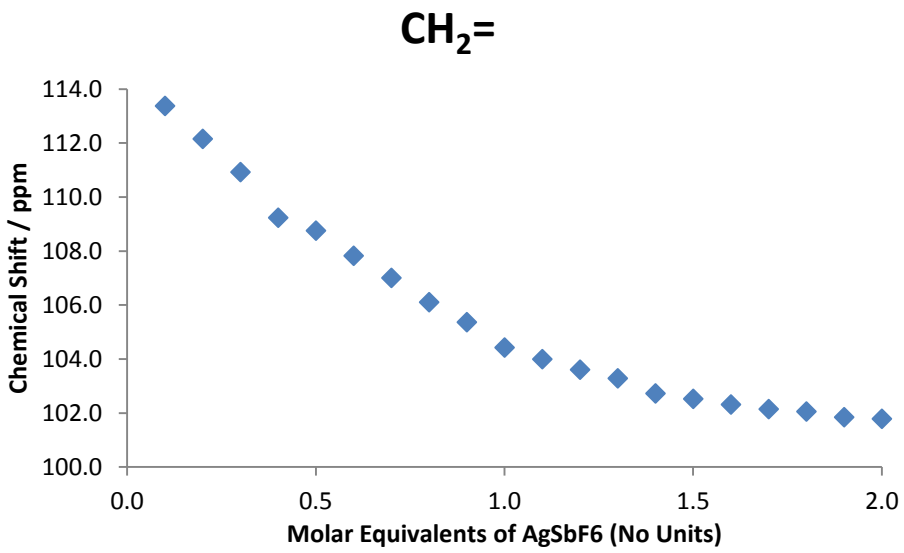

Fig. S12 Plot of chemical shift changing on the CH_2= carbon of **Octene** with increasing amounts of $AgSbF_6$

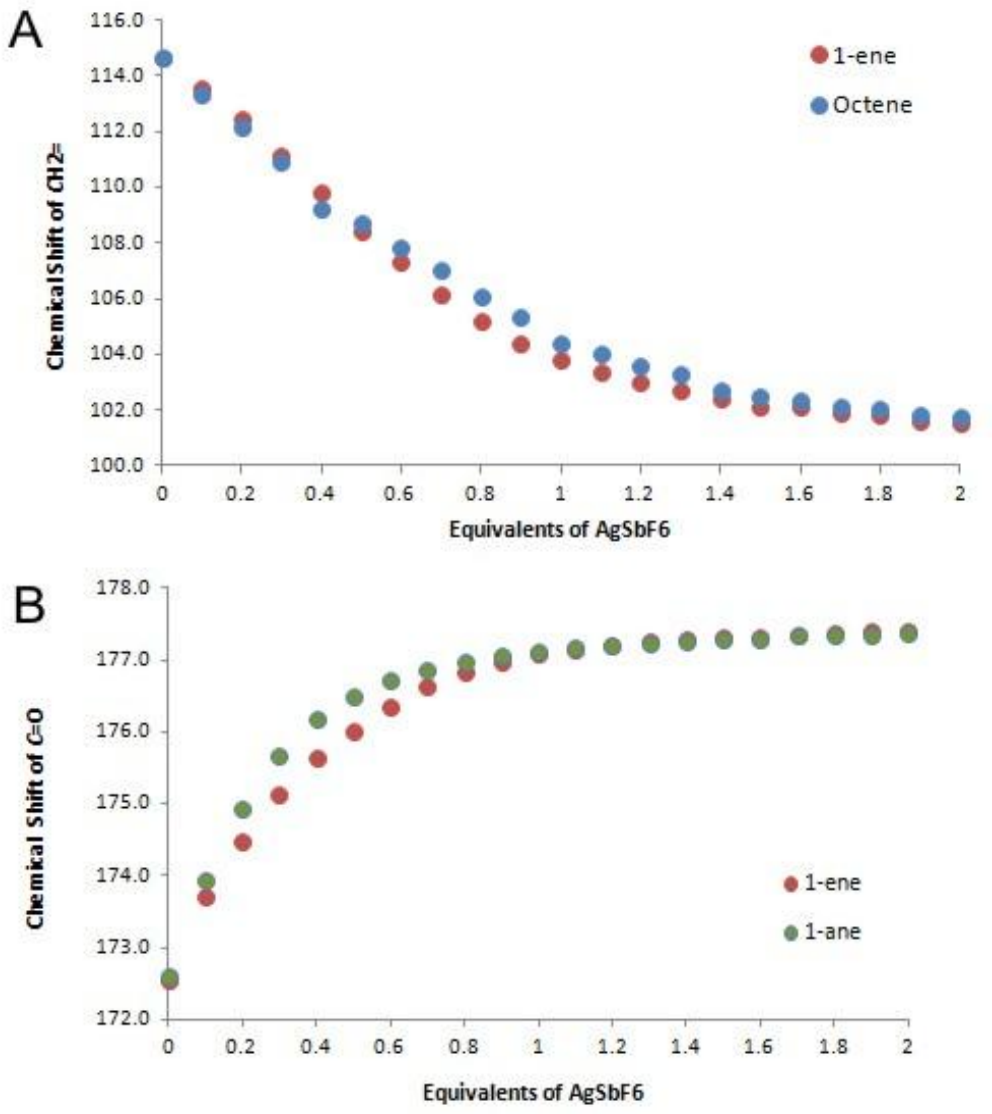

Fig. S13. Composite graphs showing chemical shift of A, alkene carbons and B, amide carbonyls on **1-ene**, **1-ane** and **Octene** when titrated with $AgSbF_6$

^{13}C NMR Spectra of Native G1-ene Gel Before and After Salt Addition

A gel was formed with 50 mg of **G1-ene** (4.46×10^{-5} mol) and 0.75 mL EtOAc. For the other samples a gel was formed with 50 mg of **G1-ene** and 0.5 mL EtOAc, then either $AgSbF_6$ (153 mg, 4.46×10^{-4} mol) or $LiPF_6$ (68 mg, 4.46×10^{-4}) was added in 0.25 mL EtOAc. The samples were left overnight before the spectra were recorded.

5. Calculation of Stability Constants

Binding constants could be fitted to data produced for CH_2= carbons on compound **2** and **Octene** using the WinEQNMR2 program.[4] Different starting values were found to converge on the stated constants. The fit plots produced by winEQNMR2 are shown below.

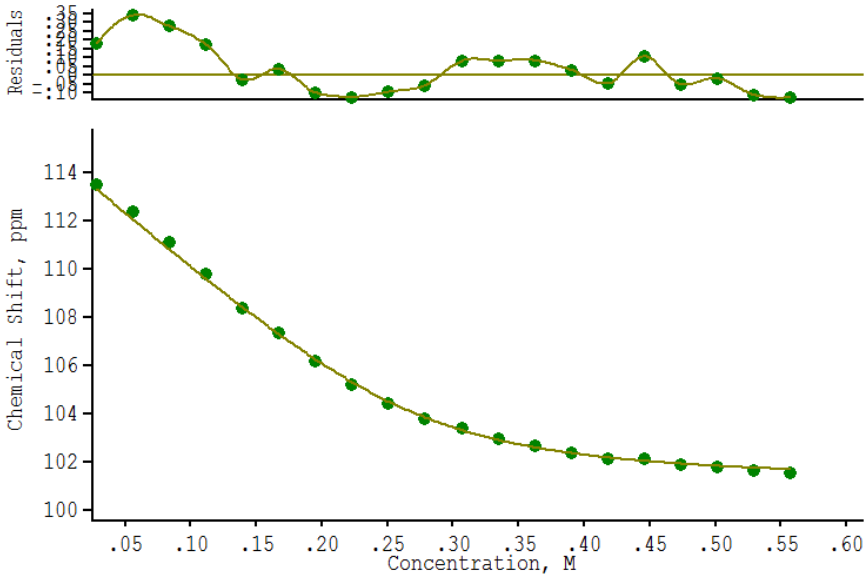

Fig. S14 Fit plot with residuals shown for CH_2= carbon of compound **2** (points = experimental data, curve = theoretical data)

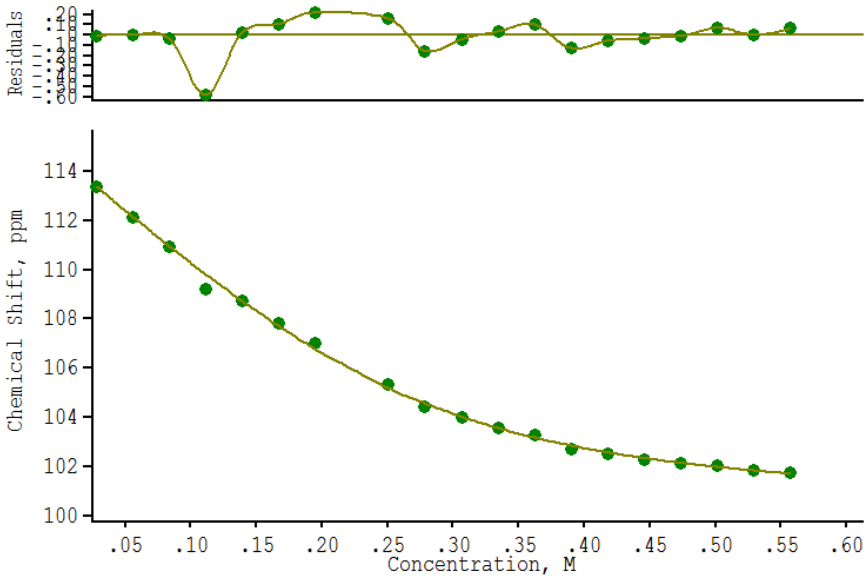

Fig. S15 Fit plot with residuals shown for CH_2= carbon of compound **Octene** (points = experimental data, curve = theoretical data)

References

1 (*a*) J. R. Moffat, I. A Coates, F. J. Leng and D. K. Smith, *Langmuir*, 2009, **25**, 8786-8793; (*b*) J. R. Moffat and D. K. Smith, *Chem. Commun.*, 2009, 316-318.

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