

Electronic Supplementary information for A magnetic self-contained thermochromic system with convenient temperature range

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Table of contents

Materials.....	2
Synthesis of the <i>N</i> -[2-(dimethylamino)ethyl]glucosamide intermediate.....	2
Synthesis of the <i>N</i> -[2-(dimethylamino)ethyl]glycolamide intermediate.....	2
Synthesis of the <i>N</i> -[2-(dimethylamino)ethyl]hexylamide intermediate.....	3
Synthesis of the [N ₁ 1 2GA 8]Br ligand.....	3
Synthesis of the [N ₁ 1 2GA 8][NTf ₂] ligand.....	3
Synthesis of the [N ₁ 1 2GlyA 8]Br ligand.....	4
Synthesis of the [N ₁ 1 2Hex 8]Br ligand.....	4
Preparation of the thermochromic solution.....	5
Preparation of the thermochromic film.....	5
Mass spectrometric measurements.....	5
Differential scanning calorimetry.....	5
Thermogravimetric analysis.....	5
UV-vis measurements.....	6
Preparation of the sample for the Evans method.....	6
NMR measurements.....	6
Figure S1-DSC analysis of : a) the <i>N</i> -[2-(dimethylamino)ethyl]glucosamide intermediate; b) the [N ₁ 1 2GA 8]Br ligand; c) the [N ₁ 1 2GA 8][NTf ₂] ligand; d) the [N ₁ 1 2GlyA 8]Br ligand; e) the [N ₁ 1 2Hex 8]Br ligand.....	8

Figure S2- TGA analysis of: a) the <i>N</i> -[2-(dimethylamino)ethyl]glucosamide intermediate; b) [N _{1 1 2GA 8}]Br ligand; c) [N _{1 1 2GA 8}][NTf ₂] ligand; d) the [N _{1 1 2GlyA 8}]Br ligand; e)) the [N _{1 1 2Hex 8}]Br ligand.....	10
Figure S3- ¹ H and ¹³ C NMR spectra: a) <i>N</i> -[2-(dimethylamino)ethyl]glucosamide intermediate; b) <i>N</i> -[2-(dimethylamino)ethyl]glycolamide intermediate; c)the <i>N</i> -[2-(dimethylamino)ethyl]hexylamide intermediate; d) the [N _{1 1 2GA 8}]Br IL ligand e) the [N _{1 1 2GA 8}][NTf ₂] IL ligand f) the [N _{1 1 2GlyA 8}]Br IL ligand; g)) the [N _{1 1 2Hex 8}]Br IL ligand.	13
Figure S4- UV-vis spectra for the solution composed by Co(NTf ₂) ₂ in [N _{2 2 2 4}][NTf ₂].....	19
Figure S5- UV-vis spectra of the Co(NTf ₂) ₂ + [N _{1 1 2GlyA 8}]Br in [N _{2 2 2 4}][NTf ₂] solution.....	19
Figure S6- UV-vis spectra of the Co(NTf ₂) ₂ + [N _{1 1 2HexA 8}]Br in [N _{2 2 2 4}][NTf ₂] solution.	20
Figure S7- Colour transition of Co(NTf ₂) ₂ + [N _{1 1 2GA 8}]Br in [N _{2 2 2 4}][NTf ₂] solution in the 15 to 100 °C range.	20
Figure S8- UV-vis spectra of the Co(NTf ₂) ₂ + [N _{1 1 2GA 8}]Br in [N _{2 2 2 4}][NTf ₂] solution recorded during 52 days.	21
Figure S9- Trend of the μ _{eff} calculated with the Evans method, at variable temperature.....	21
Figure S10- ¹ H NMR spectra recorded at variable temperatures for the calculation of the Evans method, herein, the zoomed area from 3.25 to 4.10 ppm is presented.	23
Figure S11- UV-vis spectra of the Co(NTf ₂) ₂ + [N _{1 1 2GA 8}]Br + PMMA film recorded for 20 cycles....	24
Figure S12- UV-vis spectra of the Co(NTf ₂) ₂ + [N _{1 1 2GA 8}]Br + PMMA film recorded for the fresh film, after 2 months and after 7 months: a) at 45 °C; b) at 50 °C.....	24

Materials

Glucono- δ -lactone (Sigma Aldrich, $\geq 99.0\%$), *N,N*-dimethylethylenediamine (TCI, $>98.0\%$), 2-ethylhexyl bromide (Sigma Aldrich, 95.0%), [N_{2,2,2,4}][NTf₂] (Iolitec, 99.0%), Co(NTf₂)₂ (Alfa Aesar), poly(methyl methacrylate) (Sigma Aldrich), ethyl glycolate (Sigma Aldrich, 98%), hexanoyl chloride (Sigma Aldrich, 97%) and lithium bis{(trifluoromethyl)sulfonyl}amide salt (TCI, $>98.0\%$) were purchased and used without further purification.

Dichloromethane (Merck, $>99.8\%$), 1-butanol (Merck, $>99.8\%$), methanol (Merck, HPLC grade), ethyl acetate (Merck, 98.8%) and *t*-butanol (Merck, 99.5%) were purchased and used without further purification.

Synthesis of the *N*-[2-(dimethylamino)ethyl]glucosamide intermediate

The glucono- δ -lactone (8.42 mmol) was solubilised in methanol (70 mL) in two-neck round bottomed flask and it was placed in an oil bath at $60\text{ }^{\circ}\text{C}$. The *N,N*-dimethylethylenediamine (9.26 mmol) was slowly added to the reaction mixture. After 24 h, the reaction was stopped and the solvent removed under vacuum. The yellow oil obtained was dissolved in a mixture of ethyl ethanoate/ethanol (50/50 v/v, 50 mL), obtaining a white solid. The solvent was removed under vacuum. To wash the solid product, ethyl ethanoate (50 mL) was added. The mixture was filtered using a Büchner funnel under vacuum, and the solid was collected. The product was dried *in vacuo* for 24 h.

Yield: 86.0% ; T_m (DSC): $91.8\text{ }^{\circ}\text{C}$.

¹H NMR (400 MHz; DMSO-*d*₆); δ (ppm): 7.53 (t, 1H, $J = 8\text{ Hz}$); 5.42 (s, 1H); 4.31 (s, 1H); 3.97 (d, 1H); 3.89 (s, 1H); 3.56 (m, 1H); 3.47 (m, 2H); 3.35 (m, 2H); 3.18 (m, 2H); 2.31 (td, 2H, $J = 4\text{ Hz}$); 2.14 (s, 6H). ¹³C NMR (400 MHz; DMSO-*d*₆); δ (ppm): 173.8; 74.0; 72.5; 71.9; 70.6; 63.9; 58.4; 45.5; 36.6.

Mass for [C₁₀H₂₃N₂O₆]⁺: 267.1556.

Synthesis of the *N*-[2-(dimethylamino)ethyl]glycolamide intermediate

The ethyl glycolate (10 mmol), *N,N*-dimethylethylenediamine (12 mmol) and distilled water (5 mL) were placed in a sealed screw cap tube. The reaction was stirred at room temperature for 3.5 hours. After this time, the reaction mixture was transferred to a round bottomed flask and N₂ was blown into the reaction for 1 h. The residual solvent was removed under vacuum and a white solid was obtained. The product was dried *in vacuo* for 24 h.^[1]

Yield: 70.0% .

¹H NMR (400 MHz; DMSO-*d*₆); δ (ppm): 7.55 (s, 1H); 5.52 (bs, 1H); 3.77 (s, 2H); 3.19 (q, 2H); 2.30 (t, 2H, $J = 8\text{ Hz}$); 2.14 (s, 6H). ¹³C NMR (400 MHz; DMSO-*d*₆); δ (ppm): 172.0; 58.5; 45.5; 36.4.

Synthesis of the *N*-[2-(dimethylamino)ethyl]hexylamide intermediate

The *N,N*-dimethylethylenediamine (2.27 mmol) was dissolved in chloroform (10 mL) in a round bottomed flask and it was placed in ice to maintain the temperature equal to 5 °C. Hexanoyl chloride (2.29 mmol) was added dropwise in 8 minutes. The mixture was stirred at room temperature for two hours. After this time, the reaction was complete and chloroform was removed under vacuum. The oil obtained was subjected to extraction with ethyl ethanoate (30 mL). After the extraction, the mixture was washed with a saturated aqueous sodium bicarbonate solution (10 mL) and, then, with saturated brine (10 mL). After washing the residual solvent was removed under vacuum and a white solid was obtained. The product was dried *in vacuo* for 24 h.⁸³

Yield: 70.9%.

¹H NMR (300 MHz; CDCl₃); δ (ppm): 6.04 (s, 1H); 3.30 (q, 2H, *J* = 3); 2.39 (t, 2H, *J* = 6 Hz); 2.22 (s, 6H); 2.14 (m, 2H); 1.62 (m, 2H); 1.30 (d, 4H); 0.88 (t, 3H, *J* = 6 Hz). ¹³C NMR (300 MHz; CDCl₃); δ (ppm): 172.9; 57.6; 44.8; 36.4; 36.3; 31.2; 25.2; 22.1 13.6.

Synthesis of the [N_{1 1 2GA 8}]Br ligand

The *N*-[2-(dimethylamino)ethyl]glucosamide intermediate (2.5 mmol) was placed with methanol (4 mL) in a round bottomed flask and heated at reflux (60 °C). The 2-ethylhexyl bromide (3.75 mmol) was slowly added to the reaction mixture. The alkylation was stopped when the ¹H NMR of the mixture did not show the signal of the amide (chemical shift: 7.53 ppm) related to the intermediate and only the amide signal of the ionic liquid (chemical shift: 8.04 ppm) appeared. The solvent was removed under vacuum and the ionic liquid was washed with ethyl ethanoate (20 mL). The ionic liquid was dried *in vacuo* for 24 h.

The product was obtained as light yellow oil. Yield: 90.2%; *T_g* (DSC): -16.6 °C (heating); -22.6 °C (cooling).

¹H NMR (600 MHz, DMSO-*d*₆); δ (ppm): 8.04 (t, 1H, *J* = 6 Hz); 5.48 (s, 1H); 4.34 (m, 4H); 3.96 (m, 1H); 3.87 (m, 1H); 3.50 (m, 3H); 3.42 (m, 4H); 3.32 (m, 4H); 2.96 (s, 6H); 1.80 (s, 1H); 1.27 (m, 10H); 0.82 (m, 6H). ¹³C NMR (600 MHz, DMSO-*d*₆); δ (ppm): 173.8; 74.0; 72.7; 72.0; 70.6; 69.1; 63.7; 62.9; 50.3; 33.4; 32.9; 32.8; 28.6; 28.0; 26.1; 22.8; 14.4; 10.6.

Mass for [N_{1 1 2GA 8}]₂⁺Br⁻: 837.4880.

Synthesis of the [N_{1 1 2GA 8}][NTf₂] ligand

[N_{1 1 2GA 8}]Br ionic liquid (0.60 mmol) IL (0.60 mmol) was dissolved in 1-butanol (4 mL) in a round bottomed flask and stirred at room temperature for 24 h. Li(NTf₂) (0.64 mmol) was slowly added to the solution and white precipitate was formed. This precipitate was separated by filtration and the solution was passed through alumina oxide. The organic phase was placed in a separatory funnel and washed with distilled water. The organic phase was recovered and the sodium sulfate anhydrous

was added to remove the residue of water. Sodium sulfate was removed by filtration. The organic solvent was removed under vacuum. The ionic liquid was dried in vacuo for 24 h.

The product was obtained as yellow oil. Yield: 72.6%. T_g (DSC): -15.9 °C.

¹H NMR (600 MHz; DMSO-*d*₆); δ (ppm): 7.88 (t, 1H, *J* = 6 Hz); 5.48 (d, 1H); 4.60 (d, 1H); 4.55 (d, 1H); 4.50 (d, 1H); 4.36 (s, 1H); 4.00 (t, 1H, *J* = 6 Hz); 3.92 (s, 1H); 3.59 (d, 1H); 3.50 (s, 2H); 3.26 (t, 3H, *J* = 6 Hz); 3.14 (m, 3H); 2.97 (s, 6H); 1.33 (m, 10H); 0.87 (m, 6H). ¹³C NMR (600 MHz; DMSO-*d*₆); δ (ppm): 173.8; 123.1; 121.0; 118.9; 116.7; 74.0; 72.7; 72.0; 70.6; 69.1; 63.7; 60.8; 50.3; 35.1; 33.4; 32.8; 28.0; 26.1; 22.8; 19.1; 14.4; 10.5.

Mass for [N_{1 1 2GA 8}]²⁺[NTf₂]⁻: 1038.4789.

Synthesis of the [N_{1 1 2GlyA 8}]Br ligand

The *N*-[2-(dimethylamino)ethyl]glycolamide intermediate was placed with methanol (4 mL) in a round bottomed flask and heated at reflux (60 °C). The 2-ethylhexyl bromide (1.4 mmol) was slowly added to the reaction mixture. The alkylation was stopped when the ¹H NMR of the mixture did not show the signal of the amide (chemical shift: 7.55 ppm) related to the intermediate and only the amide signal of the ionic liquid (chemical shift: 8.14 ppm) appeared. The solvent was removed under vacuum and the ionic liquid was washed with ethyl ethanoate (20 mL). The ionic liquid was dried *in vacuo* for 24 h.

The product was obtained as light yellow oil. Yield: 98%; T_g: -29.5°C (heating) -38.7 °C (cooling).

¹H NMR (400 MHz, DMSO-*d*₆); δ (ppm): 8.14 (t, 1H, *J* = 8 Hz); 5.61 (d, 1H); 3.83 (s, 2H); 3.55 (q, 2H); 3.42 (m, 2H); 3.22 (m, 2H); 3.06 (s, 6H); 2.71 (s, 1H); 1.28 (m, 8H); 0.88 (m, 6H). ¹³C NMR (400 MHz; DMSO-*d*₆); δ (ppm): 172.9; 68.9; 62.7; 61.9; 50.3; 33.0; 32.9; 32.7; 28.0; 26.0; 22.8; 14.4; 10.5.

Mass for [N_{1 1 2GlyA 8}]₂⁺ Br⁻: 599.3939.

Synthesis of the [N_{1 1 2Hex 8}]Br ligand

The *N*-[2-(dimethylamino)ethyl]hexylamide intermediate was placed with methanol (4 mL) in a round bottomed flask and heated at reflux (60 °C). The 2-ethylhexyl bromide (1.6 mmol) was slowly added to the reaction mixture. The alkylation was stopped when the ¹H NMR of the mixture did not show the signal of the amide (chemical shift: 6.04 ppm) related to the intermediate and only the amide signal of the ionic liquid (chemical shift: 8.14 ppm) appeared. The solvent was removed under vacuum and the ionic liquid was washed with ethyl ethanoate (20 mL). The ionic liquid was dried *in vacuo* for 24 h.

The product was obtained as light yellow oil. Yield: 69.8%; T_g: -48.7 °C (heating); -51.0 °C (cooling).

¹H NMR (400 MHz, DMSO-*d*₆); δ (ppm): 8.14 (t, 1H, *J* = 8 Hz); 3.47 (m, 2H); 3.22 (t, 2H, *J* = 4 Hz); 3.06 (s, 6H); 2.80 (s, 1H); 2.10 (t, 2H, *J* = 8 Hz); 1.90 (s, 1H); 1.50 (q, 3H, *J* = 8 Hz); 1.27 (m, 11H);

0.88 (m, 9H). ^{13}C NMR (400 MHz; DMSO- d_6); δ (ppm): 172.1; 67.7; 61.6; 49.1; 41.8; 34.5; 32.1; 31.8; 31.6; 30.2; 26.9; 24.9; 24.1; 21.7; 21.2; 13.2; 13.1; 9.4.

Mass for $[\text{N}_{11}\text{HexA}_8\text{L}]^{2+} \text{Br}^-$: 677.5308.

Preparation of the thermochromic solution

$\text{Co}(\text{NTf}_2)_2$ salt (5.75 mg, $9.28 \cdot 10^{-3}$ mmol) was dissolved in 600 mg of $[\text{N}_{2224}][\text{NTf}_2]$. In order to assist solubilisation, ultrasound bath (VWR ultrasonic cleaning bath and Decon ultrasonics Ltd.) was used for 30 min. A pink homogeneous solution was obtained, to this solution $[\text{N}_{11}\text{GA}_8]\text{Br}$ (12.77 mg, $2.78 \cdot 10^{-2}$ mmol) was added. The mixture was heated at 90 °C for 1.5 h. The solution turned blue at 90 °C and switched back to pink at room temperature.

Preparation of the thermochromic film

$[\text{N}_{11}\text{GA}_8]\text{Br}$ ligand (48 mg, 0.10 mmol) and $\text{Co}(\text{NTf}_2)_2$ (23 mg, 0.03 mmol) were solubilised in DCM (3 mL). Poly(methyl methacrylate) (PMMA) (390 mg) was solubilised in DCM (8 mL). In both cases, to obtain homogeneous solutions, the mixtures were sonicated for 30 min. After the solutions cooled down, they were mixed and pink solution was obtained. This solution was placed in a petri dish (diameter: 10 cm). The solvent slowly evaporated at room temperature. A pink homogeneous film was obtained, that was subsequently removed from the glass by peeling.

Mass spectrometric measurements

ESMS-mass spectrometric measurements were carried out using a Waters ICI Premier instrument with an Adylon Triversa NanoMate injection system (cone voltage 50 V, source 120 °C). Positive ions were detected. For each sample, methanol was used as a solvent.

Differential scanning calorimetry

DSC measurements were carried out using TA Instruments Modulated DSC Q 2000 V24.4 Build 116 with a refrigerated cooling system RCS 90 capable of controlling the temperature down to 220 K. Samples were weighed and hermetically sealed in aluminum pans. Heating and cooling rates were 5 °C min^{-1} for the ionic liquid sample. The maximum heating temperature was varied depending on the thermal stability of the sample. The minimum cooling temperature was set at -20 °C under dinitrogen atmosphere. Two heating-cooling cycles were performed.

Thermogravimetric analysis

Thermogravimetric analysis was performed using TGA/DSC thermogravimetric analyser from Mettler-Toledo, Inc. The samples were measured in alumina crucibles, at a heating rate of 5 K min^{-1} under a dinitrogen atmosphere. The onset of the weight loss in each thermogram was used as a measure of the decomposition temperature (point at 5 wt% loss of the sample).

UV-vis measurements

The spectra of the solution were recorded with a Beckman Coulter DU 800 spectrophotometer equipped with a Peltier temperature controller. The solution was placed in a quartz cuvette with light path of 0.2 cm. The spectra were recorded in the wavelength range 250-900 nm. The spectra of the film were recorded using the Agilent Cary 60 UV-Vis spectrophotometer equipped with a temperature control block, where the quartz cuvette was placed. The film was placed inside of the quartz cuvette with a light path of 0.2 cm. The spectra were recorded in the wavelength range 300-800 nm.

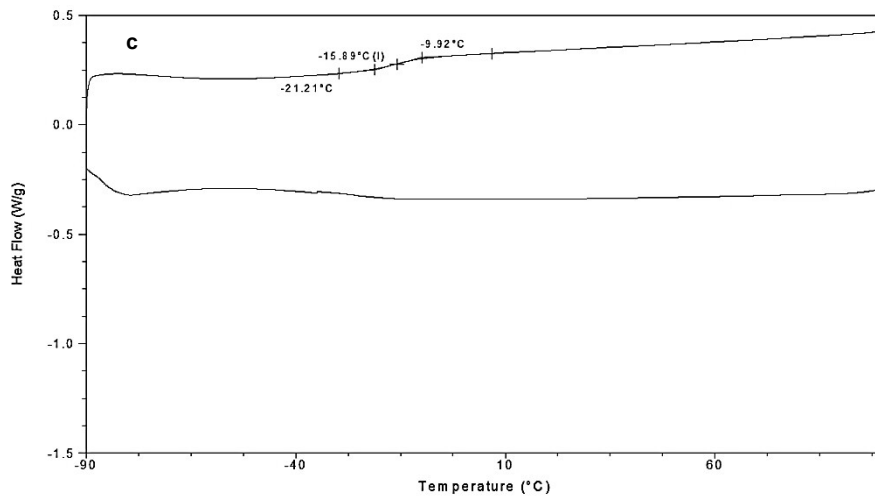
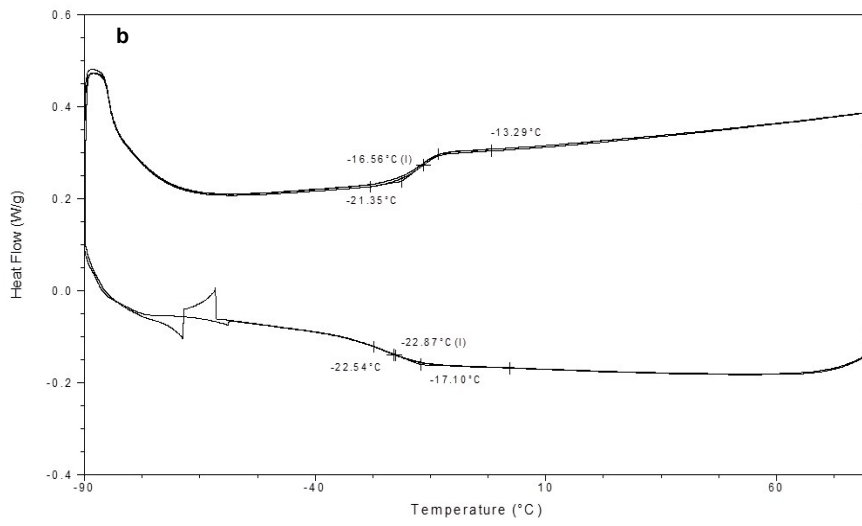
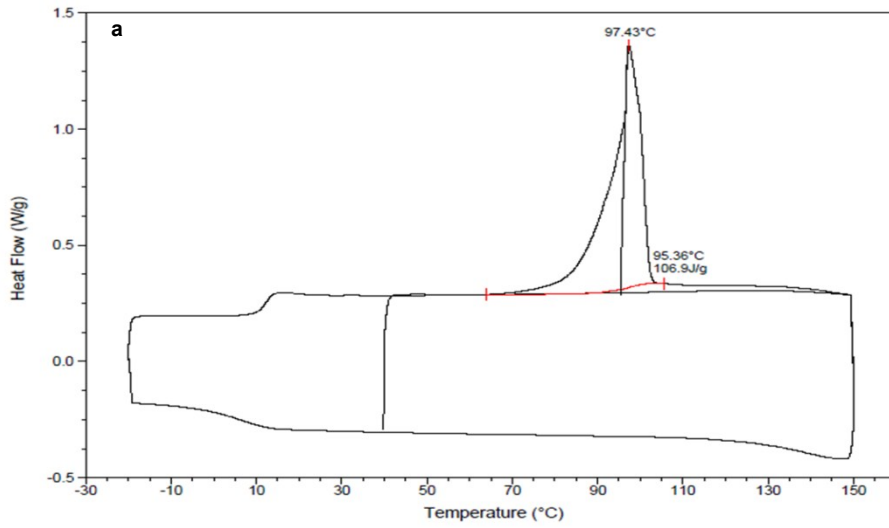
Preparation of the sample for the Evans method

The solution was prepared following the procedure described in the section: preparation of the thermochromic solution. *t*-butanol (0.2 mL) was added to this solution and the obtained mixture was transferred into an NMR tube. Additionally, two capillaries with the references (*t*-butanol and DMSO- d_6) were placed inside the NMR tube. The X_m and the μ_{eff} were calculated following a procedure previously reported.^{[2],[3]}

NMR measurements

^1H NMR and ^{13}C NMR spectra were recorded using Bruker-spectroscopin 400 ultrashield and the Ascend™ 600 Bruker nuclear magnetic resonance spectrometers. Chemical shifts were reported relative to SiMe_4 . The VT ^{59}Co NMR were recorded using the Ascend™ 600 Bruker with an internal solvent reference ($\text{K}_3[\text{Co}(\text{CN})_6]$ in D_2O in a sealed silica capillary). The spectra were recorded from 293.15 to 363.15 K; for each 10 K gradient, the sample was equilibrated for 20 min.

The VT ^1H NMR spectra for the Evans method were recorded using the Ascend™ 600 Bruker with two internal solvents references (DMSO- d_6 and *t*-butanol). For each 10 K gradient, the sample was equilibrated for 20 min.



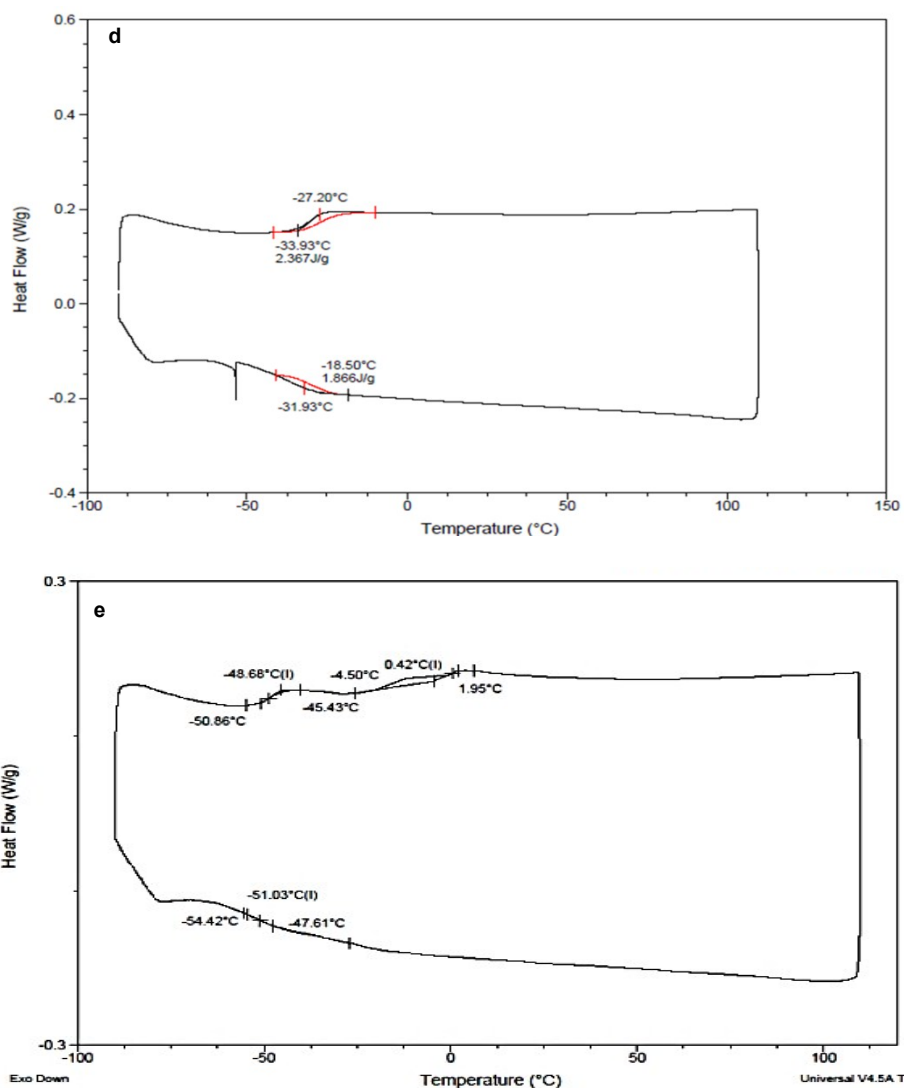
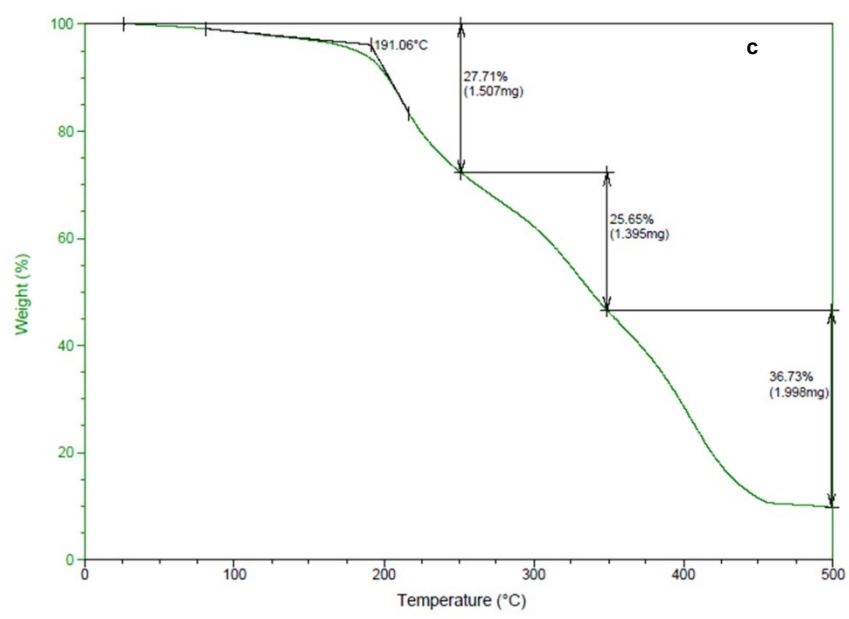
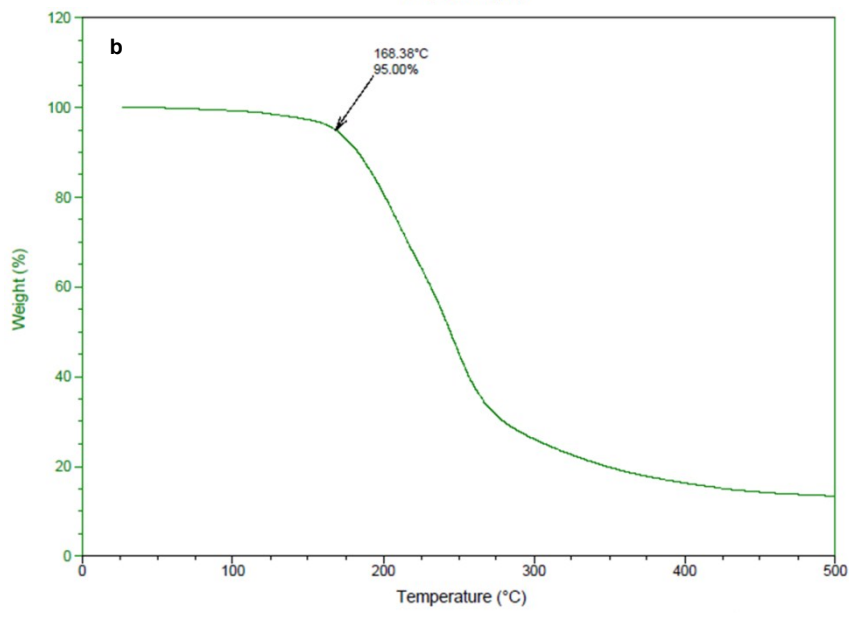
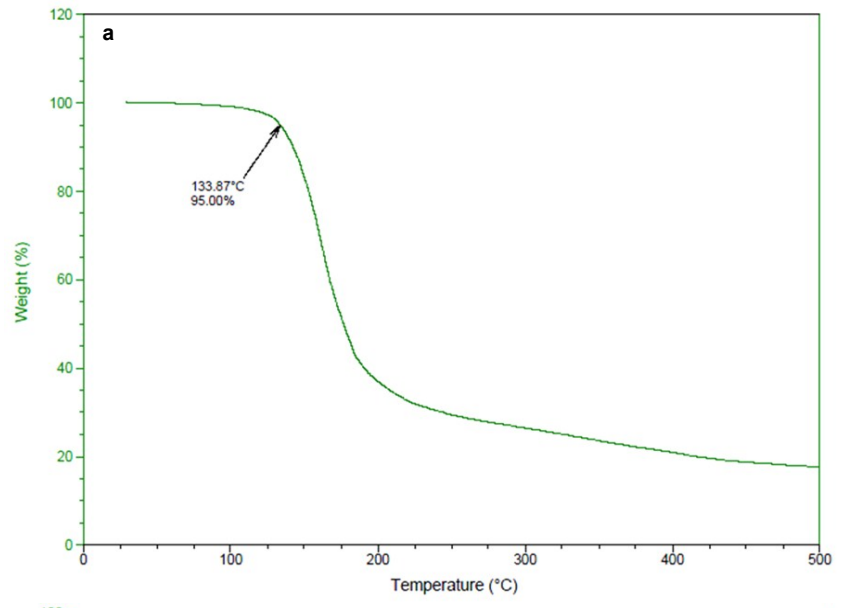


Figure S1-DSC analysis of : a) the *N*-[2-(dimethylamino)ethyl]glucosamide intermediate; b) the [N_{1,1,2GA}8]Br ligand; c) the [N_{1,1,2GA}8][NTf₂] ligand; d) the [N_{1,1,2GlyA}8]Br ligand; e) the [N_{1,1,2Hex}8]Br ligand.



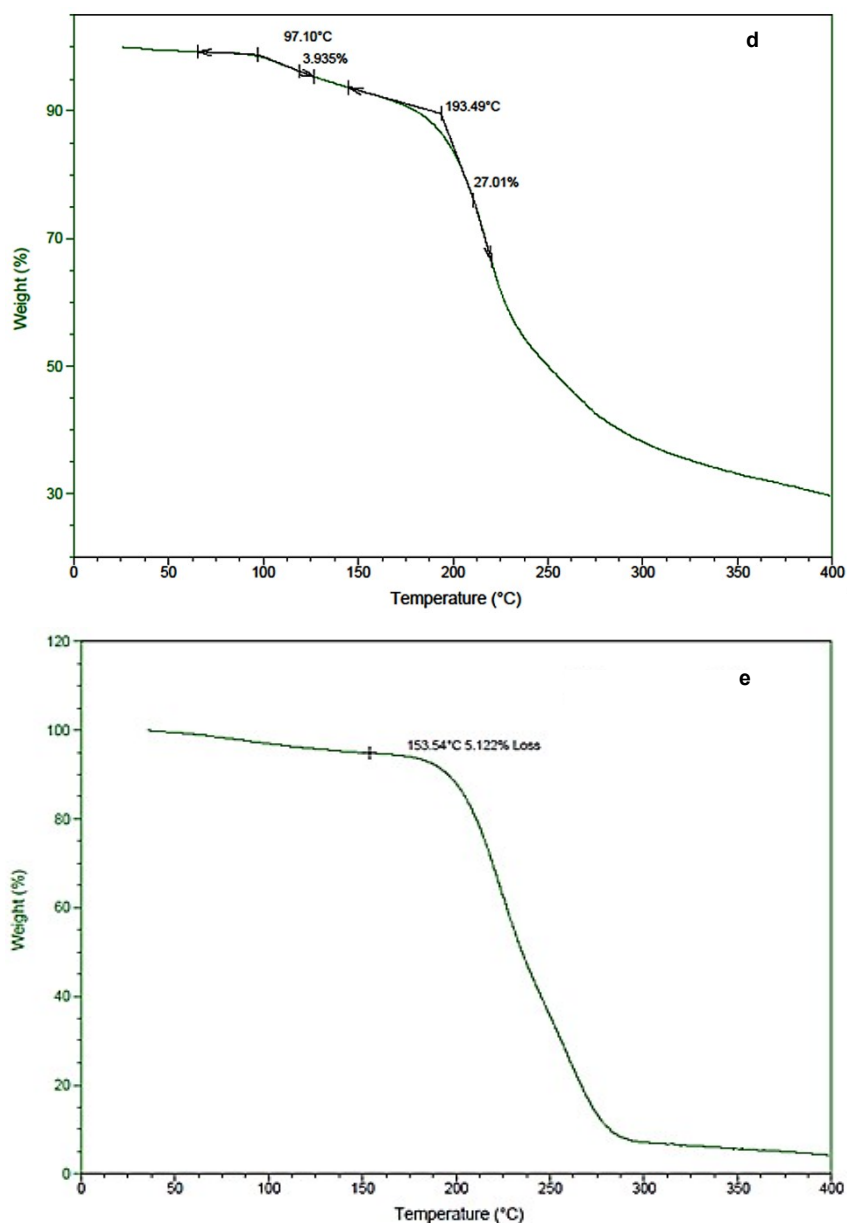
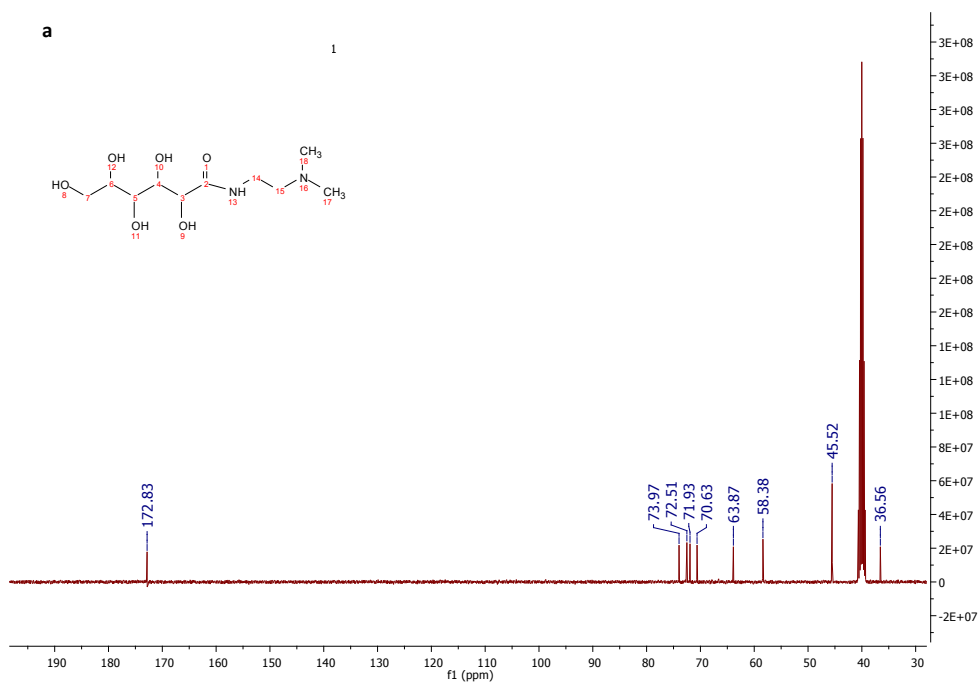
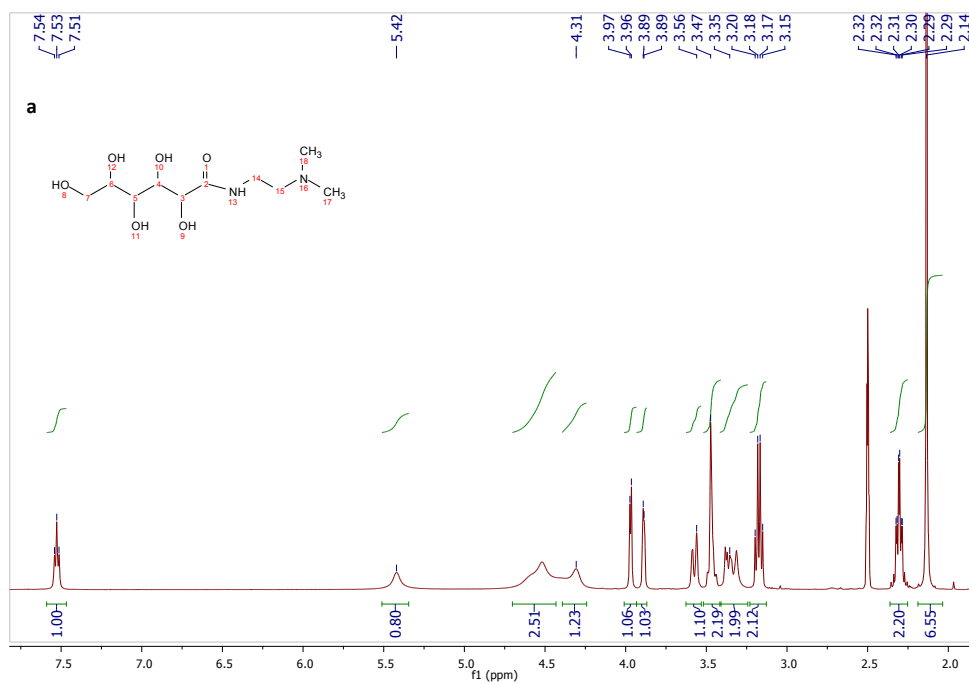
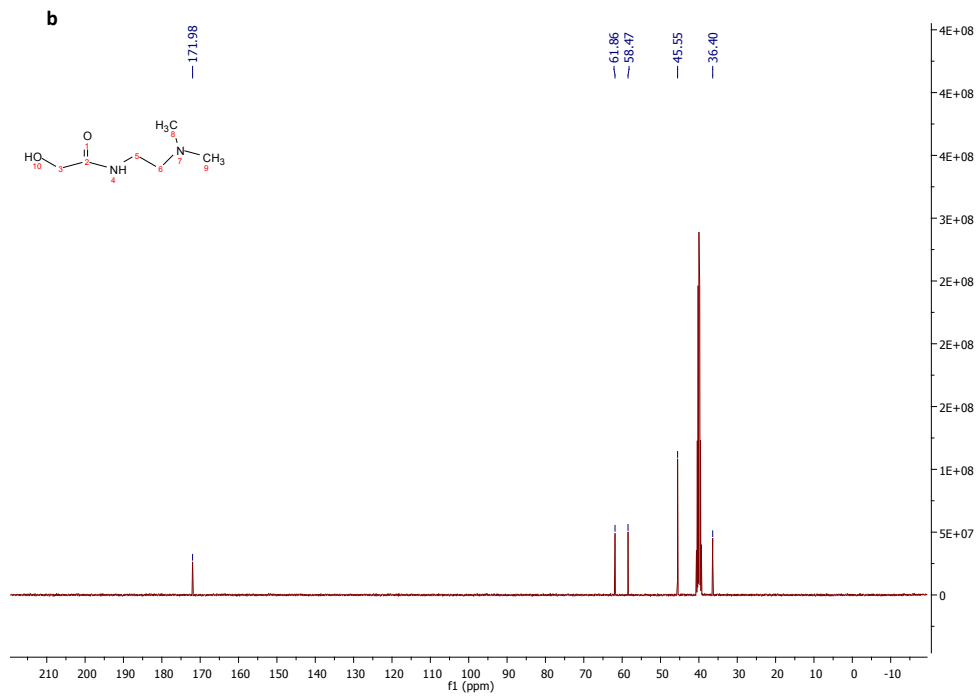
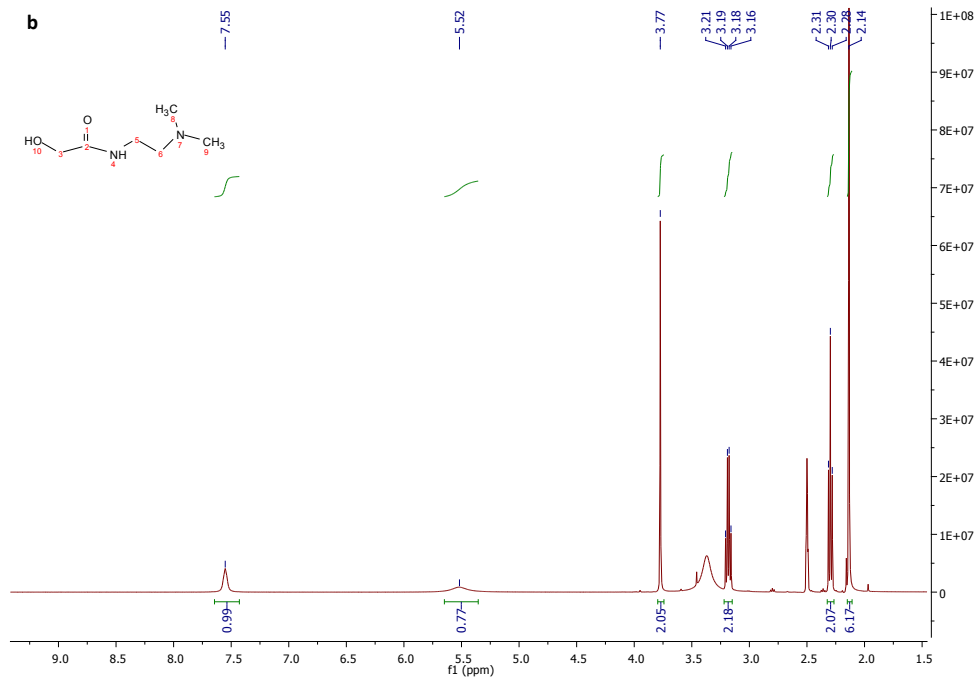
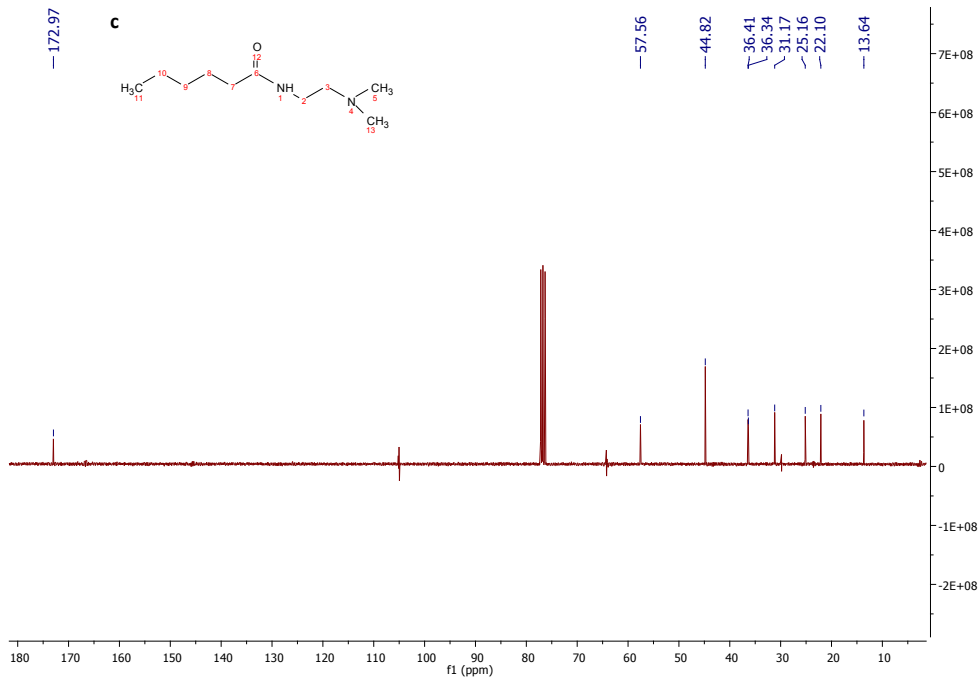
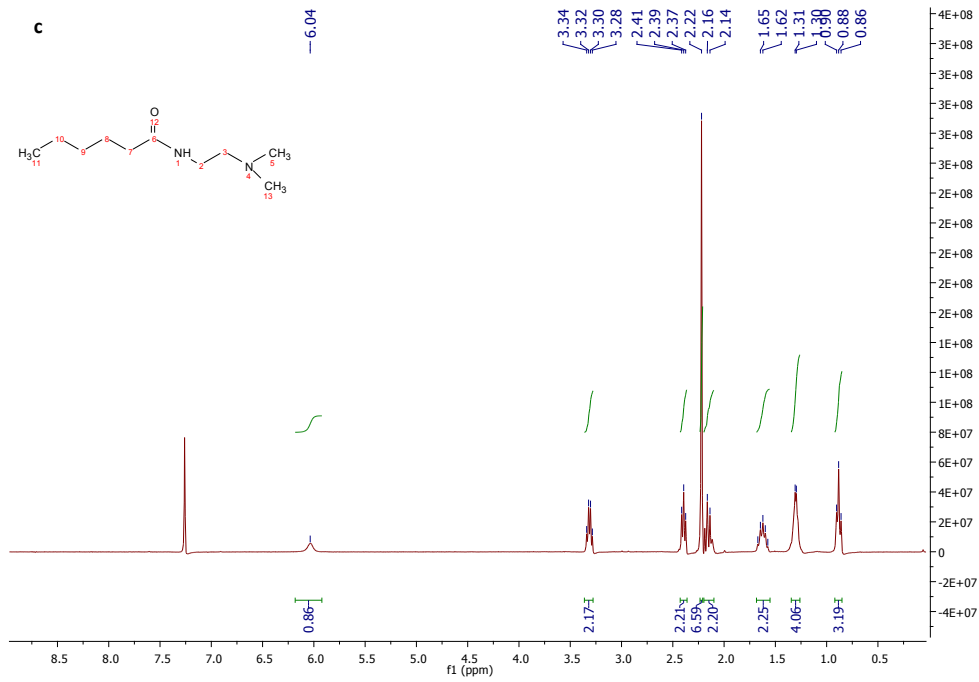
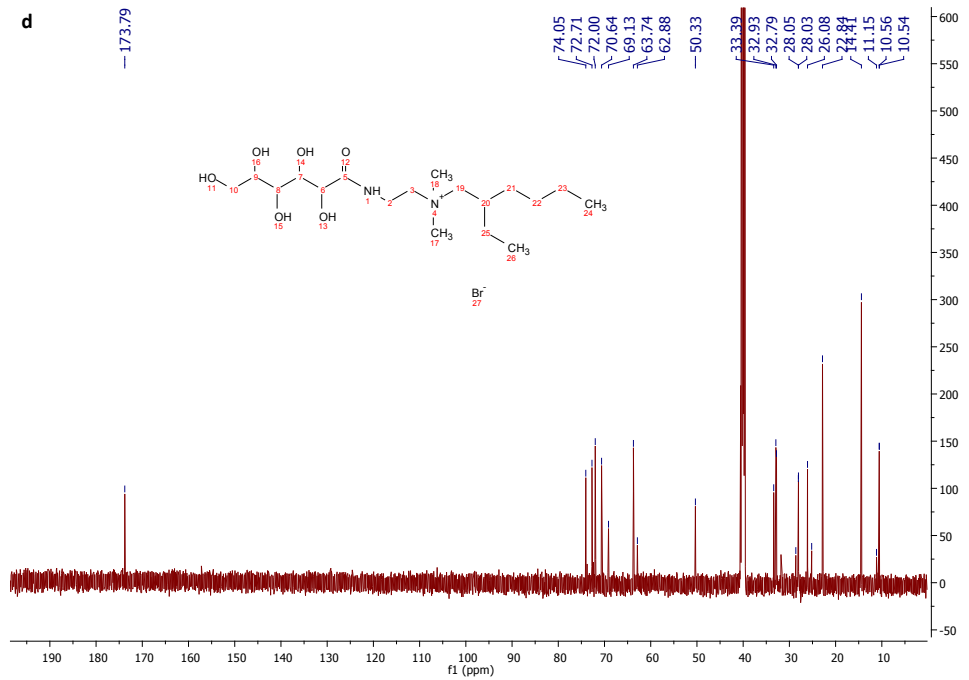
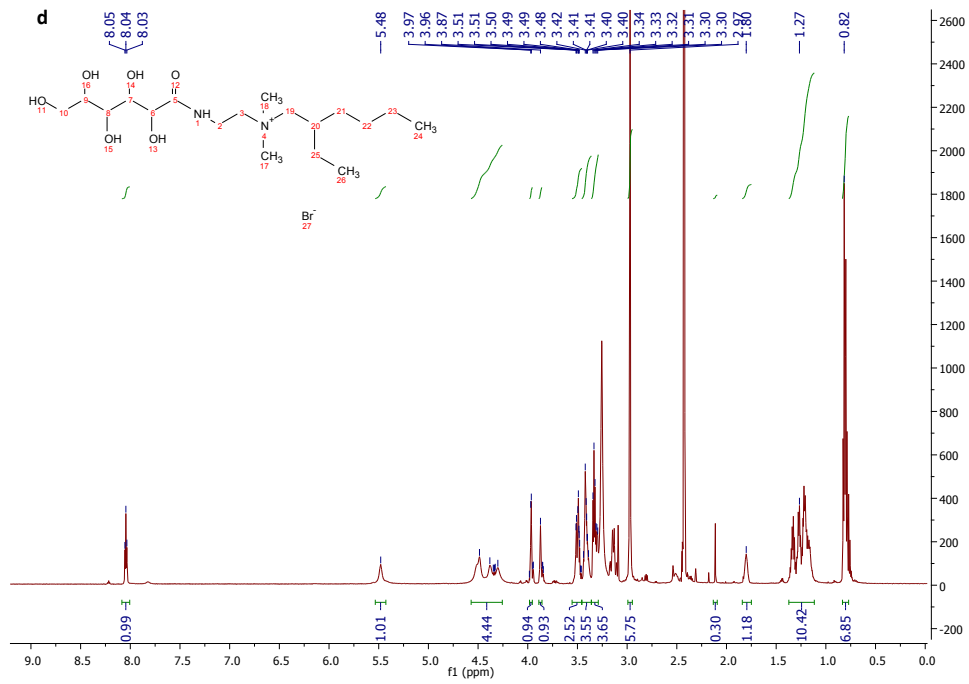


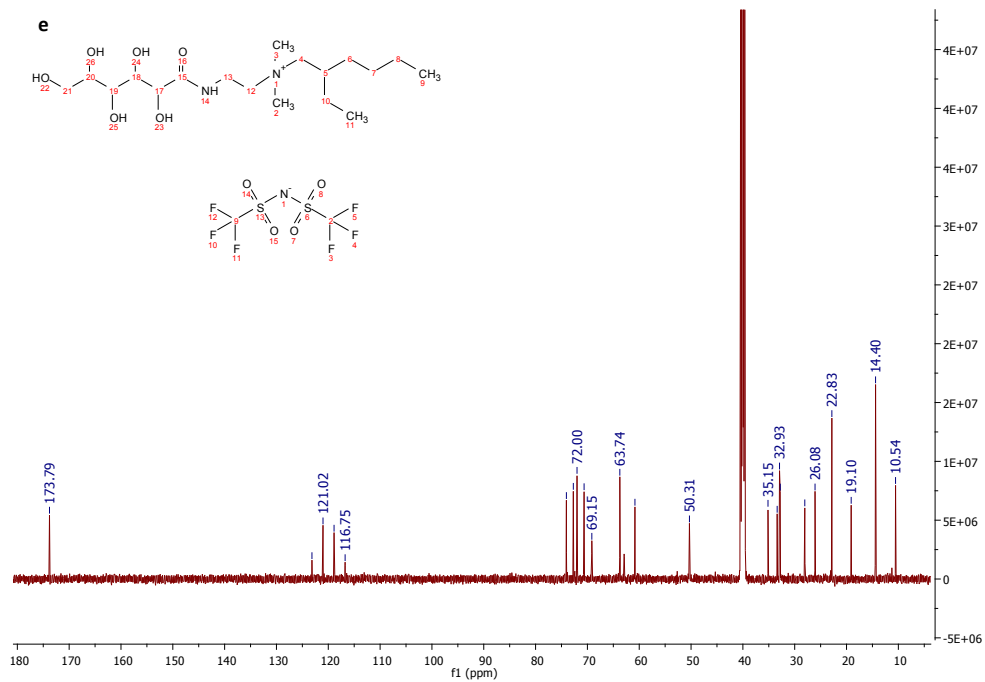
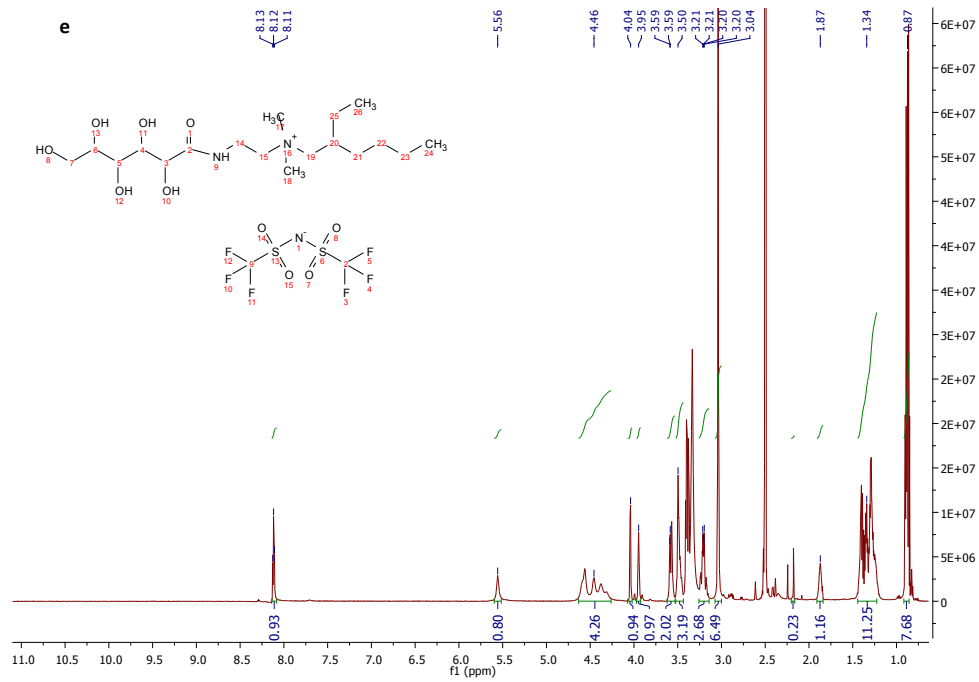
Figure S2- TGA analysis of: a) the *N*-[2-(dimethylamino)ethyl]glucosamide intermediate; b) [N_{1,1,2GA,8}]Br ligand; c) [N_{1,1,2GA,8}][NTf₂] ligand; d) the [N_{1,1,2GlyA,8}]Br ligand; e) the [N_{1,1,2Hex,8}]Br ligand.

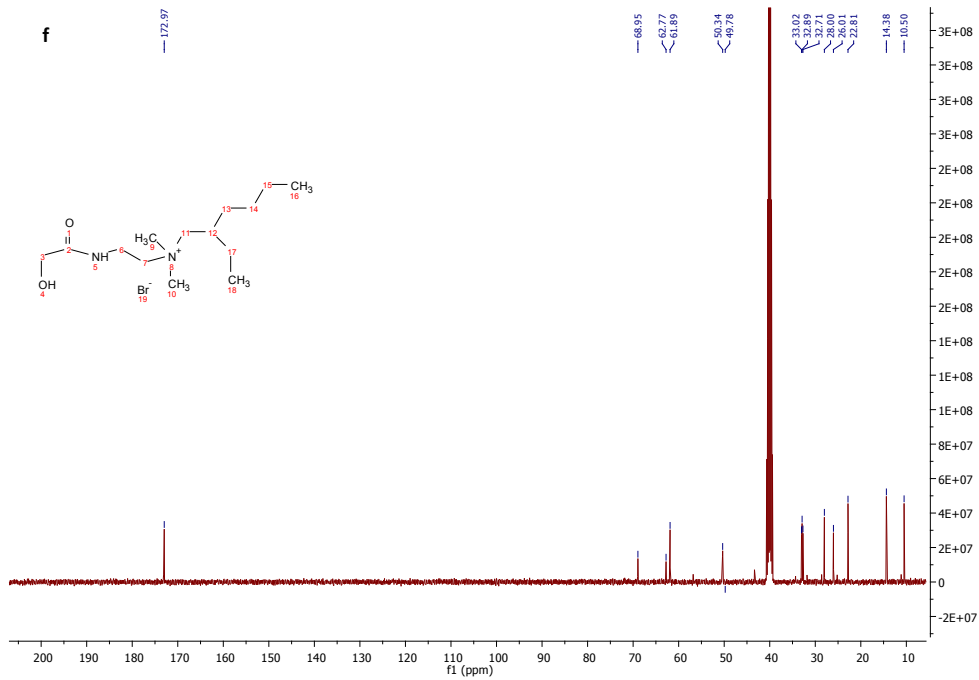
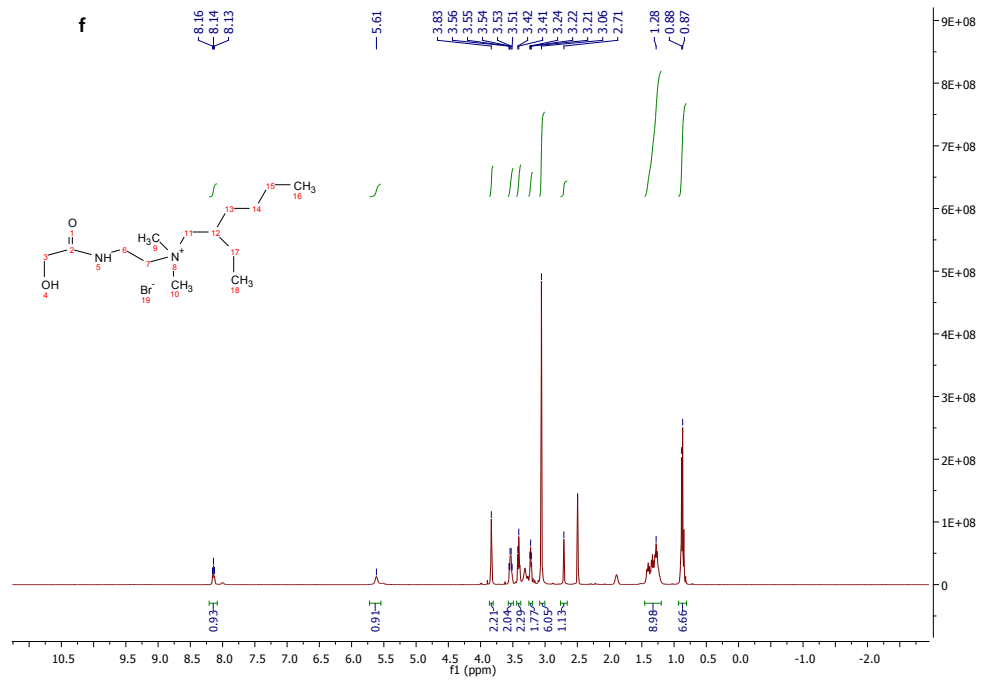












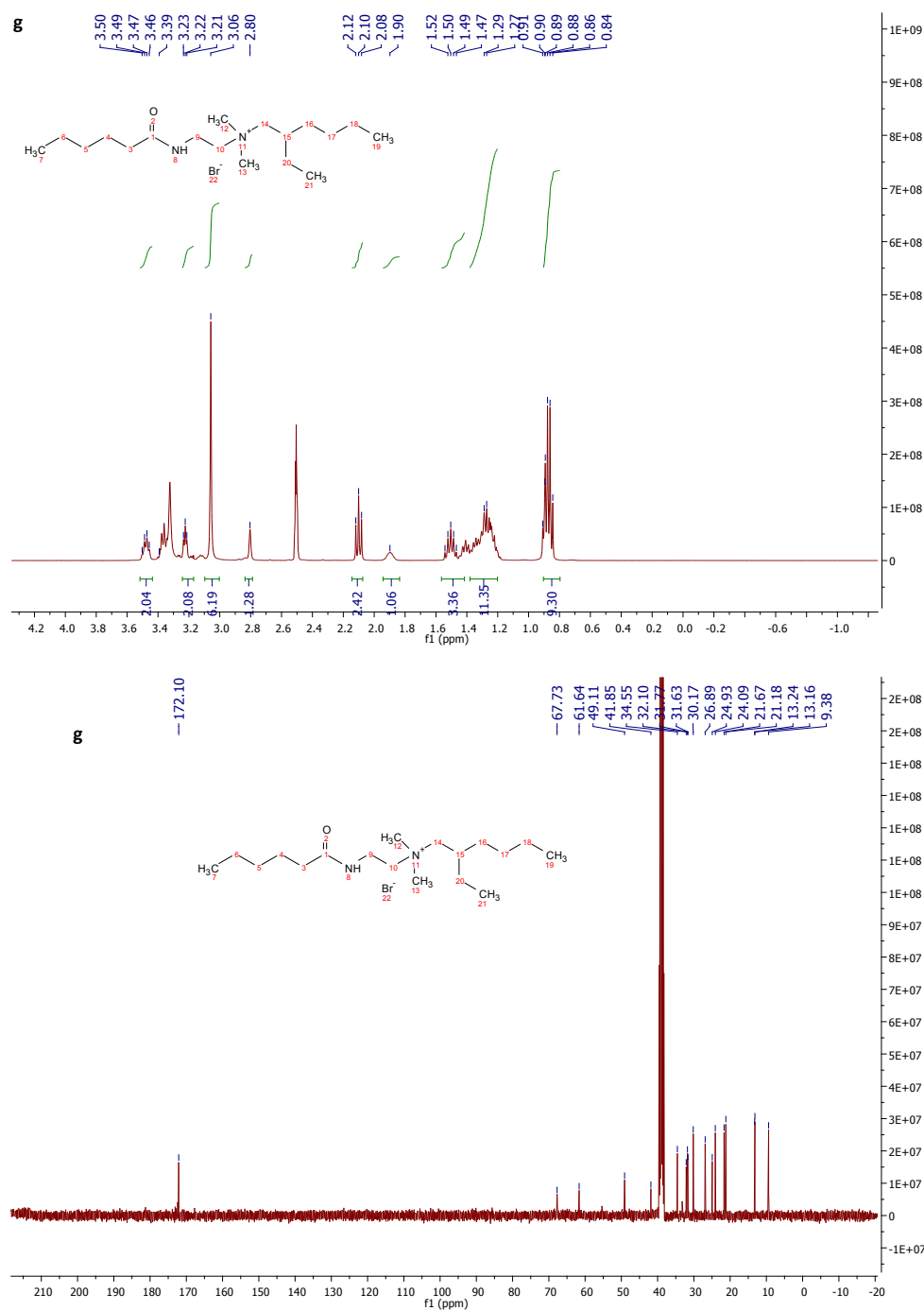


Figure S3- ^1H and ^{13}C NMR spectra: a) *N*-[2-(dimethylamino)ethyl]glucosamide intermediate; b) *N*-[2-(dimethylamino)ethyl]glycolamide intermediate; c) the *N*-[2-(dimethylamino)ethyl]hexylamide intermediate; d) the $[\text{N}_{1\ 1\ 2\text{GA}\ 8}]\text{Br}$ IL ligand e) the $[\text{N}_{1\ 1\ 2\text{GA}\ 8}][\text{Ntf}_2]$ IL ligand f) the $[\text{N}_{1\ 1\ 2\text{GlyA}\ 8}]\text{Br}$ IL ligand; g) the $[\text{N}_{1\ 1\ 2\text{Hex}\ 8}]\text{Br}$ IL ligand.

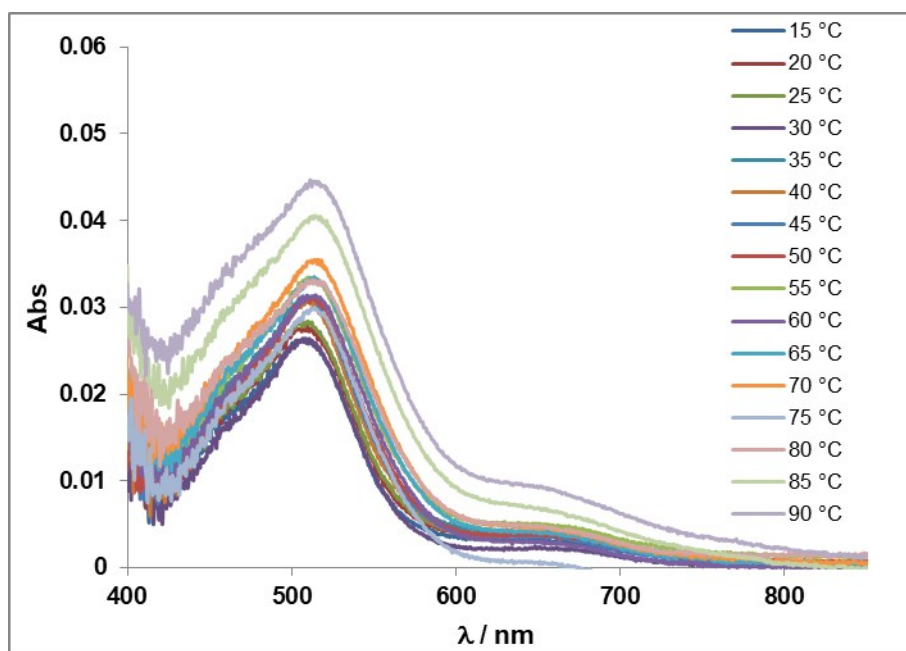


Figure S4- UV-vis spectra for the solution composed by $\text{Co}(\text{NTf}_2)_2$ in $[\text{N}_{2,2,2,4}][\text{NTf}_2]$.

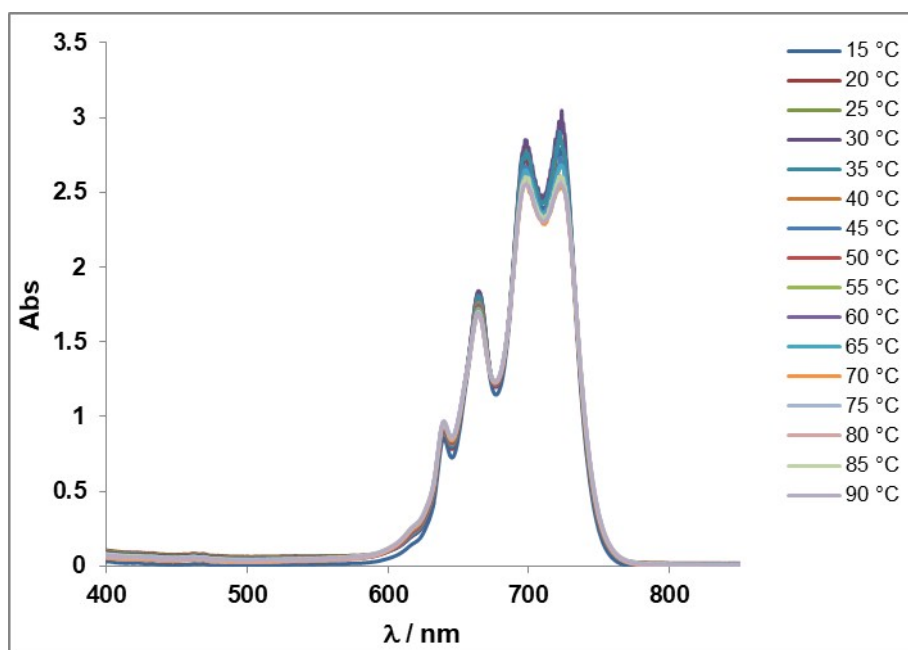


Figure S5- UV-vis spectra of the $\text{Co}(\text{NTf}_2)_2 + [\text{N}_{1,1,2\text{GlyA},8}]\text{Br}$ in $[\text{N}_{2,2,2,4}][\text{NTf}_2]$ solution.

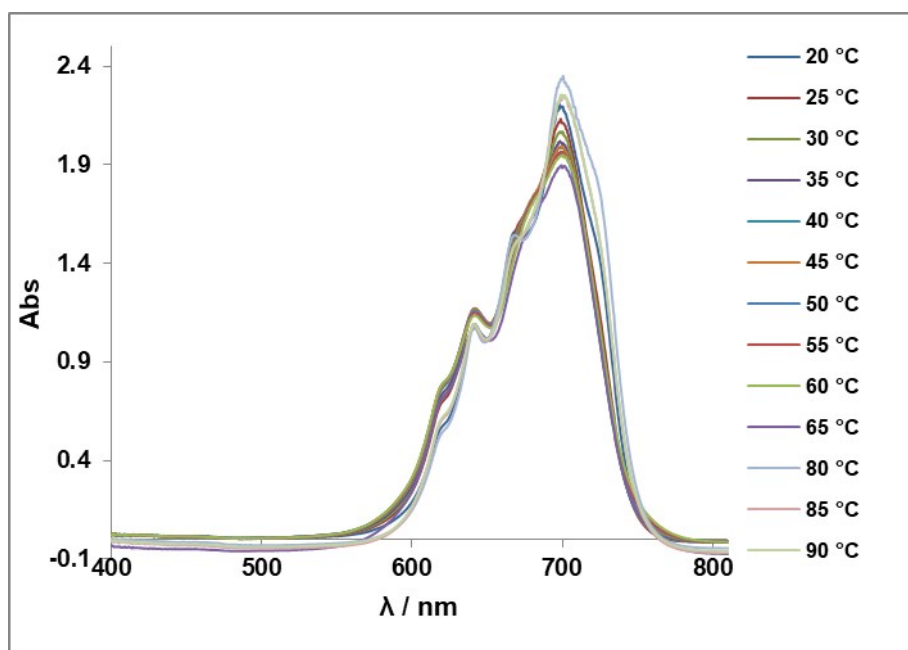


Figure S6- UV-vis spectra of the $\text{Co}(\text{NTf}_2)_2 + [\text{N}_{1,1,2\text{HexA},8}]\text{Br}$ in $[\text{N}_{2,2,2,4}][\text{NTf}_2]$ solution.

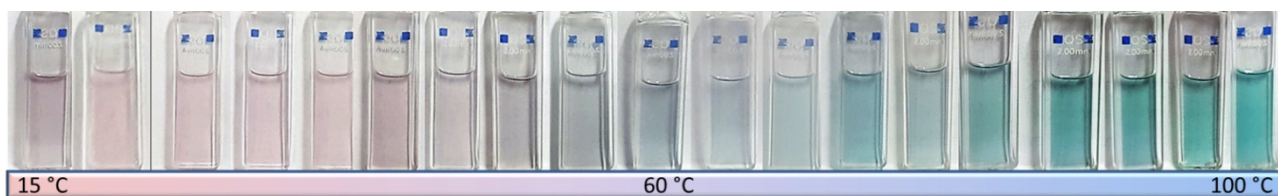


Figure S7- Colour transition of $\text{Co}(\text{NTf}_2)_2 + [\text{N}_{1,1,2\text{GA},8}]\text{Br}$ in $[\text{N}_{2,2,2,4}][\text{NTf}_2]$ solution in the 15 to 100 °C range.

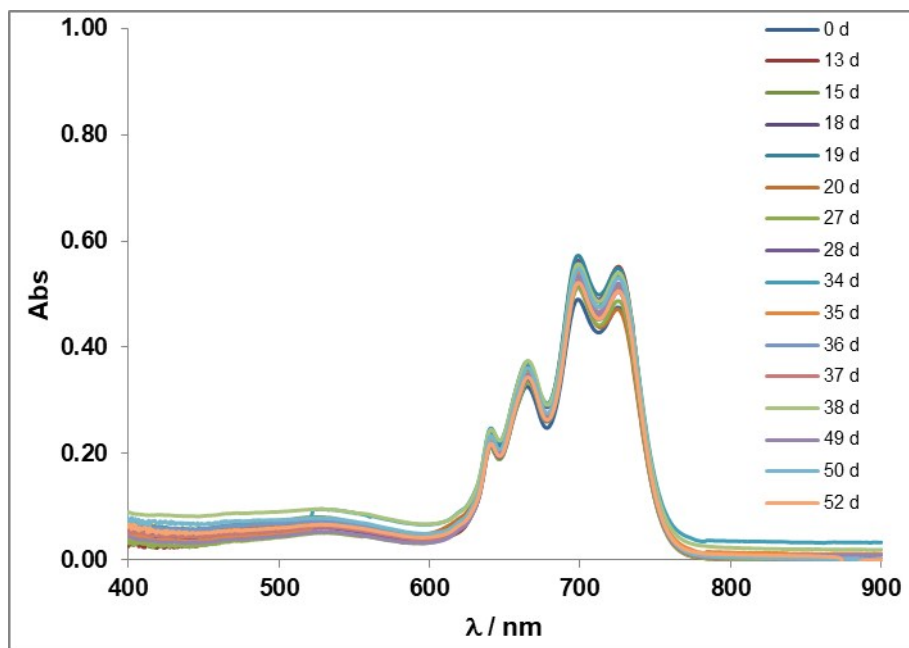


Figure S8- UV-vis spectra of the $\text{Co}(\text{NTf}_2)_2 + [\text{N}_{1.12}\text{GA}_8]\text{Br}$ in $[\text{N}_{2.22.4}][\text{NTf}_2]$ solution recorded during 52 days.

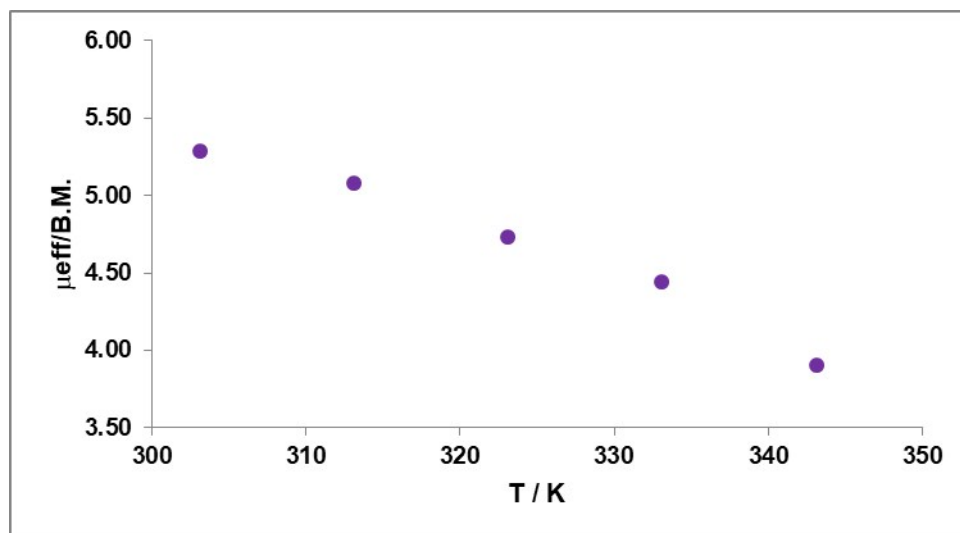
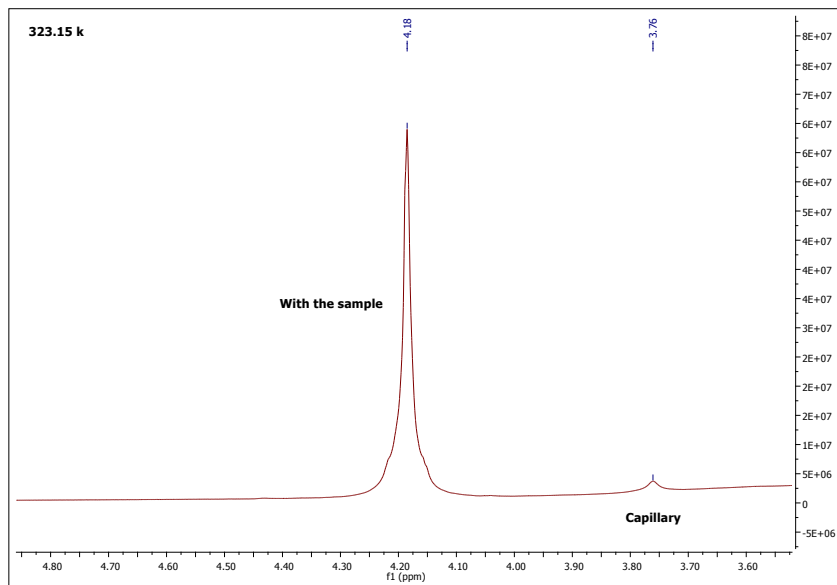
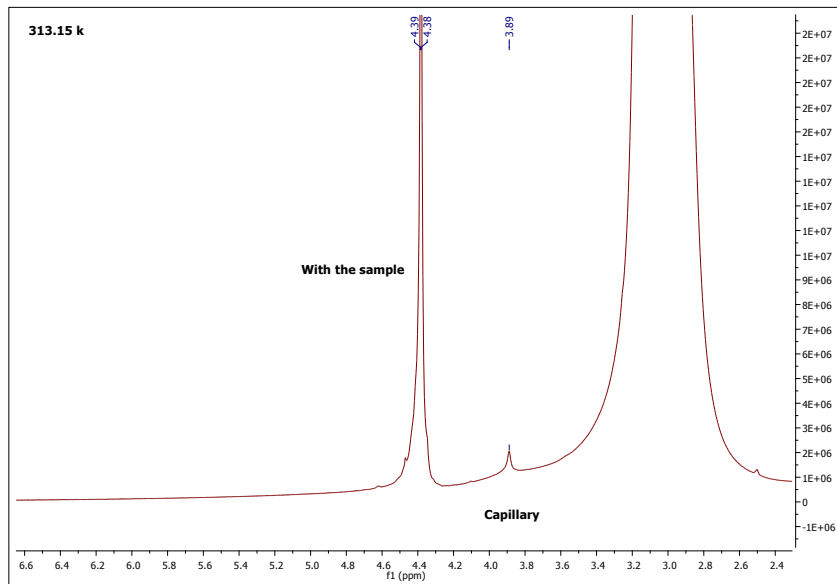
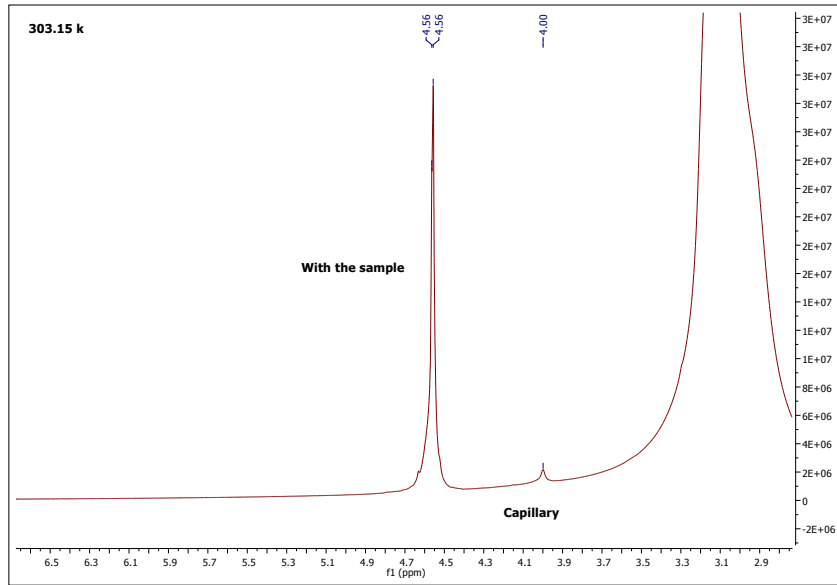


Figure S9- Trend of the μ_{eff} calculated with the Evans method, at variable temperature.



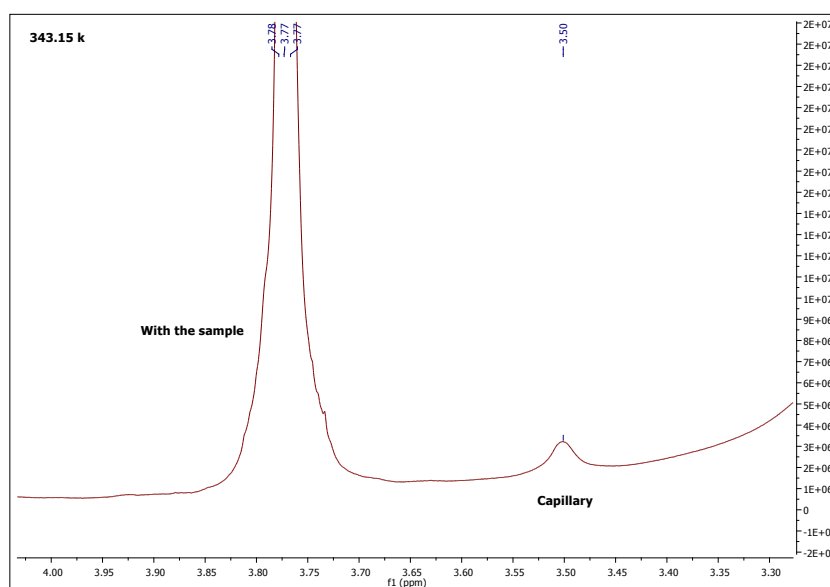
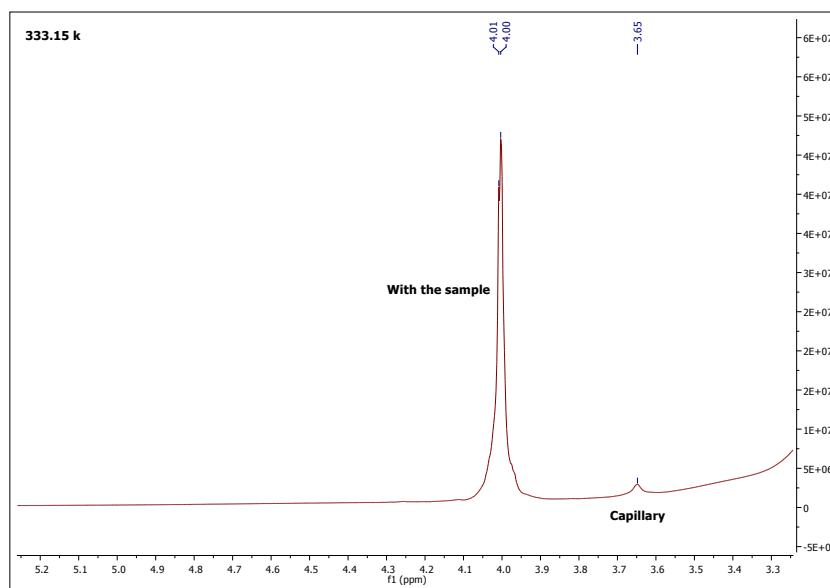


Figure S10-¹H NMR spectra recorded at variable temperatures for the calculation of the Evans method, herein, the zoomed area from 3.25 to 4.10 ppm is presented.

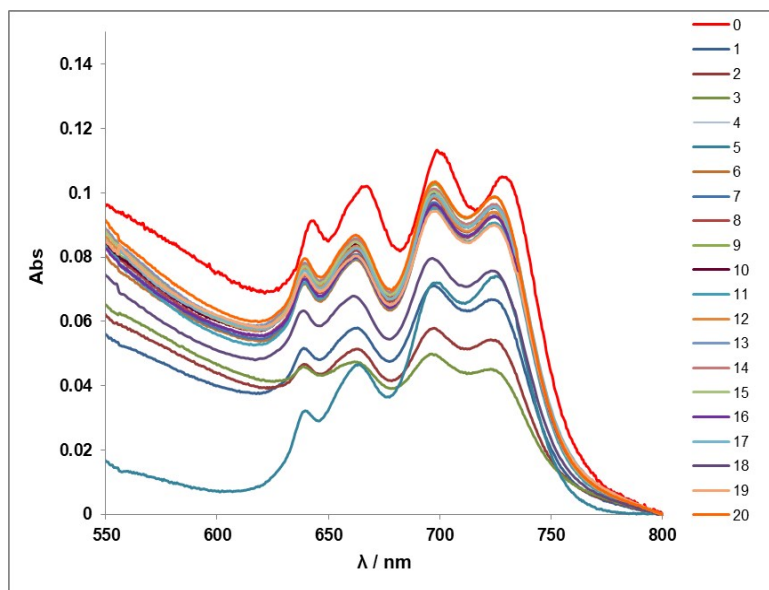


Figure S11- UV-vis spectra of the $\text{Co}(\text{NTf}_2)_2 + [\text{N}_{1,1,2\text{GA},8}]\text{Br} + \text{PMMA}$ film recorded for 20 cycles.

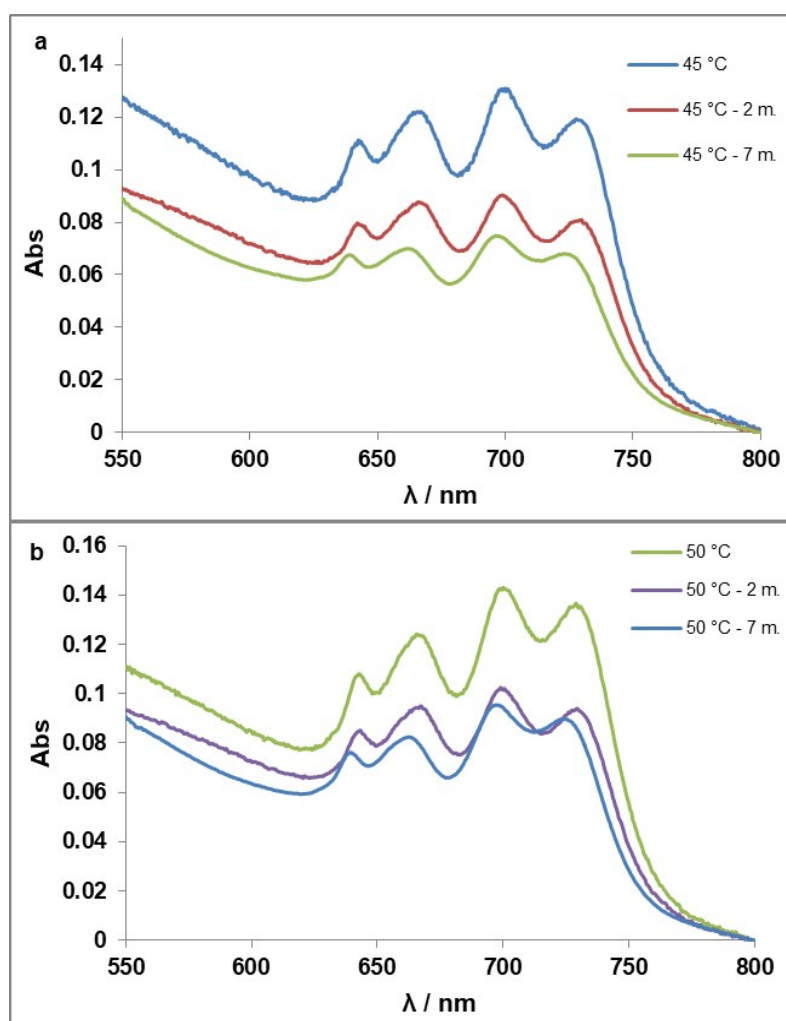


Figure S12- UV-vis spectra of the $\text{Co}(\text{NTf}_2)_2 + [\text{N}_{1,1,2\text{GA},8}]\text{Br} + \text{PMMA}$ film recorded for the fresh film, after 2 months and after 7 months: a) at 45 °C; b) at 50 °C.