Towards the Prediction of Global Solution State Properties for Hydrogen Bonded, Self-Associating Amphiphiles

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**Experimental**

**General remarks:** All reactions were performed under slight positive pressure of nitrogen using oven dried glassware. NMR spectra were determined using a Jeol ECS-400, Bruker or Bruker AV II or NEO 400 MHz spectrometer with the chemical shifts reported in parts per million (ppm), calibrated to the centre of the solvent peak set. All solvents and starting materials were purchased from commercial sources or chemical stores where available, used as purchased unless stated otherwise. High resolution mass spectra were collected using a Bruker microTOF-Q mass spectrometer or a SYNAPT G2-S Mass Spectrometer. Melting points were recorded in open capillaries using a Stuart SMP10 melting point apparatus and are uncorrected. Shimadzu IR-Affinity 1, and reported in wavenumbers (cm⁻¹). DLS and zeta potential studies were performed using a Malvern Zetasizer Nano ZS. Tensiometry performed using a Biolin Scientific Theta Attension optical tensiometer with data analysis conducted using one attension software. Single Crystal X-Ray structures were collected using a Rigaku Oxford Diffraction Supernova diffractometer. Data were collected using Cu Ka radiation at 100 K. Structures were solved with the ShelXT45 or ShelXS structure solution programs via direct methods and refined with ShelXL46 on least squares minimisation.

**DLS studies:** Studies conducted with compounds 1 - 15 and 17 - 27 were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution. Sample sizes were kept to 1 mL. All solvents used for DLS studies were filtered to remove particulates from the solvents. Samples were heated to the appropriate temperature and allowed to equilibrate for 2 minutes and then a series of 10 ‘runs’ were performed with each sample to give enough data to derive an appropriate average. In some instances, the raw correlation data indicated that a greater amount of time may be needed for the samples to reach a stable state. For this reason, only the last 9 ‘runs’ were included in the average size distribution calculations.

**Zeta potential studies:** All solvents used for zeta potential studies were filtered to remove particulates from the solvents. Samples were heated to the appropriate temperature and allowed to equilibrate for 2 minutes and then a series of 10 ‘runs’ at 25 °C were performed with each sample to give enough data to derive an appropriate average. In some instances, the raw correlation data
indicated that a greater amount of time may be needed for the samples to reach a stable state. For this reason, only the last 9 ‘runs’ were included in the average size distribution calculations.

**Low level computational studies:** All calculated parameters relating to logP, polarization or electrostatic potential maps were calculated using spartan’16 from optimised geometries obtained at the PM6 level.\(^1\)\(^2\)

**High level computational self-association studies:** Preliminary conformer searches for selected molecules were conducted using the MM2 and/or MMFF94 force fields intrinsic to Chem3D (version 15, Perkin Elmer Informatics). However, both the MM2 and MMFF94 searches performed poorly in predicting the H-bonded minimum energy conformers, consequently many of the molecular conformations identified were the result of systematic manual modifications to the bond angles and the urea dihedral angles (N-C-N) in particular. Molecular and self-associated complexes were then geometry optimised using the PM6-D3H4X Hamiltonian\(^3\)\(^4\) through the MOPAC 2016\(^5\) interface to Chem3D. Solvent effects (for DMSO \(\delta= 46.826\) and water, \(\delta=78.355\))\(^6\) were modelled through the implicit COSMO method in MOPAC 2016. All molecular models were subject to vibrational analysis following optimisation; all final structures reported displayed no negative frequencies except for certain the dimeric complexes which possessed relatively flat potential energy surfaces. For these complexes conformers with one small negative frequency were deemed acceptable for report.

**HRMS studies:** Samples were dissolved in HPLC methanol at a concentration of 1 mg/mL before being diluted 1 in 100 in methanol. 10 \(\mu\)L of sample was injected into a flowing stream of 10 mM ammonium acetate in 95 % methanol in water (flow rate: 0.02 ml/min) and the flow directed into the electrospray source of the mass spectrometer. Mass spectra were acquired in the negative ion mode and data processed in Bruker’s Compass Data Analysis software or Mass Lynx software utilising a lock mass.

**Tensiometry studies:** Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution. All solutions underwent an annealing process and were allowed to rest for approximately 2 minutes before undergoing analysis. Surfactant adsorption behaviour and critical micelle concentrations (CMCs) are determined by surface tension measurements using axisymmetric drop shape analysis with a pendant-drop apparatus. A succession of 3 droplets were measured for each sample and an average for these measurements reported.

**Self-association constant calculation:** All association constants were calculated using the freely available Bindfit programme (http://app.supramolecular.org/bindfit/). All the data relating to the calculation of the association constants can be accessed online, through the links given for each association event.

**Compounds 1 and 17:** These compounds were synthesised in line with previously published methods.\(^7\)

**Compounds 4, 7, 8, 15 and 16:** These compounds were synthesised in line with previously published methods.\(^8\)

**Compounds 28 - 31:** These compounds were synthesised in line with previously published methods.\(^9\)
**Compound 2:** TBA hydroxide (1N) in methanol (4.00 mL, 4.00 mM) was added to 2-aminoethanesulfonic acid (0.50 g, 4.00 mM) and taken to dryness overnight. 1-isocyanto-4-(trifluoromethyl)benzene (0.58 mL, 4.00 mM) was added to a stirring solution of the TBA salt in chloroform (25 mL), heated at reflux for 3 hrs and taken to dryness, dissolved in chloroform (50 mL) and washed with water (50 mL). The organic phase was then taken to dryness. The pure product was obtained by flash chromatography 100 % ethyl acetate followed by 100 % methanol. The methanol fraction was taken to dryness with further addition of TBAOH in methanol (1N) as necessary to give the pure product as a white solid with a yield of 60 % (1.34 g, 2.41 mM); melting point: 180 °C; 1H NMR (400 MHz, 298.15 K, DMSO-d_6): δ: 6.93 (s, 1H), 7.60 (d, J = 8.71 Hz, 2H), 7.53 (d, J = 8.81 Hz, 2H), 6.53 (t, J = 5.33 Hz, 1H), 3.38 (t, 2H), 3.15 (t, 8H), 2.56 (t, 2H), 1.60 - 1.45 (m, 8H), 1.40 - 1.20 (m, 8H), 0.92 (t, J = 7.33 Hz, 12H); 13C(1H) NMR (100 MHz, 298.15 K, DMSO-d_6): δ: 155.2 (CO), 145.1 (ArC), 125.2 (q, J = 269.42 Hz, CF_3), 126.2 (m, ArCH), 121.60 (q, J = 31.62 Hz, ArC), 117.6 (ArCH), 58.0 (CH_3), 51.3 (CH_2), 36.6 (CH_2), 23.5 (CH_2), 19.7 (CH_2), 13.9 (CH_3); IR (film): ν = 3116 (NH stretch), 1697, 1176, 1033, 883; HRMS for the sulfonate-urea ion ([C_{10}H_{13}F_3N_3O_5S]^- (ESI)): m/z: act: 311.0311 [M] cal: 311.0319 [M]

**Compound 3:** TBA hydroxide (1N) in methanol (2.00 mL, 2.00 mM) was added to 3-amino-1-propane sulfonic acid (0.28 g, 2.00 mM) and taken to dryness overnight. 1-Isocyanto-4-(trifluoromethyl)benzene (0.29 mL, 2.00 mM) was added to a stirring solution of the TBA salt in chloroform (12.5 mL), heated at reflux overnight and taken to dryness, dissolved in chloroform (50 mL) and washed with water (50 mL). The organic phase was then taken to dryness. The pure product was obtained by flash chromatography 100 % ethyl acetate followed by 100 % methanol. The methanol fraction was taken to dryness with further addition of TBAOH in methanol (1N) as necessary to give the pure product as a white solid with a yield of 56 % (0.63 g, 1.11 mM); melting point: 180 °C; 1H NMR (400 MHz, 298.15 K, DMSO-d_6): δ: 8.93 (s, 1H), 7.55 (d, J = 8.80 Hz, 2H), 7.50 (d, J = 8.88 Hz, 2H), 6.41 (t, J = 5.75 Hz, 1H), 3.14 - 3.09 (m, 10H), 2.44 - 2.37 (m, 2H), 1.75 - 1.61 (m, 2H), 1.52 - 1.50 (m, 8H), 1.36 - 1.12 (m, 8H), 0.89 (t, J = 7.34 Hz, 12H); 13C(1H) NMR (100 MHz, 298.15 K, DMSO-d_6): δ: 155.4 (CO), 145.1 (ArC), 126.3 (q, J = 258.31 Hz, CF_3), 126.3 - 126.2 (m, ArCH), 121.09 (q, J = 31.78 Hz, ArC), 117.6 (ArCH), 58.0 (CH_3), 49.5 (CH_2), 38.7 (CH_2), 26.5 (CH_2), 23.5 (CH_2), 19.7 (CH_2), 13.9 (CH_3); IR (film): ν = 3116 (NH stretch), 1697, 1176, 1031, 879; HRMS for the sulfonate-urea ion ([C_{11}H_{12}F_3N_3O_5S]^- (ESI)): m/z: act: 325.9465 [M] cal: 325.04575 [M]

**Compound 5:** TBA hydroxide (1N) in methanol (4.00 mL, 4.00 mM) was added to 2-aminoethanesulfonic acid (0.50 g, 4.00 mM) and taken to dryness overnight. 4-(Trifluoromethyl) phenyl isothiocyanate (0.82 mL, 4.00 mM) was added to a stirring solution of the TBA salt in chloroform (25 mL), heated at reflux for 3 hrs and taken to dryness, dissolved in chloroform (50 mL) and washed with water (50 mL). The organic phase was then taken to dryness. The pure product was obtained by flash chromatography 100 % ethyl acetate followed by 100 % methanol. The methanol fraction was taken to dryness with further addition of TBAOH in methanol (1N) as necessary to give the pure product as a white solid with a yield of 60 % (1.97 g, 3.30 mM); melting point: 138 °C; 1H NMR (400 MHz, 298.15 K, DMSO-d_6): δ: 10.23 (s, 1H), 8.23 (s, 1H), 7.75 (d, J = 8.52 Hz, 2H), 7.62 (d, J = 9.08 Hz, 2H), 3.76 (d, J = 5.33 Hz, 2H), 3.16 (t, J = 16.80 Hz, 8H), 2.69 (t, J = 12.32 Hz, 2H), 1.66 - 1.42 (m, 8H), 1.42 - 1.12 (m, 8H), 0.93 (t, J = 7.34 Hz, 12H); 13C(1H) NMR (100 MHz, 298.15 K, DMSO-d_6): δ: 180.2 (CS), 143.9 (ArC), 126.5 (q, J = 250.56 Hz, CF_3), 126.0 - 125.0 (m, ArCH), 123.7 (q, J = 31.76, Hz, ArC), 122.1 (ArCH), 58.0 (CH_3), 49.9 (CH_3), 41.5 (CH_3), 23.5 (CH_2), 19.7 (CH_3), 13.9 (CH_3); IR (film): ν = 3327 (NH stretch), 1610, 1168, 1037, 883; HRMS for the sulfonate-urea ion ([C_{10}H_{13}F_3N_3O_5S]^- (ESI)): m/z: act: 327.0090 [M] cal: 327.0083 [M]

**Compound 6:** TBA hydroxide (1N) in methanol (2.00 mL, 2.00 mM) was added to 3-amino-1-propane sulfonic acid (0.28 g, 2.00 mM) and taken to dryness overnight. 4- Phenyl (trifluoromethyl) isothiocyanate (0.41 g, 2.00 mM) was added to a stirring solution of the TBA salt in chloroform (12.5
mL), heated at reflux overnight and taken to dryness, dissolved in chloroform (50 mL) and washed with water (50 mL). The organic phase was then taken to dryness. The pure product was obtained by flash chromatography 100% ethyl acetate followed by 100% methanol. The methanol fraction was taken to dryness with further addition of TBAOH in methanol (1N) as necessary to give the pure product as a white solid with a yield of 76% (0.89 g, 1.11 mM); melting point: 149 °C; 1H NMR (400 MHz, 333.15 K, DMSO-d6): δ: 9.95 (s, 1H), 8.25 (s, 1H), 7.77 (d, J = 8.10 Hz, 2H), 7.62 (d, J = 8.66 Hz, 2H), 3.56 (d, J = 5.29 Hz, 2H), 3.21 - 3.10 (m, 8H), 1.94 - 1.75 (m, 2H), 1.60 - 1.52 (m, 9H, 8H), 1.39 - 1.20 (m, 8H), 0.93 (t, J = 7.33 Hz, 12H); 13C{1H} NMR (100 MHz, 298.15 K, DMSO-d6): δ: 180.7 (CS), 144.4 (ArC), 124.9 (q, J = 269.92 Hz, CF3), 125.8 - 125.8 (m, ArCH), 123.7 (q, J = 47.79 Hz, ArC), 121.9 (ArCH), 58.0 (CH3), 49.6 (CH3), 43.3 (CH3), 25.2 (CH3), 23.5 (CH3), 19.7 (CH3), 14.0 (CH3); IR (film): v: = 3323 (NH stretch), 1614, 1170, 1033, 883; HRMS for the sulfonate-urea ion ([C11H12F3N2O2S] (ESI)): m/z: act: 341.3438 [M]+ cal: 341.0234 [M]+.

**Compound 9:** 1-Isocyanoate-4-(trifluoromethyl) benzene (0.58 mL, 4.00 mM) was added to a stirring solution of aminomethanesulfonic acid (0.44 g, 4.00 mM) in anhydrous pyridine (20 mL) under an inert atmosphere. The mixture was heated to 60 °C overnight. The pyridinium salt was then removed by filtration. Yield: 82% (0.56 g, 1.49 mM). The pyridinium salt (0.38 g, 1.00 mM) was dissolved in a solution of TMA hydroxide pentahydrate (0.10 g, 1.00 M) and H2O (0.45 g) to give the pure product as a white solid with a yield of 97% (0.36 g, 0.97 mM); melting point: > 200 °C; 1H NMR (400 MHz, 298.15 K, DMSO-d6): δ: 9.18 (s, 1H), 7.55 (s, 4H), 6.68 (s, 1H), 3.89 (d, J = 5.89 Hz, 2H), 3.09 (s, 12H); 13C{1H} NMR (100 MHz, 298.15 K, DMSO-d6): δ: 154.7 (CO), 144.7 (ArC), 126.5 - 126.1 (m, ArCH), 124.5 (q, J = 269.39 Hz, CF3), 121.3 (q, J = 31.77 Hz, ArC), 117.7 (ArCH), 56.4 (CH3), 54.9 (CH3); IR (film): v: = 3113 (NH stretch), 1697, 1182, 1033, 839; HRMS for the sulfonate-urea ion ([C9H9F3N2O2S] (ESI)): m/z: act: 297.0164 [M]+ cal: 297.0162 [M].

**Compound 10:** The compound was produced with an analogous method to that described with the synthesis of compound 9. The pyridinium salt (0.38 g, 1.00 mM) was dissolved in a solution of 25% TEA hydroxide in H2O (0.26 g, 1.00 mM) to give the pure product as a white solid with a yield of 97% (0.41 g, 0.97 mM); melting point: 165 °C; 1H NMR (400 MHz, 298.15 K, DMSO-d6): δ: 9.33 (s, 1H), 7.78 - 7.18 (m, 5H), 4.01 (s, 2H), 3.18 (d, J = 3.7 Hz, 8H), 1.13 (s, 12H); 13C{1H} NMR (100 MHz, 298.15 K, DMSO-d6): δ: 154.7 (CO), 144.9 (ArC), 126.1 - 126.0 (m, ArCH), 124.5 (q, J = 269.49 Hz, CF3), 121.2 (q, J = 31.47 Hz, ArC), 117.7 (ArCH), 56.4 (CH3), 51.9 (CH3), 7.5 (CH3); IR (film): v: = 3120 (NH stretch), 1697, 1182, 1037, 842; HRMS for the sulfonate-urea ion ([C9H9F3N2O2S] (ESI)): m/z: act: 297.0174 [M]+ cal: 297.0162 [M].

**Compound 11:** The compound was produced with an analogous method to that described with the synthesis of compound 9. The pyridinium salt (0.38 g, 1.00 mM) was dissolved in a solution of 25% TPA hydroxide in H2O (0.36 g, 1.00 mM) to give the pure product as a white solid with a yield of 97% (0.47 g, 0.97 mM); melting point: 145 °C; 1H NMR (400 MHz, 298.15 K, DMSO-d6): δ: 9.19 (s, 1H), 7.56 (s, 4H), 6.69 (s, 1H), 3.89 (d, J = 5.87 Hz, 2H), 3.23 - 2.95 (m, 8H), 1.65 - 1.61 (m, 8H), 0.89 (t, J = 7.27 Hz, 12H); 13C{1H} NMR (100 MHz, 298.15 K, DMSO-d6): δ: 154.7 (CO), 144.8 (ArC), 126.2 (m, ArCH), 124.6 (q, J = 269.33 Hz, CF3), 121.2 (q, J = 31.69 Hz, ArC), 117.6 (ArCH), 59.8 (CH3), 56.4 (CH3), 15.3 (CH3), 11.0 (CH3); IR (film): v: = 3118 (NH stretch), 1697, 1182, 1039, 856; HRMS for the sulfonate-urea ion ([C9H9F3N2O2S] (ESI)): m/z: act: 297.0156 [M]+ cal: 297.0162 [M].

**Compound 12:** The compound was produced with an analogous method to that described with the synthesis of compound 9. The pyridinium salt (0.38 g, 1.00 mM) was dissolved in a solution of 20% TPeA hydroxide in H2O (1.58 g, 1.00 mM) to give the pure product as a white solid with a yield of 99% (0.58 g, 0.99 mM); melting point: 90 °C; 1H NMR (400 MHz, 298.15 K, DMSO-d6): δ: 9.20 (s, 1H), 7.48 (dd, J = 23.57 Hz, 8.5 Hz, 4H), 6.89 (s, 1H), 3.88 (d, J = 5.65 Hz, 2H), 3.31 (d, J = 1.11 Hz, 4H), 3.21 - 3.01 (m, 8H), 2.45 (d, J = 1.23 Hz, 2H), 1.52 (s, 1H), 1.39 - 1.02 (m, 17H), 0.83 (t, J = 6.82 Hz, 12H); 13C{1H} NMR (100 MHz, 298.15 K, DMSO-d6): 154.7 (CO), 144.8 (ArC), 126.4 - 126.3 (m, ArCH), 125.2
(q, J = 268.78 Hz, CF₃), 121.3 (q, J = 32.40 Hz, ArC), 117.6 (ArCH), 58.1 (CH₂), 56.4 (CH₂), 28.4 (CH₃), 22.1 (CH₃), 21.2 (CH₃), 14.3 (CH₃); IR (film): ν = 2956 (NH stretch), 1695, 1182, 1031, 841; HRMS for the sulfonate-urea ion ([C₆H₆F₃N₂O₄S]⁻) (ESI): m/z: act: 297.0155 [M] cal: 297.0162 [M].

**Compound 13**: The compound was produced with an analogous method to that described with the synthesis of compound 9. The pyridinium salt (0.38 g, 1.00 mM) was dissolved in a solution of 40 % THA hydroxide in H₂O (0.93 g, 1.00 mM) to give the pure product as an oil with a yield of 98 % (0.64 g, 0.98 mM); ¹H NMR (400 MHz, 298.15 K, DMSO-d₆): δ: 9.42 (s, 1H), 7.54 (d, J = 8.24 Hz, 2H), 7.40 (d, J = 8.28 Hz, 2H), 7.23 (s, 1H), 3.96 (d, J = 5.54 Hz, 2H), 3.15 (d, J = 12.42 Hz, 8H), 1.55 (s, 8H), 1.27 (s, 24H), 0.86 (s, 12H); ¹³C(¹H) NMR (100 MHz, 298.15 K, DMSO-d₆): δ: 154.8 (CO), 144.7 (ArC), 126.2 - 126.1 (m, ArCH), 124.4 (q, J = 270.00 Hz, CF₃), 121.2 (q, J = 32.02 Hz, ArC), 117.6 (ArCH), 58.1 (CH₂), 56.4 (CH₂), 31.1 (CH₃), 25.9 (CH₂), 22.4 (CH₂), 21.5 (CH₂), 14.3 (CH₃); IR (film): ν = 3288 (NH stretch), 1695, 1182, 1035, 840; HRMS for the sulfonate-urea ion ([C₆H₆F₃N₂O₄S]⁻) (ESI): m/z: act: 297.0141 [M] cal: 297.0162 [M].

**Compound 14**: Hydrazine hydrate (2.15 mL, 4.29 mM) and 10 % palladium on carbon (0.04 g) was added to a stirred solution of compound 17 (2.21 g, 4.29 mM) in ethanol (25 mL) and heated at reflux overnight. Filtered, and taken to dryness to give a brown solid with a yield of 96 % (2.00 g, 4.11 mM); melting point: 189 °C; ¹H NMR (400 MHz, 298.15 K, DMSO-d₆): δ: 8.42 (s, 1H), 7.04 (d, J = 8.64 Hz, 2H), 6.51 (d, J = 8.64 Hz, 2H), 6.41 (t, J = 5.92 Hz, 1H), 3.88 (d, J = 5.93 Hz, 2H), 3.28 - 3.01 (m, 8H), 1.73 - 1.40 (m, 8H), 1.32 - 1.25 (m, 8H), 0.92 (t, J = 7.33 Hz, 12H); ¹³C(¹H) NMR (100 MHz, 298.15 K, DMSO-d₆): δ: 155.4 (CO), 142.4 (ArC), 131.0 (ArC), 120.1 (ArC), 115.3 (ArCH), 58.0 (CH₂), 56.7 (CH₂), 23.5 (CH₃), 19.7 (CH₃), 14.0 (CH₃); IR (film): ν = 3227 (NH stretch), 1685, 1213, 1168, 883; HRMS for the sulfonate-urea ion ([C₆H₆F₃N₂O₄S]⁻) (ESI): m/z: act: 244.0394 [M] cal: 244.0398 [M].

**Compound 19**: TBA hydroxide (1N) in methanol (1.73 mL, 1.73 mM) was added to 2-aminomethanesulfonic acid (0.19 g, 1.73 mM) and taken to dryness overnight. 4-Methoxyphenyl isothiocyanate (0.24 mL, 1.73 mM) was added to a stirred solution of the TBA salt in ethyl acetate (10 mL), heated at reflux overnight, forming an oil. The oil was decanted, dissolved in chloroform (20 mL) and washed with water (20 mL). The organic phase was then taken to dryness to give the pure product as a white solid with a yield of 50 % (0.45 g, 0.86 mM); melting point: 145 °C; ¹H NMR (400 MHz, 333.15 K, DMSO-d₆): δ: 9.79 (s, 1H), 7.56 (s, 1H), 7.36 (d, J = 7.94 Hz, 2H), 6.87 (d, J = 7.89 Hz, 2H), 4.23 (s, 8H), 3.75 (s, 3H), 1.76 - 1.46 (m, 8H), 1.47 - 1.20 (m, 8H), 0.95 (t, J = 7.25 Hz, 12H); ¹³C(¹H) NMR (100 MHz, 298.15 K, DMSO-d₆): δ: 181.1 (CS), 156.6 (Arc), 132.8 (ArC), 125.5 (ArCH), 114.1 (ArCH), 60.9 (CH₃), 58.0 (CH₂), 55.7 (CH₃), 23.5 (CH₂), 19.7 (CH₃), 14.0 (CH₃); IR (film): ν = 3234 (NH stretch), 1550, 1220, 1155, 877; HRMS for the sulfonate-urea ion ([C₆H₆F₃N₂O₄S]⁻) (ESI): m/z: act: 275.0238 [M] cal: 275.0216 [M].

**Compound 20**: TBA hydroxide (1N) in methanol (1.73 mL, 1.73 mM) was added to 2-aminomethanesulfonic acid (0.19 g, 1.73 mM) and taken to dryness overnight. Phenyl isothiocyanate (0.21 mL, 1.73 mM) was added to a stirred solution of the TBA salt in ethyl acetate (10 mL), heated at reflux overnight, forming an oil. The oil was decanted, dissolved in chloroform (20 mL) and washed with water (20 mL). The organic phase was then taken to dryness to give the pure product as a white solid with a yield of 61 % (0.51 g, 1.05 mM); melting point: 146 °C; ¹H NMR (400 MHz, 333.15 K, DMSO-d₆): δ: 9.63 (s, 1H), 7.77 (s, 1H), 7.54 (d, J = 7.84 Hz, 2H), 7.29 (t, J = 7.29 Hz, 2H), 7.07 (t, J = 7.46 Hz, 1H), 4.24 (s, 2H), 3.30 - 2.95 (m, 8H), 1.63 - 1.56 (m, 8H), 1.48 - 1.14 (m, 8H), 0.95 (t, J = 7.27 Hz, 12H); ¹³C(¹H) NMR (100 MHz, 298.15 K, DMSO-d₆): δ: 180.7 (CO), 140.1 (ArC), 128.7 (m, ArCH), 124.3 (ArCH), 123.0 (ArCH), 60.8 (CH₃), 58.0 (CH₂), 23.5 (CH₂), 19.7 (CH₃), 14.0 (CH₃) IR (film): ν = 3317 (NH stretch), 1651, 1232, 1159, 883; HRMS for the sulfonate-urea ion ([C₆H₆F₃N₂O₄S]⁻) (ESI): m/z: act: 245.0116 [M] cal: 245.0060 [M].
**Compound 21:** TBA hydroxide (1N) in methanol (4.00 mL, 4.00 mM) was added to 2-aminomethanesulfonic acid (0.44 g, 4.00 mM) and taken to dryness overnight. To a stirring solution of the TBA salt in acetonitrile (15 mL) 4-nitrophenyl isothiocyanate (0.73 g, 4.00 mM) was added, heated at reflux overnight and taken to dryness, dissolved in ethyl acetate (20 mL) and left-over night at 2 °C. The pure product was obtained as crystals with a yield of 89 % (1.32 g, 3.60 mM); melting point: 145 °C; 1H NMR (400 MHz, 333.15 K, DMSO-d$_6$): δ: 10.50 (bs, 1H), 8.33 (bs, 1H), 8.14 (d, J = 7.68 Hz, 2H), 7.96 (s, 2H), 4.33 (s, 2H), 3.25 - 3.14 (m, 8H), 1.61 - 1.60 (m, 8H), 1.36 - 1.31 (m, 8H), 0.94 (t, J = 6.54 Hz, 12H); 13C(¹H) NMR (100 MHz, 298.15 K, DMSO-d$_6$): δ: 180.2 (C(S)), 147.0 (CO), 142.3 (ArC), 124.9 (ArCH), 121.7 (ArC), 120.7 (ArCH), 60.6 (CH$_3$), 58.0 (CH$_3$), 23.5 (CH$_3$), 19.7 (CH$_3$), 14.0 (CH$_3$); IR (film): ν = 3224 (NH stretch), 1550, 1228, 1165, 852; HRMS for the sulfonate-urea ion ([C$_9$H$_7$N$_2$O$_2$S]⁻) (ESI): m/z: act: 290.0001 [M⁻] cal: 289.9911 [M⁻].

**Compound 22:** 1-Isocyanato-4-(trifluoromethyl) benzene (0.29 mL, 2.00 mM) was added to a stirring solution of tert-butyl 2-aminocacetate (0.27 mL, 2.00 mM) in chloroform (10 mL) and left at RT overnight. The mixture was reduced in volume to 5 mL. Hexane was added dropwise and the precipitate removed by filtration to give the pure product as a white solid with a yield of 45 % (0.29 g, 0.91 mM); melting point: 110 °C; 1H NMR (400 MHz, 298.15 K, DMSO-d$_6$): δ: 9.23 (s, 1H), 7.73 – 7.60 (d, J = 9.28 Hz 2H), 7.58 (d, J = 9.32 Hz 2H), 6.53 (t, J = 5.90 Hz, 1H), 3.77 (d, J = 5.91 Hz, 2H), 1.42 (s, 9H); 13C(¹H) NMR (100 MHz, 298.15 K, DMSO-d$_6$): δ: 170.2 (CO), 155.3 (CO), 144.5 (ArC), 126.5 - 126.4 (m, ArCH), 122.9 (q, J = 339.98 Hz, CF$_3$), 121.6 (q, J = 31.88 Hz, ArC), 117.8 (ArCH), 81.1 (C), 42.4 (CH$_3$), 28.2 (CH$_3$); IR (film): ν = 2993 (NH stretch), 1730, 1442, 1319, 1219; HRMS for the carboxylate-urea ([C$_9$H$_7$F$_3$N$_2$O$_3$]⁻) (ESI): m/z: act: 317.1097 [M⁻] cal: 318.1191 [M⁻].

**Compound 23:** Trifluoroacetic acid (5 mL) was added to a stirring solution of compound 22 (0.15 g, 0.47 mM) in dichloromethane (10 mL) and left at RT for 30 minutes. Additional dichloromethane (10 mL) was added and the organic layer was washed with sodium hydroxide (20 mL, 6 M). The aqueous phase was then taken to dryness, dissolved in H$_2$O (20 mL), neutralised by the dropwise addition of Hydrochloric acid (2M), with the precipitate removed by filtration to give the pure product as a white solid with a yield of 65 % (0.08 g, 0.31 mM); melting point: > 200 °C; 1H NMR (400 MHz, 298.15 K, DMSO-d$_6$): δ: 9.22 (s, 1H), 7.58 (s, 4H), 6.51 (t, J = 5.64 Hz, 1H), 3.79 (d, J = 5.71 Hz, 2H); 13C(¹H) NMR (100 MHz, 298.15 K, DMSO-d$_6$): δ: 172.4 (CO), 155.3 (CO), 144.5 (ArC), 126.5 - 126.4 (m, ArCH), 123.4 (q, J = 269.45 Hz, CF$_3$), 121.7 (q, J = 31.76 Hz, ArC), 117.8 (ArCH), 41.8 (CH$_3$); IR (film): ν = 2962 (NH stretch), 1685, 1448, 1319, 882; HRMS for the carboxylate-urea ([C$_9$H$_7$F$_3$N$_2$O$_3$]⁻) (ESI): m/z: act: 261.0501 [M⁻] cal: 262.0565 [M⁻].

**Compound 24:** Compound 23 (0.05 g, 0.17 mM) was dissolved in a solution of TBA hydroxide (1N) in methanol (0.17 mL) and taken to dryness to give the pure product as a white solid with a yield of 83 % (0.07 g, 0.14 mM); melting point: > 200°C; 1H NMR (400 MHz, 298.15 K, DMSO-d$_6$): δ: 9.51 (s, 1H), 7.73 (d, J = 8.74 Hz, 2H), 7.42 (d, J = 8.74 Hz, 2H), 6.49 (s, 1H), 3.38 (d, J = 4.00 Hz, 2H), 3.20 - 3.07 (m, 8H), 1.67 - 1.44 (m, 8H), 1.40 - 1.18 (m, 8H), 0.92 (t, J = 7.34 Hz, 12H); 13C(¹H) NMR (100 MHz, 298.15 K, DMSO-d$_6$): δ: 172.2 (CO), 155.2 (CO), 145.0 (ArC), 126.1 (ArCH), 121.6 (q, J = 269.31 Hz, CF$_3$), 120.4 (q, J = 31.33 Hz, ArC), 117.3 (ArCH), 58.0 (CH$_3$), 44.8 (CH$_3$), 23.5 (CH$_3$), 19.7 (CH$_3$), 14.0 (CH$_3$); IR (film): ν = 2958 (NH stretch), 1734, 1436, 1321, 948; HRMS for the carboxylate-urea ion ([C$_9$H$_7$F$_3$N$_2$O$_3$]⁻) (ESI): m/z: act: 261.0501 [M⁻] cal: 262.0565 [M⁻].

**Compound 25:** 4-(Trifluoromethyl)phenyl isothiocyanate (0.41 g, 2.00 mM) was added to a stirring solution of tert-butyl 2-aminocacetate (0.27 mL, 2.00 mM) in chloroform (10 mL) and left at RT overnight. The mixture was reduced in volume to 5 mL. Hexane was added dropwise and the precipitate removed by filtration to give the pure product as a white solid with a yield of 77 %, (0.52 g, 1.54 mM); melting point: 135 °C; 1H NMR (400 MHz, 298.15 K, DMSO-d$_6$): δ: 10.27 (bs, 1H), 8.23 (t, J = 5.53 Hz, 1H), 7.75 (d, J = 8.64 Hz, 2H), 7.67 (d, J = 8.72 Hz, 2H) 4.18 (d, J = 5.50 Hz, 2H), 1.43 (s, 9H); 13C(¹H) NMR (100 MHz, 298.15 K, DMSO-d$_6$): δ: 181.6 (CO), 169.0 (CO), 143.5 (ArC), 126.3 -
126.2 (m, ArCH), 124.8 (q, J = 269.76 Hz, CF$_3$), 124.2 (q, J = 31.96 Hz, ArC), 122.5 (ArCH), 81.4 (C), 46.6 (CH$_2$), 28.2 (CH$_3$); IR (film): v = 3035 (NH stretch), 1734, 1508, 1323, 1224; HRMS for the carboxylate-urea (C$_{14}$H$_2$F$_3$N$_2$O$_2$S) (ESI): m/z: act: 333.0874 [M] cal: 334.0963 [M].

**Compound 26**: Trifluoroacetic acid (5 mL) was added to a stirring solution of Compound 25 (0.30 g, 0.90 mM) in dichloromethane (10 mL) and left at RT for 30 minutes. Additional dichloromethane (10 mL) was added and the organic layer washed with sodium hydroxide (20 mL, 6 M). The aqueous phase was then taken to dryness, dissolved in H$_2$O (20 mL), neutralised by the dropwise addition of hydrochloric acid (2M), and the precipitate removed by filtration to give the pure product as a solid with a yield of 100%.

**Compound 27**: Compound 26 (0.10 g, 0.35 mM) was dissolved in a solution of TBA hydroxide (1N) in methanol (0.35 mL, 0.35 mM) and taken to dryness to give the pure product as a white solid with a yield of 62% (0.11 g, 0.21 mM); melting point: > 200°C; $^1$H NMR (400 MHz, 298.15 K, DMSO-$d_6$): δ: 12.30 (s, 1H), 8.77 (s, 1H), 8.38 (d, J = 8.09 Hz, 2H), 7.55 (d, J = 8.28 Hz, 2H), 3.73 (s, 2H), 3.22 - 3.01 (m, 8H), 1.66 - 1.43 (m, 8H), 1.43 - 1.15 (m, 8H), 0.92 (t, J = 7.33 Hz, 12H); $^{13}$C($^1$H) NMR (100 MHz, 298.15 K, DMSO-$d_6$): δ: 178.7 (CS), 170.3 (CO), 145.7 (ArC), 126.5 - 125.5 (m, ArCH), 125.1 (q, J = 269.86 Hz, CF$_3$), 122.2 (q, J = 31.9 Hz, ArC), 120.3 (ArCH), 58.0 (CH$_3$), 50.0 (CH$_2$), 23.5 (CH$_2$), 19.7 (CH$_3$), 13.9 (CH$_3$); IR (film): v = 2970 (NH stretch), 1734, 1435, 1323, 983; HRMS for the carboxylate-urea ion (C$_{10}$H$_6$F$_3$N$_2$O$_2$S) (ESI): m/z: act: 277.0264 [M] cal: 278.0337 [M].

**Compounds 32, 34 - 39**: One equivalent of the appropriate hydroxide salt was added to ethane sulfonic acid (0.22 g, 2.0 mM) in methanol (1 mL) and taken to dryness to give the pure product as a white solid/clear oil with a yield of 100%.

**Tetramethylammonium hexafluorophosphate**: One equivalent of tetramethylammonium hydroxide was added to hexafluorophosphoric acid (2.0 mM) in methanol (1 mL) and taken to dryness to give the pure product as a white solid with a yield of 100%.

**Pyridinium hexafluorophosphate**: One equivalent of pyridine was added to hexafluorophosphoric acid (2.0 mM) in methanol (1 mL) and taken to dryness to give the pure product as a white solid with a yield of 100%.

**Compound 33**: One equivalent of pyridine was added to ethane sulfonic acid (0.22 g, 2.0 mM) and taken to dryness to give the pure product as a white solid with a yield of 100%.
NMR Characterisation

Figure S2 - $^1$H NMR of compound 1 in DMSO-$d_6$ conducted at 298.15 K.

Figure S3 - $^1$H NMR of compound 2 in DMSO-$d_6$ conducted at 298.15 K.
Figure S4 - $^{13}$C NMR of compound 2 in DMSO-$d_6$ conducted at 298.15 K.

Figure S5 - $^1$H NMR of compound 3 in DMSO-$d_6$ conducted at 298.15 K.
Figure S6 - $^{13}$C NMR of compound 3 in DMSO-$d_6$ conducted at 298.15 K.

Figure S7 - $^1$H NMR of compound 4 in DMSO-$d_6$ conducted at 298.15 K.
Figure S8 - $^1$H NMR of compound 4 in DMSO-$d_6$ conducted at 333.15 K.

Figure S9 - $^1$H NMR of compound 5 in DMSO-$d_6$ conducted at 298.15 K.
Figure S10 - $^{13}$C NMR of compound 5 in DMSO-$d_6$ conducted at 298.15 K.

Figure S11 - $^1$H NMR of compound 6 in DMSO-$d_6$ conducted at 298.15 K.
Figure S12 - $^{13}$C NMR of compound 6 in DMSO-$d_6$ conducted at 298.15 K.

Figure S13 - $^1$H NMR of compound 7 in DMSO-$d_6$ conducted at 298.15 K.
Figure S14 - $^{1}$H NMR of compound 8 in DMSO-$d_6$ conducted at 298.15 K.

Figure S15 - $^{1}$H NMR of compound 9 in DMSO-$d_6$ conducted at 298.15 K.
Figure S16 - $^{13}$C NMR of compound 9 in DMSO-$d_6$ conducted at 298.15 K.

Figure S17 - $^1$H NMR of compound 10 in DMSO-$d_6$ conducted at 298.15 K.
Figure S18 - $^{13}$C NMR of compound 10 in DMSO-$d_6$ conducted at 298.15 K.

Figure S19 - $^1$H NMR of compound 11 in DMSO-$d_6$ conducted at 298.15 K.
Figure S20 - $^{13}$C NMR of compound 11 in DMSO-$d_6$ conducted at 298.15 K.

Figure S21 - $^1$H NMR of compound 12 in DMSO-$d_6$ conducted at 298.15 K.
Figure S22 - $^{13}$C NMR of compound 12 in DMSO-$d_6$ conducted at 298.15 K.

Figure S23 - $^1$H NMR of compound 13 in DMSO-$d_6$ conducted at 298.15 K.
Figure S24 - $^{13}$C NMR of compound 13 in DMSO-$d_6$ conducted at 298.15 K.

Figure S25 - $^1$H NMR of compound 14 in DMSO-$d_6$ conducted at 298.15 K.
Figure S26 - $^{13}$C NMR of compound 14 in DMSO-$d_6$ conducted at 298.15 K.

Figure S27 - $^1$H NMR of compound 15 in DMSO-$d_6$ conducted at 298.15 K.
Figure S28 - $^1$H NMR of compound 16 in DMSO-$d_6$ conducted at 298.15 K.

Figure S29 - $^1$H NMR of compound 17 in DMSO-$d_6$ conducted at 298.15 K.
Figure S30 - $^1$H NMR of compound 18 in DMSO-$d_6$ conducted at 298.15 K.

Figure S31 - $^1$H NMR of compound 19 in DMSO-$d_6$ conducted at 298.15 K.
Figure S32 - $^1$H NMR of compound 19 in DMSO-$d_6$ conducted at 333.15 K.

Figure S33 - $^{13}$C NMR of compound 19 in DMSO-$d_6$ conducted at 298.15 K.
Figure S34 - $^1$H NMR of compound 20 in DMSO-$d_6$ conducted at 298.15 K.

Figure S35 - $^1$H NMR of compound 20 in DMSO-$d_6$ conducted at 333.15 K.
Figure S36 - $^{13}$C NMR of compound 20 in DMSO-$d_6$ conducted at 298.15 K.

Figure S37 - $^1$H NMR of compound 21 in DMSO-$d_6$ conducted at 298.15 K.
Figure S38 - $^1$H NMR of compound 21 in DMSO-$d_6$ conducted at 333.15 K.

Figure S39 - $^{13}$C NMR of compound 21 in DMSO-$d_6$ conducted at 298.15 K.
Figure S40 - $^1$H NMR of compound 22 in DMSO-$d_6$ conducted at 298.15 K.

Figure S41 - $^{13}$C NMR of compound 22 in DMSO-$d_6$ conducted at 298.15 K.
Figure S42 - $^1$H NMR of compound 23 in DMSO-$d_6$ conducted at 298.15 K.

Figure S43 - $^{13}$C NMR of compound 23 in DMSO-$d_6$ conducted at 298.15 K.
Figure S44 - $^1$H NMR of compound 24 in DMSO-$d_6$ conducted at 298.15 K.

Figure S45 - $^{13}$C NMR of compound 24 in DMSO-$d_6$ conducted at 298.15 K.
Figure S46 - $^1$H NMR of compound 25 in DMSO-$d_6$ conducted at 298.15 K.
Figure S47 - $^{13}$C NMR of compound 25 in DMSO-$d_6$ conducted at 298.15 K.

Figure S48 - $^1$H NMR of compound 26 in DMSO-$d_6$ conducted at 298.15 K.
Figure S49 - $^{13}$C NMR of compound 26 in DMSO-$d_6$ conducted at 298.15 K.

Figure S50 - $^1$H NMR of compound 27 in DMSO-$d_6$ conducted at 298.15 K.
Figure S51 - $^{13}$C NMR of compound 27 in DMSO-$d_6$ conducted at 298.15 K.

Figure S52 - $^1$H NMR of compound 28 in DMSO-$d_6$ conducted at 298.15 K.
Figure S53 - $^1$H NMR of compound 29 in DMSO-d$_6$ conducted at 298.15 K.

Figure S54 - $^1$H NMR of compound 30 in DMSO-d$_6$ conducted at 298.15 K.
Figure S55 - $^1$H NMR of compound 31 in DMSO-$d_6$ conducted at 298.15 K.

Figure S56 - $^1$H NMR of compound 32 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.
Figure S57 - Enlarged $^1$H NMR of compound 32 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.

Figure S58 - $^1$H NMR of compound 33 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.
Figure S59 - Enlarged $^1$H NMR of compound 33 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.

Figure S60 - $^1$H NMR of compound 34 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.
Figure S61 - Enlarged $^1$H NMR of compound 34 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.

Figure S62 - $^1$H NMR of compound 35 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.
Figure S63 - Enlarged $^1$H NMR of compound 35 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.

Figure S64 - $^1$H NMR of compound 36 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.
Figure S65 - Enlarged $^1$H NMR of compound 36 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.

Figure S66 - $^1$H NMR of compound 37 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.
Figure S67 - Enlarged $^1$H NMR of compound 37 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.

Figure S68 - $^1$H NMR of compound 38 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.
Figure S69 - Enlarged $^1$H NMR of compound 38 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.

Figure S70 - $^1$H NMR of compound 39 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.
Figure S71 - Enlarged $^1$H NMR of compound 39 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.

Figure S72 - $^1$H NMR of tetramethylammonium hexafluorophosphate in DMSO-$d_6$ conducted at 298.15 K.
Figure S73 - $^1$H NMR of pyridinium hexafluorophosphate in DMSO-$d_6$ conducted at 298.15 K.
$^1$H DOSY NMR experiments

Figure S74 - $^1$H DOSY NMR of compound 1 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K. Anionic component highlighted in blue, TBA counter cation highlighted in red.
Table S1 - Diffusion data obtained from $^1$H DOSY NMR of compound 1 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.

| Peak name | F2 [ppm] | lo       | error     | D [m$^2$/s] | error     |
|-----------|----------|----------|-----------|-------------|-----------|
| 1         | 9.250    | 8.46e+08 | 2.168e+04 | 4.79e-12    | 2.021e-16 |
| 2         | 7.560    | 2.69e+09 | 1.492e+04 | 4.79e-12    | 4.365e-17 |
| 3         | 7.497    | 2.33e+09 | 1.295e+04 | 4.82e-12    | 4.403e-17 |
| 4         | 6.951    | 1.15e+09 | 1.667e+04 | 4.81e-12    | 1.143e-16 |
| 5         | 3.939    | 2.30e+09 | 1.292e+04 | 4.79e-12    | 4.421e-17 |
| 6         | 3.165    | 7.13e+09 | 1.705e+04 | 5.15e-12    | 1.992e-17 |
| 7         | 1.567    | 8.17e+09 | 2.011e+04 | 5.11e-12    | 2.041e-17 |
| 8         | 1.306    | 9.83e+09 | 2.011e+04 | 5.11e-12    | 1.697e-17 |
| 9         | 0.939    | 1.62e+10 | 1.860e+04 | 5.11e-12    | 9.535e-18 |
Figure S75 - $^1$H DOSY NMR of compound 4 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K. Anionic component highlighted in blue, TBA counter cation highlighted in red. Solvent peaks omitted from diffusion spectrum.
Table S2 - Diffusion data obtained from $^1$H DOSY NMR of compound 4 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.

| Peak name | $F_2$ [ppm] | $lo$  | error        | $D$ [m$^2$/s] | error        |
|-----------|-------------|-------|--------------|---------------|--------------|
| 1         | 11.055      | 1.01e+08 | 1.993e+04   | 1.98e-10     | 8.562e-14   |
| 2         | 10.263      | 3.33e+08 | 1.923e+04   | 1.97e-10     | 2.684e-14   |
| 3         | 8.764       | 1.06e+08 | 2.093e+04   | 1.97e-10     | 8.551e-14   |
| 4         | 8.155       | 3.46e+08 | 2.027e+04   | 1.97e-10     | 2.523e-14   |
| 5         | 7.883       | 6.96e+08 | 1.990e+04   | 1.96e-10     | 9.546e-15   |
| 6         | 7.726       | 2.89e+08 | 1.781e+04   | 1.97e-10     | 2.653e-14   |
| 7         | 7.640       | 1.32e+09 | 1.783e+04   | 1.96e-10     | 5.825e-15   |
| 8         | 4.343       | 8.28e+08 | 1.922e+04   | 1.96e-10     | 9.963e-15   |
| 9         | 4.095       | 2.58e+08 | 1.993e+04   | 1.96e-10     | 3.315e-14   |
| 10        | 3.171       | 3.21e+09 | 1.684e+04   | 2.04e-10     | 2.328e-15   |
| 11        | 1.575       | 3.49e+09 | 1.905e+04   | 2.03e-10     | 2.418e-15   |
| 12        | 1.317       | 4.27e+09 | 1.577e+04   | 2.03e-10     | 2.050e-15   |
| 13        | 0.942       | 6.86e+09 | 1.555e+04   | 2.03e-10     | 1.003e-15   |
Figure S76 - $^1$H DOSY NMR of compound 24 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K. Anionic component highlighted in blue, TBA counter cation highlighted in red, solvents (DMSO, H$_2$O) highlighted in green.
Table S3 - Diffusion data obtained from $^1$H DOSY NMR of compound 24 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K.

| Peak name | F2 [ppm]   | Io      | error    | D [m2/s]  | error    |
|-----------|------------|---------|----------|-----------|----------|
| 1         | 10.692     | 4.89e+09| 1.071e+06| 1.70e-10  | 8.175e-14|
| 2         | 7.672      | 2.56e+10| 1.469e+06| 1.70e-10  | 2.173e-14|
| 3         | 7.129      | 4.69e+09| 1.021e+06| 1.71e-10  | 8.186e-14|
| 4         | 5.803      | 2.15e+10| 1.613e+06| 7.18e-10  | 1.103e-13|
| 5         | 3.461      | 1.19e+10| 1.060e+06| 1.74e-10  | 3.393e-14|
| 6         | 3.192      | 2.93e+10| 1.129e+06| 2.05e-10  | 1.712e-14|
| 7         | 2.533      | 4.32e+08| 1.253e+06| 5.54e-10  | 3.341e-13|
| 8         | 1.604      | 3.37e+10| 1.212e+06| 2.04e-10  | 1.592e-14|
| 9         | 1.331      | 4.20e+10| 1.145e+06| 2.05e-10  | 1.219e-14|
| 10        | 0.960      | 6.61e+10| 1.052e+06| 2.05e-10  | 7.328e-15|
Figure S77 - $^1$H DOSY NMR of compound 27 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K. Anionic component highlighted in blue, TBA counter cation highlighted in red. Solvent peaks omitted from diffusion spectrum.
Table S4 - Diffusion data obtained from $^1$H DOSY NMR of compound 27 (55.56 mM) in DMSO-$d_6$ conducted at 298.15 K

| Peak name | F2 [ppm] | I0 | error | D [m$^2$/s] | error |
|-----------|----------|----|--------|-------------|-------|
| 1         | 8.411    | 4.98e+09 | 1.239e+05 | 1.53e-10 | 8.265e-15 |
| 2         | 7.552    | 5.02e+09 | 1.244e+05 | 1.54e-10 | 8.276e-15 |
| 3         | 3.719    | 4.34e+09 | 1.079e+05 | 1.53e-10 | 8.269e-15 |
| 4         | 3.160    | 1.35e+10 | 1.538e+05 | 1.87e-10 | 4.558e-15 |
| 5         | 1.660    | 1.56e+10 | 1.731e+05 | 1.87e-10 | 4.473e-15 |
| 6         | 1.288    | 2.09e+10 | 1.852e+05 | 1.87e-10 | 3.544e-15 |
| 7         | 0.922    | 3.49e+10 | 1.604e+05 | 1.87e-10 | 1.835e-15 |
Quantitative $^1$H NMR experiments

Figure S78 - $^1$H NMR spectrum ($d_1 = 60$ s) of compound 1 (0.030 g, 109.80 mM) and dichloromethane (5 µl, 0.08 mM) in DMSO-$d_6$. No apparent loss of compound observed upon comparative signal integration.

Figure S79 - $^1$H NMR spectrum ($d_1 = 60$ s) of compound 4 (0.030 g, 110.60 mM) and dichloromethane (5 µl, 0.08 mM) in DMSO-$d_6$. No apparent loss of compound observed upon comparative signal integration.
Figure S80 - $^1$H NMR spectrum ($d_1 = 60$ s) of compound 24 (0.014 g, 54.6 mM) and dichloromethane (5 µl, 0.08 mM) in DMSO-$d_6$. No apparent loss of compound observed upon comparative signal integration.

Figure S81 - $^1$H NMR spectrum ($d_1 = 60$ s) of compound 27 (0.029 g, 110.60 mM) and dichloromethane (5 µl, 0.08 mM) in DMSO-$d_6$. No apparent loss of compound observed upon comparative signal integration.
Figure S82 - $^1$H NMR spectrum (d$_1$ = 60 s) of compound 1 (0.003 g, 5.80 mM) and ethanol (25 µl, 0.43 mM) in D$_2$O, 1:19. An apparent 51% loss of compound was observed upon comparative signal integration.

Figure S83 - $^1$H NMR spectrum (d$_1$ = 60 s) of compound 4 (0.003 g, 6.10 mM) and ethanol (25 µl, 0.43 mM) in D$_2$O, 1:19. An apparent 50% loss of compound was observed upon comparative signal integration.
Figure S84 - $^1$H NMR spectrum (d$_1$ = 60 s) of compound 24 (0.003 g, 6.30 mM) and ethanol (25 µl, 0.43 mM) in D$_2$O, 1:19. An apparent 68 % loss of compound was observed upon comparative signal integration.

Figure S85 - $^1$H NMR spectrum (d$_1$ = 60 s) of compound 27 (0.003 g, 6.01 mM) and ethanol (25 µl, 0.43 mM) in D$_2$O, 1:19. An apparent 59 % loss of compound was observed upon comparative signal integration.
**¹H NMR self-association studies**

Figure S86 - ¹H NMR stack plot of compound 1 in a DMSO-<sub>d6</sub>0.5 % H<sub>2</sub>O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S87 - Enlarged ¹H NMR stack plot of compound 1 in a DMSO-<sub>d6</sub>0.5 % H<sub>2</sub>O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S88 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 1 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 1 - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.**

**Equal K/Dimerization model**

$K_e = 5.31 \text{ M}^{-1} \pm 0.6180 \%$  \hspace{1cm} $K_{\text{dim}} = 2.66 \text{ M}^{-1} \pm 0.3090 \%$

[http://app.supramolecular.org/bindfit/view/d6af9b53-56d3-41af-9eb1-1089d2ebed98](http://app.supramolecular.org/bindfit/view/d6af9b53-56d3-41af-9eb1-1089d2ebed98)

**CoEK model**

$K_e = 12.95 \text{ M}^{-1} \pm 0.7180 \%$  \hspace{1cm} $K_{\text{dim}} = 6.48 \text{ M}^{-1} \pm 0.3590 \%$  \hspace{1cm} $\rho = 0.50 \pm 2.1072 \%$

[http://app.supramolecular.org/bindfit/view/01e930a4-468d-42b7-b512-879b89a19e47](http://app.supramolecular.org/bindfit/view/01e930a4-468d-42b7-b512-879b89a19e47)
Figure S89 - $^1$H NMR stack plot of compound 2 in a DMSO-$d_6$ 0.5 % $H_2O$ solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S90 - Enlarged $^1$H NMR stack plot of compound 2 in a DMSO-$d_6$ 0.5 % $H_2O$ solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S91 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 2 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 2 - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.**

**Equal K/Dimerization model**

$K_e = 0.18 \text{ M}^{-1} \pm 1.9926 \%$  \hspace{1cm} $K_{d_{	ext{dim}}} = 0.09 \text{ M}^{-1} \pm 0.9963 \%$

[http://app.supramolecular.org/bindfit/view/611ab18c-91b8-452a-9291-06723b77b27d](http://app.supramolecular.org/bindfit/view/611ab18c-91b8-452a-9291-06723b77b27d)

**CoEK model**

$K_e = 4.01 \text{ M}^{-1} \pm 12.0440 \%$  \hspace{1cm} $K_{d_{	ext{dim}}} = 2.00 \text{ M}^{-1} \pm 6.0220 \%$  \hspace{1cm} $\rho = 0.39 \pm 20.3336 \%$

[http://app.supramolecular.org/bindfit/view/9ff706a-1be8-42e0-9add-c45df6b8775f](http://app.supramolecular.org/bindfit/view/9ff706a-1be8-42e0-9add-c45df6b8775f)
Figure S92 - $^1$H NMR stack plot of compound 3 in a DMSO-d$_6$ 0.5 % H$_2$O. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S93 - Enlarged $^1$H NMR stack plot of compound 3 in a DMSO-d$_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Self-association constant calculation

Compound 3 - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.

Equal K/Dimerization model

$K_e = 6.60 \text{ M}^{-1} \pm 1.9895 \%$ \quad $K_{\text{dim}} = 3.30 \text{ M}^{-1} \pm 0.9947 \%$

http://app.supramolecular.org/bindfit/view/80983541-35ea-4fc8-ba61-db06ca69b722

CoEK model

$K_e = 19.97 \text{ M}^{-1} \pm 2.7078 \%$ \quad $K_{\text{dim}} = 9.98 \text{ M}^{-1} \pm 1.3539 \%$ \quad $\rho = 0.34 \pm 11.5687 \%$

http://app.supramolecular.org/bindfit/view/f8516087-4785-4676-8b8c-8ac3bc6ec9e6

Figure S94 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 3 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).
Figure S95 - $^1$H NMR stack plot of compound 5 in a DMSO-d$_6$ 0.5 % H$_2$O. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S96 - Enlarged $^1$H NMR stack plot of compound 5 in a DMSO-d$_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S97 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 5 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 5 - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.**

*Equal K/Dimerization model*

\[ K_e = 0.30 \text{ M}^{-1} \pm 4.2417 \% \quad K_{\text{dim}} = 0.15 \text{ M}^{-1} \pm 2.1208 \% \]

[http://app.supramolecular.org/bindfit/view/a78e4b05-98d6-4e0a-a472-36cb6e950e11](http://app.supramolecular.org/bindfit/view/a78e4b05-98d6-4e0a-a472-36cb6e950e11)

*CoEK model*

\[ K_e = 1.86 \text{ M}^{-1} \pm 50.9685 \% \quad K_{\text{dim}} = 0.93 \text{ M}^{-1} \pm 25.4842 \% \quad \rho = 0.52 \pm 66.2743 \% \]

[http://app.supramolecular.org/bindfit/view/20409611-869d-4a35-b403-8ce0c8ff9fe2](http://app.supramolecular.org/bindfit/view/20409611-869d-4a35-b403-8ce0c8ff9fe2)
Figure S98 - $^1$H NMR stack plot of compound 6 in a DMSO-d$_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S99 - Enlarged $^1$H NMR stack plot of compound 6 in a DMSO-d$_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S100 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 6 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 6 - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.**

*Equal K/Dimerization model*

$K_e = 5.14 \text{ M}^{-1} \pm 2.1382$ %  \hspace{1cm} $K_{\text{dim}} = 2.57 \text{ M}^{-1} \pm 1.3691$ %

[http://app.supramolecular.org/bindfit/view/5ae5efa4-d195-4f17-ad13-dd563321d23b](http://app.supramolecular.org/bindfit/view/5ae5efa4-d195-4f17-ad13-dd563321d23b)

*CoEK model*

$K_e = 14.13 \text{ M}^{-1} \pm 4.3952$ %  \hspace{1cm} $K_{\text{dim}} = 7.07 \text{ M}^{-1} \pm 2.1976$ %  \hspace{1cm} $\rho = 0.44 \pm 14.0401$ %

[http://app.supramolecular.org/bindfit/view/bef26f74-77ff-4256-bd56-7f4492ed5a9f](http://app.supramolecular.org/bindfit/view/bef26f74-77ff-4256-bd56-7f4492ed5a9f)
Figure S101 - $^1$H NMR stack plot of compound 9 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S102 - Enlarged $^1$H NMR stack plot of compound 9 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S103 – Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 9 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 9** - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.

*Equal K/Dimerization model*

\[ K_e = 13.46 \text{ M}^{-1} \pm 0.6559 \% \quad K_{\text{dim}} = 6.73 \text{ M}^{-1} \pm 0.3280 \% \]

[http://app.supramolecular.org/bindfit/view/663e8a71-6640-464a-90de-6683e7305d91](http://app.supramolecular.org/bindfit/view/663e8a71-6640-464a-90de-6683e7305d91)

*CoEK model*

\[ K_e = 18.24 \text{ M}^{-1} \pm 1.0369 \% \quad K_{\text{dim}} = 9.12 \text{ M}^{-1} \pm 0.5184 \% \quad \rho = 0.75 \pm 3.3727 \% \]

[http://app.supramolecular.org/bindfit/view/e52669a4-9408-4dd8-9dd3-182c5bec7de6](http://app.supramolecular.org/bindfit/view/e52669a4-9408-4dd8-9dd3-182c5bec7de6)
Figure S104 - $^1$H NMR stack plot of compound 10 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S105 - Enlarged $^1$H NMR stack plot of compound 10 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S106 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 10 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 10** - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.

**Equal K/Dimerization model**

$K_e = 6.33 \text{ M}^{-1} \pm 0.8868 \%$  \quad $K_{d_{\text{dim}}} = 3.16 \text{ M}^{-1} \pm 0.4434 \%$

[http://app.supramolecular.org/bindfit/view/803ae004-5fd7-441f-b193-a904f7934214](http://app.supramolecular.org/bindfit/view/803ae004-5fd7-441f-b193-a904f7934214)

**CoEK model**

$K_e = 12.02 \text{ M}^{-1} \pm 2.0491 \%$  \quad $K_{d_{\text{dim}}} = 6.01 \text{ M}^{-1} \pm 1.0246 \%$  \quad $\rho = 0.61 \pm 5.5007 \%$

[http://app.supramolecular.org/bindfit/view/3c74e0d7-8d08-4c52-ab97-3f329b57c46a](http://app.supramolecular.org/bindfit/view/3c74e0d7-8d08-4c52-ab97-3f329b57c46a)
Figure S107 - $^1$H NMR stack plot of compound 11 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S108 - Enlarged $^1$H NMR stack plot of compound 11 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S109 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 11 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 11** - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.

**Equal K/Dimerization model**

$K_e = 6.58 \text{ M}^{-1} \pm 1.1817 \%$  
$K_{dim} = 3.29 \text{ M}^{-1} \pm 0.5908 \%$

[http://app.supramolecular.org/bindfit/view/39722541-1459-456f-a641-186f57d3eacd](http://app.supramolecular.org/bindfit/view/39722541-1459-456f-a641-186f57d3eacd)

**CoEK model**

$K_e = 14.94 \text{ M}^{-1} \pm 2.1054 \%$  
$K_{dim} = 7.47 \text{ M}^{-1} \pm 8.1683 \%$  
$\rho = 0.50 \pm 6.7425 \%$

[http://app.supramolecular.org/bindfit/view/c6b1dbf0-cde9-4293-8f15-10c6c2a3cf4e](http://app.supramolecular.org/bindfit/view/c6b1dbf0-cde9-4293-8f15-10c6c2a3cf4e)
Figure S110 - $^1$H NMR stack plot of compound 12 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S111 - Enlarged $^1$H NMR stack plot of compound 12 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S112 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 12 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 12 - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.**

*Equal K/Dimerization model*

$$K_e = 4.11 \text{ M}^{-1} \pm 0.5004 \%$$

$$K_{\text{dim}} = 2.05 \text{ M}^{-1} \pm 0.2502 \%$$

[Link](http://app.supramolecular.org/bindfit/view/30b20e66-3dc5-4558-a3cc-3c701883387e)

*CoEK model*

$$K_e = 8.84 \text{ M}^{-1} \pm 1.3367 \%$$

$$K_{\text{dim}} = 4.42 \text{ M}^{-1} \pm 0.6684 \%$$

$$\rho = 0.60 \pm 3.0443 \%$$

[Link](http://app.supramolecular.org/bindfit/view/e991d3e2-20cc-4ba4-80ed-afaacef703b5)
Figure S113 - $^1$H NMR stack plot of compound 13 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S114 - Enlarged $^1$H NMR stack plot of compound 13 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S115 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 13 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

Self-association constant calculation

Compound 13 - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.

Equal K/Dimerization model

$K_e = 5.03 \text{ M}^{-1} \pm 0.9186 \%$ \hspace{1cm} $K_{dm} = 2.51 \text{ M}^{-1} \pm 0.4582 \%$

http://app.supramolecular.org/bindfit/view/4c947200-18e8-44e1-abf1-de45cecd25df

CoEK model

$K_e = 9.60 \text{ M}^{-1} \pm 2.6644 \%$ \hspace{1cm} $K_{dm} = 4.80 \text{ M}^{-1} \pm 1.3322 \% \hspace{1cm} \rho = 0.9 \pm 6.2664 \%$

http://app.supramolecular.org/bindfit/view/4e1c358a-1031-411f-983d-90287bd92e70
Figure S116 - $^1$H NMR stack plot of compound 14 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S117 - Enlarged $^1$H NMR stack plot of compound 14 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S118 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 14 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 14 - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated combining the data gathered from both NH.**

*Equal K/Dimerization model*

- $K_e = 3.62 \text{ M}^{-1} \pm 1.4514 \%$
- $K_{\text{dim}} = 1.81 \text{ M}^{-1} \pm 0.7257 \%$

[Link](http://app.supramolecular.org/bindfit/view/fbf5eb94-aa6f-4cbc-8ecf-cb89db0283dc)

*CoEK model*

- $K_e = 4.59 \text{ M}^{-1} \pm 8.2825 \%$
- $K_{\text{dim}} = 2.30 \text{ M}^{-1} \pm 4.1412 \%$
- $\rho = 0.86 \pm 13.4410 \%$

[Link](http://app.supramolecular.org/bindfit/view/6e3dc7a1-4d48-4c5c-9fe3-680fca65e123)
Figure S119 - $^1$H NMR stack plot of compound 22 in a DMSO-$d_6$ 0.5 % H$_2$O. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S120 - Enlarged $^1$H NMR stack plot of compound 22 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S121 - Graph illustrating $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 22 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K). The change in chemical shift is too small enable the self-association constant to be calculated.
Figure S122 - $^1$H NMR stack plot of compound 23 in a DMSO-$d_6$ 0.5 % H$_2$O. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S123 - Enlarged $^1$H NMR stack plot of compound 23 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S124 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 23 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 23 - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.**

*Equal K/Dimerization model*

$K_e = 5.62 \text{e-}4 \text{ M}^{-1} \pm 1.2078 \text{e-}4 \%$  
$K_{\text{dim}} = 2.81 \text{e-}4 \text{ M}^{-1} \pm 6.0389 \text{e-}5 \%$

[http://app.supramolecular.org/bindfit/view/8ee9bf55-7b9e-4dec-ae15-609fb8ebf9a3](http://app.supramolecular.org/bindfit/view/8ee9bf55-7b9e-4dec-ae15-609fb8ebf9a3)

*CoEK model*

$K_e = 7.12 \text{ M}^{-1} \pm 18.3708 \%$  
$K_{\text{dim}} = 3.56 \text{ M}^{-1} \pm 9.1854 \%$  
$\rho = 0.07 \pm 58.3987 \%$

[http://app.supramolecular.org/bindfit/view/de79dbdc-bb5d-4152-881e-1daead5698c7](http://app.supramolecular.org/bindfit/view/de79dbdc-bb5d-4152-881e-1daead5698c7)
Figure S125 - $^1$H NMR stack plot of compound 24 in a DMSO-$d_6$ 0.5 % H$_2$O. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S126 - Enlarged $^1$H NMR stack plot of compound 24 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S127 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 24 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 24 - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.**

*Equal K/Dimerization model*

\[
K_e = 82.78 \text{ M}^{-1} \pm 2.5313 \% \\
K_{\text{dim}} = 41.39 \text{ M}^{-1} \pm 1.2657 \%
\]

[http://app.supramolecular.org/bindfit/view/2bb99c66-416f-49c8-8a5e-4cbaa0d76147](http://app.supramolecular.org/bindfit/view/2bb99c66-416f-49c8-8a5e-4cbaa0d76147)

*CoEK model*

\[
K_e = 101.81 \text{ M}^{-1} \pm 2.5572 \% \\
K_{\text{dim}} = 50.90 \text{ M}^{-1} \pm 1.2786 \% \\
\rho = 2.57 \pm 11.5817 \%
\]

[http://app.supramolecular.org/bindfit/view/9e0a4b28-c4ff-4c8d-ba68-b0fabc3de8f](http://app.supramolecular.org/bindfit/view/9e0a4b28-c4ff-4c8d-ba68-b0fabc3de8f)
Figure S128 - $^1$H NMR stack plot of compound 25 in a DMSO-$d_6$ 0.5 % H$_2$O. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S129 - Enlarged $^1$H NMR stack plot of compound 25 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S130 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 25 in DMSO-$d_6$ 0.5% H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 25 - Dilution study in DMSO-$d_6$ 0.5% H$_2$O.** Values calculated from data gathered from both NH.

*Equal K/Dimerization model*

\[ K_e = 11.90 \text{ M}^{-1} \pm 1.5194 \% \quad K_{\text{dim}} = 5.95 \text{ M}^{-1} \pm 0.7597 \% \]

[http://app.supramolecular.org/bindfit/view/53cc2518-deff-4532-9e18-67f9bd0c59e8](http://app.supramolecular.org/bindfit/view/53cc2518-deff-4532-9e18-67f9bd0c59e8)

*CoEK model*

\[ K_e = 23.75 \text{ M}^{-1} \pm 1.7369 \% \quad K_{\text{dim}} = 11.87 \text{ M}^{-1} \pm 0.8685 \% \quad \rho = 0.46 \pm 7.5306 \% \]

[http://app.supramolecular.org/bindfit/view/a49ba9f9-8815-4849-93a7-2841a2575f51](http://app.supramolecular.org/bindfit/view/a49ba9f9-8815-4849-93a7-2841a2575f51)
Figure S131 - $^1$H NMR stack plot of compound 26 in a DMSO-$d_6$ 0.5 % H$_2$O. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S132 - Enlarged $^1$H NMR stack plot of compound 26 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S133 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 26 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

*Compound 26* - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.

*Equal K/Dimerization model*

\[ K_e = 10.81 \text{ M}^{-1} \pm 3.5045 \% \quad K_{\text{dim}} = 5.40 \text{ M}^{-1} \pm 1.7522 \% \]

[http://app.supramolecular.org/bindfit/view/aa5fa670-4533-4b7b-b741-e3176349d4f3](http://app.supramolecular.org/bindfit/view/aa5fa670-4533-4b7b-b741-e3176349d4f3)

*CoEK model*

\[ K_e = 4.59 \text{ M}^{-1} \pm 20.8121 \% \quad K_{\text{dim}} = 2.30 \text{ M}^{-1} \pm 10.4061 \% \quad \rho = 1.88 \pm 31.0686 \% \]

[http://app.supramolecular.org/bindfit/view/22a940f7-8289-4c34-a9f8-b9a646651bb3](http://app.supramolecular.org/bindfit/view/22a940f7-8289-4c34-a9f8-b9a646651bb3)
Figure S134 - $^1$H NMR stack plot of compound 27 in a DMSO-$d_6$ 0.5 % H$_2$O. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.

Figure S135 - Enlarged $^1$H NMR stack plot of compound 27 in a DMSO-$d_6$ 0.5 % H$_2$O solution. Samples were prepared in series with an aliquot of the most concentrated solution undergoing serial dilution.
Figure S136 - Graph illustrating the $^1$H NMR down-field change in chemical shift of urea NH resonances with increasing concentration of compound 27 in DMSO-$d_6$ 0.5 % H$_2$O (298.15 K).

**Self-association constant calculation**

**Compound 27** - Dilution study in DMSO-$d_6$ 5 % H$_2$O. Values calculated from data gathered from both NH.

**Equal K/Dimerization model**

$K_e = 209.34 \text{ M}^{-1} \pm 1.2548 \%$ \quad $K_{\text{dim}} = 104.67 \text{ M}^{-1} \pm 0.6274 \%$

[http://app.supramolecular.org/bindfit/view/7fa20ef7-0dc5-4dff-b81d-5457f6b2140c](http://app.supramolecular.org/bindfit/view/7fa20ef7-0dc5-4dff-b81d-5457f6b2140c)

**CoEK model**

$K_e = 226.07 \text{ M}^{-1} \pm 1.3871 \%$ \quad $K_{\text{dim}} = 113.04 \text{ M}^{-1} \pm 0.6935 \%$ \quad $\rho = 1.18 \pm 3.2623 \%$

[http://app.supramolecular.org/bindfit/view/0be23f65-5265-4cc4-a392-eb0bf3952332](http://app.supramolecular.org/bindfit/view/0be23f65-5265-4cc4-a392-eb0bf3952332)
Table S5 - $^1$H NMR resonances of the ethane sulfonate portion of compounds 32-39.

| Compound | Ethane sulfonate cation | Concentration (mM) |
|----------|-------------------------|-------------------|
|          |                         | 55.56             | 5.56  | 0.56  |
|          |                         | CH$_2$ (ppm) | CH$_3$ (ppm) | CH$_2$ (ppm) | CH$_3$ (ppm) | CH$_2$ (ppm) | CH$_3$ (ppm) |
| 32       | Sodium                  | 2.4807         | 1.0890 | 2.3754 | 1.0520 | 2.3410 | 1.0416 |
| 33       | Pyridinium              | 2.4385         | 1.0687 | 2.3818 | 2.0486 | 2.3593 | 1.0410 |
| 34       | TMA                     | 2.3684         | 1.0468 | 2.3566 | 1.0416 | 2.3535 | 1.0404 |
| 35       | TEA                     | 2.3636         | 1.0440 | 2.3675 | 1.0449 | 2.3596 | 1.0422 |
| 36       | TPA                     | 2.3630         | 1.0446 | 2.3547 | 1.0407 | 2.3529 | 1.0398 |
| 37       | TBA                     | 2.3599         | 1.0471 | 2.3566 | 1.0446 | 2.3560 | 1.0440 |
| 38       | TPeA                    | 2.3648         | 1.0453 | 2.3581 | 1.0419 | 2.3590 | 1.0416 |
| 39       | THA                     | 2.3666         | 1.0459 | 2.3569 | 1.0413 | 2.3550 | 1.0404 |
\(^1\)H NMR titration studies

![Graph illustrating the \(^1\)H NMR down-field change in chemical shift of the sulfonate-CH\(_2\) signal corresponding to compound 37 with increasing concentration of tetramethylammonium hexafluorophosphate in DMSO-\(d_6\) 0.5 % H\(_2\)O (298.15 K).](http://app.supramolecular.org/bindfit/view/267b0bd1-4050-486b-b41b-991752f8db6b)

\[ K = 9.87 \text{ M}^{-1} \pm 1.7237 \% \]
Figure S138 - Graph illustrating the $^1$H NMR down-field change in chemical shift of the sulfonate-CH$_2$ signal corresponding to compound 37 with increasing concentration of pyridinium hexafluorophosphate in DMSO-d$_6$, 0.5 % H$_2$O (298.15 K).

K = 10.71 M$^{-1}$ ± 0.6717 %

http://app.supramolecular.org/bindfit/view/96ef976e-ed3f-4dfa-9042-44f216a2682d
DLS data

Size distribution data

Figure S139 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 1 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S140 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 1 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S141 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 2 at a concentration of 5.56 mM in DMSO at (∆) 25 °C, (□) heating to 40 °C and (○) cooling to 25 °C.
Figure S142 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 2 at a concentration of 0.56 mM in DMSO at \( \Delta \) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S143 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 2 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S144 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 2 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S145 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 3 at a concentration of 5.56 mM in DMSO at ∆) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S146 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 3 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S147 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 3 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S148 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 3 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S149 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 4 at a concentration of 5.56 mM in DMSO at △) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S150 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 4 at a concentration of 0.56 mM in DMSO at △) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S151 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 4 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S152 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 4 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S153 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 5 at a concentration of 5.56 mM in DMSO at △) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S154 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 5 at a concentration of 0.56 mM in DMSO at △) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S155 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 5 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S156 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 5 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S157 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 6 at a concentration of 5.56 mM in DMSO at (A) 25 °C, (□) heating to 40 °C and (○) cooling to 25 °C.
Figure S158 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 6 at a concentration of 0.56 mM in DMSO at △) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S159 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 6 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S160 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 6 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S161 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 7 at a concentration of 5.56 mM in DMSO at △) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S162 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 7 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S163 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 7 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S164 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 7 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S165 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 8 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S166 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 8 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S167 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 8 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S168 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 8 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S169 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 9 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S170 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 9 at a concentration of 0.56 mM in DMSO at (A) 25 °C, (□) heating to 40 °C and (○) cooling to 25 °C.
Figure S171 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 9 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S172 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 9 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S173 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 10 at a concentration of 5.56 mM in DMSO at ▲) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S174 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 10 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S175 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 10 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S176 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 10 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S177 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 11 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S178 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 11 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S179 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound **11** at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S180 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound **11** at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S181 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 12 at a concentration of 5.56 mM in DMSO at △) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S182 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound \textbf{12} at a concentration of 0.56 mM in DMSO at (A) 25 °C, (□) heating to 40 °C and (○) cooling to 25 °C.
Figure S183 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 13 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S184 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 13 at a concentration of 0.56 mM in DMSO at △) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S185 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 14 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S186 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 14 at a concentration of 0.56 mM in DMSO at  \( \Delta \) 25 \( ^\circ \)C,  \( \square \) heating to 40 \( ^\circ \)C and  \( \circ \) cooling to 25 \( ^\circ \)C.
Figure S187 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 14 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S188 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 14 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S189 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 15 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S190 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 15 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S191 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 15 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S192 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 15 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S193 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 17 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S194 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 17 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S195 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 17 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S196 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 17 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S197 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 19 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S198 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 19 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S199 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 19 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S200 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 19 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S201 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 20 at a concentration of 5.56 mM in DMSO at A) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S202 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 20 at a concentration of 0.56 mM in DMSO at △) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S203 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 20 at a concentration of 5.56 mM in a solution of EtOH:HO 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S204 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 20 at a concentration of 0.56 mM in a solution of EtOH:HO 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S205 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 21 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S206 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 21 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S207 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 21 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S208 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 21 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S209 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 22 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S210 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 22 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S211 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 23 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S212 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 23 at a concentration of 0.56 mM in DMSO at △) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S213 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 23 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S214 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 23 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S215 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 24 at a concentration of 5.56 mM in DMSO at △) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S216 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 24 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S217 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 24 at a concentration of 5.56 mM in a solution of EtOH:H$_2$O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S218 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 24 at a concentration of 0.56 mM in a solution of EtOH:H$_2$O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S219 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 25 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S220 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 25 at a concentration of 0.56 mM in DMSO at (A) 25 °C, (□) heating to 40 °C and (○) cooling to 25 °C.
Figure S221 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 26 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S222 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 26 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S223 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 26 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S224 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 26 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Figure S225 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 27 at a concentration of 5.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S226 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 27 at a concentration of 0.56 mM in DMSO at Δ) 25 °C, □) heating to 40 °C and ○) cooling to 25 °C.
Figure S227 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 27 at a concentration of 5.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.

Figure S228 - Average intensity particle size distribution, calculated from 9 DLS runs, of aggregates formed by dissolving compound 27 at a concentration of 0.56 mM in a solution of EtOH:H₂O 1:19, after heating to 40 °C and cooling to 25 °C.
Comparative overview of DLS results

Table S6 - Average intensity particle size distribution maxima for compounds 1-31, calculated from 9 DLS runs in different solvent conditions at 5.56 mM and 0.56 mM. Samples were prepared in series, with an aliquot of the most concentrated solution undergoing serial dilution and measured after heating to 40 °C and cooling to 25 °C.

| No. | DMSO (mM) | EtOH:H₂O 1:19 (mM) | No. | DMSO (mM) | EtOH:H₂O 1:19 (mM) |
|-----|-----------|-------------------|-----|-----------|-------------------|
|     | 5.56      | 0.56              |     | 5.56      | 0.56              |
| 1   | 164       | 255               | 16  | 615       | 531               |
| 2   | 615       | 342               | 17  | 164       | 220               | 91              | 79              |
| 3   | 220       | 295               | 19  | 459       | 342               | 220             | 190,18          |
| 4   | 342,1     | 459               | 20  | 396       | 342               | 190             | 190             |
| 5   | 255       | 295               | 21  | 255       | 342               | 106,1           | 122,5560        |
| 6   | 459       | 220               | 22  | 342       | 295               | a               |
| 7   | 295       | 342               | 23  | 342       | 531               | 396             | 330,33          |
| 8   | 255       | 190               | 24  | 1106      | 342               | 220             | 190,33          |
| 9   | 459       | 396               | 25  | 459       | 712               | a               |
| 10  | 531       | 615               | 26  | 2035      | 615               | 459             | 255             |
| 11  | 342       | 615               | 27  | 342       | 295               | 164             | 106             |
| 12  | 615       | 295               |     |           | b                 | 164             | 255             |
| 13  | 531       | 531               |     |           |                   |                 |
| 14  | 396       | 342               | 30  | 1106      | 531,1             | 295             | 220             |
| 15  | 295       | 342               | 31  | 396,1     | 396               | 59,122           | 295             |

a - DLS Size distribution in a solution of EtOH:H₂O 1:19 for compounds 12, 13, 22 and 25 could not be obtained due to solubility issues.

b - DLS Size distribution in a solution of DMSO for compound 28 could not be gathered due to the inherent absorbance and fluorescent characteristics of this compound.
Zeta potential

Figure S229 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 1 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -75.8 mV.

Figure S230 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 2 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -77.6 mV.
Figure S231 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 3 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -93.7 mV.

Figure S232 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 4 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -92.3 mV.
Figure S233 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 5 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -33.5 mV.

Figure S234 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 6 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -38.2 mV.
Figure S235 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 7 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -55.4 mV.

Figure S236 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 8 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -27.7 mV.
Figure S237 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 9 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -24.4 mV.

Figure S238 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 10 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -25.7 mV.
Figure S239 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 11 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -48.3 mV.

Figure S240 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 14 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -30.2 mV.
Figure S241 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 15 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -97.9 mV.

Figure S242 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 17 (5.56 mM) in a solution EtOH:H₂O 1:19. The results from this study are ambiguous and could not be replicated.
Figure S243 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 19 (5.56 mM) in a solution EtOH:H$_2$O 1:19. Average measurement = -30.2 mV.

Figure S244 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 20 (5.56 mM) in a solution EtOH:H$_2$O 1:19. Average measurement = -66.2 mV.
Figure S245 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 21 (5.56 mM) in a solution EtOH:H₂O 1:19. The results from this study are ambiguous and could not be replicated.

Figure S246 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 23 (5.56 mM) in a solution EtOH:H₂O 1:19. The results from this study are ambiguous and could not be replicated.
Figure S247 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 24 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -37.3 mV.

Figure S248 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 26 (5.56 mM) in a solution EtOH:H₂O 1:19. Average measurement = -22.6 mV.
Figure S249 - Phase plot obtained during the measurement of 9 zeta potential transfer standard (PTS) runs of compound 27 (5.56 mM) in a solution EtOH:H_{2}O 1:19. Average measurement = -3.89 mV.
Single Crystal X-Ray structures

Figure S250 - Crystal data for compound 2: red = oxygen; yellow = sulfur; blue = nitrogen; white = hydrogen; grey = carbon; green = fluorine. CCDC 1589886, C_{26}H_{48}F_{3}N_{3}O_{5}S (M = 571.73): monoclinic, space group P 21/c, a = 9.5166(2) Å, b = 20.0606(3) Å, c = 16.0871(3) Å, α = 90°, β = 95.510(2)°, γ = 90°, V = 3056.98(10) Å³, Z = 4, T = 270(1) K, CuKα = 1.5418 Å, Dcalc = 1.242 g/cm³, 50907 reflections measured (7.064 ≤ 2θ ≤ 133.188), 5404 unique (R_int = 0.0585, R_sigma = 0.0259) which were used in all calculations. The final R₁ was 0.0375 (I > 2σ(I)) and wR₂ was 0.0958 (all data).
Figure S251 - Crystal data for compound 3: red = oxygen; yellow = sulfur; blue = nitrogen; white = hydrogen; grey = carbon; green = fluorine. CCDC 1589882, C_{27}H_{48}F_{3}N_{3}O_{4}S (M = 567.74): monoclinic, space group P 21, a = 9.6443(3) Å, b = 31.9367(9) Å, c = 19.9817(6) Å, α = 90°, β = 101.941(3)°, γ = 90°, V = 6021.4(3) Å³, Z = 8, T = 100(1) K, CuKα = 1.5418 Å, Dcalc = 1.253 g/cm³, 41806 reflections measured (5.300 ≤ 2θ ≤ 133.198), 21243 unique (R_{int} = 0.0968, R_{sigma} = 0.1258) which were used in all calculations. The final R_{1} was 0.1151 (I > 2σ(I)) and wR_{2} was 0.3301 (all data).
Crystal data for compound 5: red = oxygen; yellow = sulfur; blue = nitrogen; white = hydrogen; grey = carbon; green = fluorine. CCDC 1589887, C_{26}H_{46}F_{3}N_{3}O_{3}S_{2} (M = 569.78): monoclinic, space group P 21/n, \(a = 17.8100(12) \ \text{Å}, \ b = 9.7869(7) \ \text{Å}, \ c = 19.6552(13) \ \text{Å}, \ \alpha = 90^\circ, \ \beta = 116.887(8)^\circ, \ \gamma = 90^\circ, \ V = 3055.6(4) \ \text{Å}^3, \ Z = 4, \ T = 270(1) \ \text{K}, \ \text{CuK}\alpha = 1.5418 \ \text{Å}, \ D_{\text{calc}} = 1.239 \ \text{g/cm}^3, \ 47851 \ \text{reflections measured} (5.568 \leq 2\Theta \leq 133.200), 5394 \ \text{unique} (R_{\text{int}} = 0.1287, R_{\text{sigma}} = 0.0656) \ \text{which were used in all calculations}. \ \text{The final} R_1 = 0.0713 \ \text{(I > 2σ(I)) and wR}_2 = 0.1864 \ \text{(all data)}.\n
Crystal data for compound 6: red = oxygen; yellow = sulfur; blue = nitrogen; white = hydrogen; grey = carbon; green = fluorine. CCDC 1589888, C_{27}H_{48}F_{3}N_{3}O_{3}S_{2} (M = 583.80): monoclinic, space group P 21/n, \(a = 9.6068(5) \ \text{Å}, \ b = 21.7563(9) \ \text{Å}, \ c = 14.6928(6) \ \text{Å}, \ \alpha = 90^\circ, \ \beta = 91.199(4)^\circ, \ \gamma = 90^\circ, \ V = 3070.2(2) \ \text{Å}^3, \ Z = 4, \ T = 270(1) \ \text{K}, \ \text{CuK}\alpha = 1.5418 \ \text{Å}, \ D_{\text{calc}} = 1.263 \ \text{g/cm}^3, \ 47573 \ \text{reflections measured} (7.262 \leq 2\Theta \leq 133.170), 5436 \ \text{unique} (R_{\text{int}} = 0.1816, R_{\text{sigma}} = 0.0773) \ \text{which were used in all calculations}. \ \text{The final} R_1 = 0.0946 \ \text{(I > 2σ(I)) and wR}_2 = 0.3041 \ \text{(all data)}.\n
Figure S254 - Crystal data for compound 9: red = oxygen; yellow = sulfur; blue = nitrogen; white = hydrogen; grey = carbon; green = fluorine. CCDC 1589880, C_{33}H_{30}F_{3}N_{3}O_{4}S (M = 371.38): monoclinic, space group C 2/c, a = 32.609(1) Å, b = 5.6739(2) Å, c = 19.0078(7) Å, α = 90°, β = 102.953(3)°, γ = 90°, V = 3427.3(2) Å³, Z = 8, T = 100(1) K, CuKα = 1.5418 Å, Dcalc = 1.439 g/cm³, 13318 reflections measured (5.562 ≤ 2θ ≤ 133.186), 3036 unique (Rint = 0.0627, Rsigma = 0.0523) which were used in all calculations. The final R₁ was 0.0604 (I > 2σ(I)) and wR₂ was 0.1718 (all data).

Figure S255 - Crystal data for compound 14: red = oxygen; yellow = sulfur; blue = nitrogen; white = hydrogen; grey = carbon. CCDC 1589879, C_{24}H_{46}N_{4}O_{4}S (M = 486.71): monoclinic, space group P 21/n, a = 13.4243(13) Å, b = 14.8120(13) Å, c = 14.2467(16) Å, α = 90°, β = 106.523(11)°, γ = 90°, V = 2715.8(5) Å³, Z = 4, T = 100(1) K, CuKα = 1.5418 Å, Dcalc = 1.190 g/cm³, 13318 reflections measured (5.562 ≤ 2θ ≤ 133.186), 3036 unique (Rint = 0.0627, Rsigma = 0.0523) which were used in all calculations. The final R₁ was 0.0604 (I > 2σ(I)) and wR₂ was 0.1718 (all data).
Figure S256 - Crystal data for compound 21: red = oxygen; yellow = sulfur; blue = nitrogen; white = hydrogen; grey = carbon. CCDC 1589884, C34H44N4O5S2 (M =532.75): monoclinic, space group C 2/c, a = 18.7541(18) Å, b = 16.1936(18) Å, c = 20.683(2) Å, α = 90°, β = 105.841(11)°, γ = 90°, V = 6042.7(11) Å³, Z = 8, T = 290(1) K, CuKα = 1.5418 Å, Dcalc = 1.171 g/cm³, 26997 reflections measured (7.336 ≤ 2Θ ≤ 133.198), 5339 unique (Rint = 0.0422, Rsigma = 0.0246) which were used in all calculations. The final R1 was 0.0706 (I > 2σ(I)) and wR2 was 0.2426 (all data).

Figure S257 - Crystal data for compound 22: red = oxygen; blue = nitrogen; white = hydrogen; grey = carbon; green = fluorine. CCDC 1589885, C14H19F3N2O4 (M =336.31): triclinic, space group P -1, a = 6.4011(16) Å, b = 10.811(3) Å, c = 11.967(3) Å, α = 84.334(18)°, β = 88.945(19)°, γ = 81.70(2)°, V = 815(5) Å³, Z = 2, T = 343(1) K, CuKα = 1.5418 Å, Dcalc = 1.370 g/cm³, 9213 reflections measured (7.422 ≤ 2Θ ≤ 108.462), 1970 unique (Rint = 0.1551, Rsigma = 0.1299) which were used in all calculations. The final R1 was 0.1167 (I > 2σ(I)) and wR2 was 0.2891 (all data).
Figure S258 - Crystal data for a single crystal obtained from a solution of compound 24: red = oxygen; blue = nitrogen; white = hydrogen; grey = carbon. CCDC 1589881, C_{26}H_{45}N_{3}O_{5} (M = 476.65): monoclinic, space group P 2₁/n, a = 14.226(4) Å, b = 14.602(3) Å, c = 14.483(4) Å, α = 90°, β = 112.91(3)°, γ = 90°, V = 2771.0(13) Å³, Z = 4, T = 100(1) K, CuKα = 1.5418 Å, Dcalc = 1.150 g/cm³, 15432 reflections measured (7.390 ≤ 2Θ ≤ 117.842), 6338 unique (R_int = 0.1754, R_sigma = 0.1246) which were used in all calculations. The final R₁ was 0.0865 (I > 2σ(I)) and wR₂ was 0.2092 (all data).

Figure S259 - Crystal data for compound 26: red = oxygen; yellow = sulfur; blue = nitrogen; white = hydrogen; grey = carbon; green = fluorine. CCDC 1589883, C_{10}H_{11}F_{3}N_{2}O_{3}S (M = 296.27): monoclinic, space group P 2₁/c, a = 20.786(10) Å, b = 6.941(2) Å, c = 8.610(2) Å, α = 90°, β = 100.49(4)°, γ = 90°, V = 1221.5(8) Å³, Z = 4, T = 100(1) K, CuKα = 1.5418 Å, Dcalc = 1.611 g/cm³, 2649 reflections measured (8.625 ≤ 2Θ ≤ 133.198), 1825 unique (R_int = 0.0845, R_sigma = 0.1183) which were used in all calculations. The final R₁ was 0.1124 (I > 2σ(I)) and wR₂ was 0.3217 (all data).
### Hydrogen bonding tables from single crystal X-ray structures

Table S7 - Hydrogen bond distances and angles observed for hydrogen self-association, calculated from single crystal X-ray structures.

| Compound | Hydrogen bond donor | Hydrogen atom | Hydrogen bond acceptor | Hydrogen bond length (D•••A) (Å) | Hydrogen bond angle (D-H•••A) (°) |
|----------|---------------------|---------------|------------------------|--------------------------------|---------------------------------|
| 2        | N1                  | H1            | O2                     | 2.8954 (18)                    | 163.42 (10)                     |
| 2        | N2                  | H2            | O2                     | 3.0960 (17)                    | 149.23 (10)                     |
| 2        | N2                  | H2            | O2                     | 2.9813 (18)                    | 122.31 (16)                     |
| 3        | N1                  | H1            | O7                     | 2.889 (13)                     | 156.9 (7)                       |
| 3        | N2                  | H2            | O7                     | 2.917 (16)                     | 154.0 (7)                       |
| 3        | N3                  | H3            | O1                     | 3.105 (15)                     | 150.4 (7)                       |
| 3        | N4                  | H4            | O1                     | 2.967 (16)                     | 151.7 (7)                       |
| 3        | N5                  | H5            | O15                    | 3.096 (15)                     | 158.1 (7)                       |
| 3        | N6                  | H6            | O14                    | 2.980 (16)                     | 148.1 (7)                       |
| 3        | N7                  | H7A           | O9                     | 2.909 (13)                     | 157.5 (7)                       |
| 3        | N8                  | H8A           | O9                     | 2.916 (15)                     | 152.4 (7)                       |
| 5        | N1                  | H1            | O2                     | 2.829 (4)                      | 159.1 (2)                       |
| 5        | N2                  | H2            | O1                     | 2.918 (4)                      | 159.9 (3)                       |
| 6        | N1                  | H1            | O1                     | 3.149 (5)                      | 169.4 (3)                       |
| 6        | N2                  | H2            | O3                     | 3.013 (4)                      | 141.7 (3)                       |
| 9        | N1                  | H1            | O2                     | 2.987 (3)                      | 169.32 (18)                     |
| 9        | N2                  | H2            | O3                     | 2.862 (3)                      | 172.3 (2)                       |
| 14       | N1                  | H1A           | O3                     | 3.094 (3)                      | 154.41 (16)                     |
| 14       | N1                  | H1B           | O3                     | 3.423 (3)                      | 153.24 (17)                     |
| 14       | N2                  | H2            | O4                     | 2.927 (2)                      | 155.24 (15)                     |
| 14       | N3                  | H3            | O4                     | 2.903 (3)                      | 152.77 (15)                     |
| 21       | N1                  | H1            | O3                     | 2.860 (3)                      | 161.71 (16)                     |
| 21       | N2                  | H2            | O1                     | 2.897 (3)                      | 154.17 (16)                     |
| 23       | N1                  | H1            | O10                    | 2.831 (13)                     | 174.1 (10)                      |
| 23       | N2                  | H2            | O9                     | 2.828 (12)                     | 159.9 (9)                       |
| 23       | N3                  | H3A           | O1                     | 2.884 (15)                     | 155.2 (9)                       |
| 23       | N4                  | H4B           | O1                     | 2.812 (16)                     | 152.2 (9)                       |
Surface tension measurements and CMC calculation

Figure S260 - Calculation of CMC (10.39 mM) for compound 1 in an EtOH:H₂O 1:19 mixture using surface tension measurements.

Figure S261 - Calculation of CMC (10.70 mM) for compound 2 in an EtOH:H₂O 1:19 mixture using surface tension measurements.
Figure S262 - Calculation of CMC (8.85 mM) for compound 3 in an EtOH:H₂O 1:19 mixture using surface tension measurements.

Figure 263 - Calculation of CMC (24.14 mM) for compound 4 in an EtOH:H₂O 1:19 mixture using surface tension measurements.
Figure S264 - Calculation of CMC (6.12 mM) for compound 5 in an EtOH:H₂O 1:19 mixture using surface tension measurements.

Figure S265 - Calculation of CMC (5.61 mM) for compound 6 in an EtOH:H₂O 1:19 mixture using surface tension measurements.
Figure S266 - Calculation of CMC (96.35 mM) for compound 7 in an EtOH:H₂O 1:19 mixture using surface tension measurements.

Figure S267 - Calculation of CMC (198.42 mM) for compound 8 in an EtOH:H₂O 1:19 mixture using surface tension measurements.
Figure S268 - Calculation of CMC (209.98 mM) for compound 9 in an EtOH:H₂O 1:19 mixture using surface tension measurements.

Figure S269 - Calculation of CMC (103.13 mM) for compound 10 in an EtOH:H₂O 1:19 mixture using surface tension measurements.
Figure S270 - Calculation of CMC (34.57 mM) for compound 11 in an EtOH:H₂O 1:19 mixture using surface tension measurements.

Figure S271 - Calculation of CMC (92.67 mM) for compound 15 in an EtOH:H₂O 1:19 mixture using surface tension measurements.
Figure S272 - Calculation of CMC (30.29 mM) for compound 17 in an EtOH:H₂O 1:19 mixture using surface tension measurements.

Figure S273 - Calculation of CMC (65.83 mM) for compound 19 in an EtOH:H₂O 1:19 mixture using surface tension measurements.
Figure S274 - Calculation of CMC (74.59 mM) for compound 20 in an EtOH:H₂O 1:19 mixture using surface tension measurements.

Figure S275 - Calculation of CMC (11.21 mM) for compound 24 in an EtOH:H₂O 1:19 mixture using surface tension measurements.
Low level in-silico modelling

Computational calculations to identify primary hydrogen bond donating and accepting sites were conducted in line with studies reported by Hunter using Spartan 16.\textsuperscript{1} Calculations were performed using semi-empirical PM6 methods, after energy minimisation calculations, to identify $E_{\text{max}}$, $E_{\text{min}}$ and polarizability values. PM6 was used over AM1 in line with research conducted by Stewart.\textsuperscript{2}

Figure S276 - Electrostatic potential map calculated for the anionic component of 1. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S277 - Electrostatic potential map calculated for the anionic component of 2. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S278 - Electrostatic potential map calculated for the anionic component of 3. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.
Figure S279 - Electrostatic potential map calculated for the anionic component of 4. \( E_{\text{max}} \) and \( E_{\text{min}} \) values depicted in the Figure legends are given in KJ/mol.

Figure S280 - Electrostatic potential map calculated for the anionic component of 5. \( E_{\text{max}} \) and \( E_{\text{min}} \) values depicted in the Figure legends are given in KJ/mol.

Figure S281 - Electrostatic potential map calculated for the anionic component of 6. \( E_{\text{max}} \) and \( E_{\text{min}} \) values depicted in the Figure legends are given in KJ/mol.
Figure S282 - Electrostatic potential map calculated for the cationic component of 8. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S283 - Electrostatic potential map calculated for the cationic component of 9. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S284 - Electrostatic potential map calculated for the cationic component of 10. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.
Figure S285 - Electrostatic potential map calculated for TBA. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S286 - Electrostatic potential map calculated for the cationic component of 1. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S287 - Electrostatic potential map calculated for the cationic component of 12. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.
Figure S288 - Electrostatic potential map calculated for the cationic component of 13. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S289 - Electrostatic potential map calculated for the anionic component of 14. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S290 - Electrostatic potential map calculated for the anionic component of 15. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.
Figure S291 - Electrostatic potential map calculated for the anionic component of 17. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S292 - Electrostatic potential map calculated for the anionic component of 18. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S293 - Electrostatic potential map calculated for the anionic component of 19. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.
Figure S294 - Electrostatic potential map calculated for the anionic component of 20. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S295 - Electrostatic potential map calculated for the anionic component of 21. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S296 - Electrostatic potential map calculated for 22. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.
Figure S297 - Electrostatic potential map calculated for 23. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S298 - Electrostatic potential map calculated for the anionic component of 24. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S299 - Electrostatic potential map calculated for 25. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.
Figure S300 - Electrostatic potential map calculated for 26. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.

Figure S301 - Electrostatic potential map calculated for the anionic component of 27. $E_{\text{max}}$ and $E_{\text{min}}$ values depicted in the Figure legends are given in KJ/mol.
Mass spectrum data

Figure S302 - ESI\ mass spectrum collected for compound 1.

Figure S303 - ESI\ mass spectrum collected for compound 2.

Figure S304 - ESI\ mass spectrum collected for compound 3.
Figure S305 - ESI mass spectrum collected for compound 4.

Figure S306 - ESI mass spectrum collected for compound 5.

Figure S307 - ESI mass spectrum collected for compound 7.
Figure S308 - ESI mass spectrum collected for compound 8.

Figure S309 - ESI mass spectrum collected for compound 9.

Figure S310 - ESI mass spectrum collected for compound 10.
Figure S311 - ESI mass spectrum collected for compound 12.

Figure S312 - ESI mass spectrum collected for compound 13.

Figure S313 - ESI mass spectrum collected for compound 14.
Figure S314 - ESI mass spectrum collected for compound 17.

Figure S315 - ESI mass spectrum collected for compound 19.

Figure S316 - ESI mass spectrum collected for compound 20.
Figure S317 - ESI mass spectrum collected for compound 21.

Figure S318 - ESI mass spectrum collected for compound 22.

Figure S319 - ESI mass spectrum collected for compound 23.
Figure S320 - ESI' mass spectrum collected for compound 24.

Figure S321 - ESI' mass spectrum collected for compound 25.

Figure S322 - ESI' mass spectrum collected for compound 26.
Figure S323 - ESI mass spectrum collected for compound 27.

References

1. C. A. Hunter, Angew. Chem. Int. Ed., 2004, 43, 5310-5324.
2. J. J. P. Stewart, J. Mol. Model, 2007, 13, 1173-1213.
3. J. Řezáč, P. Hobza, J. Chem. Theory Comput., 2012, 8, 141-151.
4. J. Řezáč, P. Hobza, Chem. Phys. Lett., 2011, 506, 286-289.
5. J. J. P. Stewart, MOPAC2016. Stewart Computational Chemistry, Colorado Springs, CO, USA, http://openmopac.net/.
6. P. Winget, D. Dolney, M. Giesen, J. Cramer, D. G. Truhlar, Minnesota Solvent Descriptor Database version 1999.
7. J. R. Hiscock, G. P. Bustone, B. Wilson, K. E. Belsey and L. R. Blackholly, Soft Matter, 2016, 12, 4221-4228.
8. L. R. Blackholly, H. J. Shepherd and J. R. Hiscock, CrystEngComm, 2016, 18, 7021-7028.
9. L. J. White, N. J. Wells, L. R. Blackholly, H. J. Shepherd, B. Wilson, G. P. Bustone, T. J. Runacres, J. R. Hiscock, Chem. Sci., 2017, 8, 7620-7630.