Supporting Information for:

Design, Synthesis, and Solution Behaviour of Small Polyamines as Switchable Water Additives

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Contents:

1. Experimental Procedures:

All chemicals were obtained from either Sigma Aldrich or TCI and were used as received without further purification. Solvents were obtained from Fisher Scientific and Commercial Alcohols and were used as received without purification. NMR spectroscopy was performed using Bruker 300 and 400 MHz spectrometers. IR spectra were acquired using a Nicolet 360 FT-IR.

1.1 Salting Out of THF by Switchable Water Additives

This procedure was adapted from the method described in our earlier paper.[1] THF (1.5 g) and deionized water (1.5 g) were mixed together in a graduated cylinder. An appropriate amount of the amine additive (or inorganic salt) was dissolved in the mixture to give a 0.80 molal loading relative to water. A stir bar was added to the cylinder and the cylinder is capped with a rubber septum.

A single narrow gauge needle was inserted through the septum and into the solution. A second needle was inserted into the septum but not into the solution so that it acted as a gas outlet. CO_2 was bubbled through the solution via the first needle at a flow rate of 3 – 5 mL min^{-1} while being stirred on a magnetic plate. Flow rates were measured using a J&W Scientific ADM 2000 Intelligent Flowmeter. CO_2 was bubbled through the solution for 30 min. After CO_2 treatment, the solution had undergone a phase separation. The volumes of both phases were recorded. Bubbling CO_2 vigorously through the solution provides the potential for loss of THF from the system. The volumes of the system were monitored and any loss to blow off, if it occurred, was never more than 5% of the total THF volume.

A known mass of each layer was extracted and placed in separate NMR tubes. The samples were dissolved in d_3-acetonitrile and a known mass of ethyl acetate was added to each tube to act as an internal reference. The ^1H NMR spectra were collected using a 400 MHz Bruker NMR spectrometer. From the known mass of the standard and the integration of the THF or additive peaks, the amount of each in the NMR tubes was calculated. Using the assumptions that density of the organic layer is equal to the density of THF and that the aqueous layer contains essentially all of the amine additive, the concentrations in the NMR tubes were scaled up to that of the actual volumes to give the total amount of THF salted out from the aqueous phase and the amount of amine additive that was retained in the aqueous phase.

If desired, the phases were recombined by bubbling an inert gas, such as N_2, through the solution at the same flow rate and procedure as above while heating the mixture at 50 °C. Roughly 30 – 60 min of this treatment caused the biphasic mixture to recombine into a single phase solution.

After the salting out of THF by primary amine additives (which could not be reversed at the standard conditions used above), known volumes of each layer after separation were placed in separate NMR tubes and analyzed by ^1H NMR spectroscopy using an ethyl acetate internal standard. The THF removal or additive retention was calculated and scaled up to the total separated volume of either the organic or aqueous layer. The method was performed as opposed to the method from above as some of the amine additive would precipitate from solution after CO_2 treatment in this study, but this did not occur in all of the other salting out studies.

To establish a ceiling amount of THF that could be salted out from water by an inorganic salt, the additive salt was added to a 4 g solution of 1:1 (w/w) THF/H_2O and additional salt was continually added until a consistent volume of salted out organic was observed. In some cases additional salt was added past when the consistent volume was observed. The aqueous layer was then extracted and analyzed using ^1H NMR spectroscopy as described above. Loadings of NaCl ranged from 0.7 – 1.3 g and $(NH_4)_2SO_4$ loadings ranged from 1.4 – 1.5 g.

1.2 Salting Out of Water-Miscible Organics by α,ω-Diaminoalkane Dihydrochloride Salts

THF or acetonitrile (2.0 g) and deionized water (2.0 g) were mixed together in a graduated cylinder. An appropriate amount of α,ω-diaminoalkane dihydrochloride salt was added to the solution to give a 0.50 molal loading relative to water (1.00 molal for alkylamine hydrochloride salts). The cylinder was capped and inverted 30 – 50 times to allow for complete dissolution of the salts. Some mixtures required heating to 50 °C to speed up dissolution of the salts, but were cooled to room temperature after dissolution. If a phase separation occurred, then the volumes of the two layers were recorded.

Using the assumption that the top organic layer is comprised primarily of the organic that was salted out and the bottom aqueous contains all other components, the volume of the organic layer was multiplied by the density of the pure organic compound studied to give the mass of organic compound salted out. Comparing this amount to the original mass put into the mixture gave the percentage of organic compound salted out.

1.3 Determination of the Extent of Amine Protonation by Carbonic Acid

NMR spectroscopy was carried out using a 400 MHz Bruker NMR spectrometer. Amine additives were dissolved in D_2O and the NMR tubes were sealed with rubber septa. To introduce CO_2, two narrow gauge steel needles were inserted and gas was gently bubbled through one of them and into the solution at approximately 4-5 bubbles per second. The second needle served as a vent for the gas phase.

To establish the chemical shifts of the protonated bases, slightly more than two molar equivalents of a strong acid (HCl or HNO_3) was added to solutions of the amines in D_2O. Spectra were acquired for several replicate solutions for each amine/acid combination. An average value of each chemical shift of each protonated base was calculated along with standard deviations. If the bases, when reacted with CO_2, showed chemical shifts within this error range, they were considered to be 100 % protonated.

1.4 Synthesis of Diamine Dihydrochloride Salts

α,ω-Diaminoalkane dihydrochloride salts were synthesized from the reaction of HCl and an appropriate diamine. Diamine (5 mmol) was dissolved in 30 – 50 mL diethyl ether and, if necessary, 5 mL methanol to speed up dissolution. A slightly greater than two molar equivalent excess of 1.0 M HCl in diethyl ether was added to the solution dropwise with constant and vigorous stirring. A white precipitate immediately formed. The precipitate was collected by filtration, washed with diethyl ether and dried under vacuum. Salts without literature precedents were characterized by ^1H NMR spectroscopy in DMSO-d_6 with reference to TMS at 0 ppm. All

^{1}H NMR spectra were found to represent symmetrical molecules, indicating the presence of a dication. All other salts used were commercially available and used as received.

1,7-diaminoheptane dihydrochloride: ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ [ppm] = 8.10 (NH_3), 2.73 (4H), 1.56 (4H), 1.32 – 1.28 (6H).

1,8-diaminooctane dihydrochloride: ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ [ppm] = 7.30 (NH_3), 2.70 (4H), 1.52 (4H), 1.27 (8H). The ^{1}H NMR shifts matched those reported in the literature.[2]

1,9-diaminononane dihydrochloride: ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ [ppm] = 8.04 (NH_3), 2.73 (4H), 1.55 (4H), 1.27 (10H).

1,10-diaminodecane dihydrochloride: ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ [ppm] = 8.08 (NH_3), 2.71 (4H), 1.55 (4H), 1.26 (12H). The ^{1}H NMR shifts matched those reported in the literature.[2]

1,8-diamino-3,6-dioxaoctane dihydrochloride: ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ [ppm] = 7.55 (NH_3), 3.62-3.59 (8H), 2.92 (4H). The 1H NMR shifts matched those reported in the literature.[2]

N,N'-dimethylethylenediamine dihydrochloride: ^{1}H NMR (DMSO-d$_6$, 300 MHz): δ [ppm] = 9.51 (NH_3), 3.25 (4H), 2.57 (6H).

N,N'-dimethyl-1,6-hexanediamine dihydrochloride: ^{1}H NMR (D_2O, 400 MHz): δ [ppm] = 3.01 (4H), 2.69 (6H), 1.69 (4H), 1.42 (4H). The ^{1}H NMR shifts matched those reported in the literature.[3]

1.5 Synthesis of (1E,1'E)-N',N''-(Butane-1,4-diyl)bis(N,N-dimethylethanimidamide)

This procedure was adapted from two previously published synthetic procedures.[4,5] A 100 mL flask was equipped with a condenser and a 1 cm stirring bar and was then placed over a stirplate. 1,4-Diaminobutane (1.14 mL, 11.3 mmol, 1 eq.) and dimethylacetamide dimethylacetal (3.64 mL, 24.9 mmol, 2.2 eq.) were placed into the flask. The reaction mixture was then stirred at 600 rpm and heated to 60 °C. After 2 h the reaction mixture was allowed to cool to room temperature and the resulting methanol was removed under reduced pressure to yield a yellow oil. This crude product was then purified by high vacuum distillation. The pure product was obtained as a light yellow oil (2.32 g, 10.2 mmol, 91%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 3.09-3.19 (m, 4H), 2.79 (s, 6H), 1.80 (s, 3H), 1.45-1.53 (m, 4H). ^{13}C NMR ($CDCl_3$, 100.7 MHz): δ [ppm] = 158.7 (s), 50.0 (t), 37.9 (q), 30.2 (t), 12.3 (q). MS (EI): m/z (%) = 227.22 (3), 226.21 (21), 198.16 (7), 182.17 (7), 141.14 (14), 140.13 (21), 128.11 (10), 127.10 (30), 114.11 (23), 113.11 (28), 112.09 (52), 99.09 (27), 70.07 (45), 56.05 (100). HRMS (EI): calc. for [M]+: 226.2157, found: 226.2161.

1.6 Synthesis of 1,4-benzendiethanamine dihydrochloride

Procedure was adapted from previous literature.[6] 1,4-phenylene diacetonitrile (0.878 g, 5.62 mmol) was dissolved in 60 mL THF under nitrogen atmosphere. 1.0 M $BH_3\cdot THF$ solution

(40 mL) was added dropwise under nitrogen. The solution was refluxed for 24 h; some white precipitate formed during the reaction.

The solution was cooled to 0 °C and 40 mL of a 1:1 mixture of H_2O:THF was added very slowly dropwise. More white precipitate formed in the mixture. The mixture was warmed to room temperature and the solvents were removed *in vacuo*. The solids were then suspended in 90 mL absolute ethanol and 0.6 mL concentrated H_2SO_4. The mixture was refluxed for 30 min. The ethanol was removed *in vacuo* leaving a concentrated acidic solution. 15 mL of 1 M NaOH solution was added until the solution became basic to litmus paper. Some solid did not completely dissolve. The organic compounds were extracted from the aqueous solution by 3 x 150 mL chloroform extractions. The solution was dried over $MgSO_4$ and the solvents were removed *in vacuo* to yield a yellow liquid.

The yellow liquid was mixed with 100 mL chloroform and 12.0 mL of 2.0 M HCl in diethyl ether, forming a white precipitate. The solvent was removed *in vacuo* to yield 0.662 g of a white powder (49.7 % yield).

^{1}H NMR (D_2O, 400 MHz): δ [ppm] = 7.32 (s, 4H), 3.23 (t, J = 7.3 Hz, 4H), 2.98 (t, J = 7.3 Hz, 4H). The ^{1}H NMR shifts matched those reported in the literature.[7] ^{13}C NMR (D_2O, 100.7 MHz): δ [ppm] = 135.6 (q), 129.4 (d), 40.5 (t), 32.3 (t).

1.7 Synthesis of N1,N1'-(Butane-1,4-diyl)bis(N1,N3,N3-trimethylpropane-1,3-diamine) (hexa-methylated spermine)

The procedure was adapted from previous literature method.[8] Spermine (2.02 g, 10 mmol, 1.0 eq.) was placed in a 250 mL round-bottom flask and dissolved in 40 mL water. Afterwards, 9.72 mL (120 mmol, 12.0 eq.) formaldehyde solution (37% in H_2O) and 13.7 mL (240 mmol, 24.0 eq.) acetic acid were added and the solution was allowed to stir at room temperature for 15 min. Zn powder (7.84 g, 120 mmol, 12 eq.) was then added in small portions, which resulted in gas formation. A cold water bath was used to keep the temperature in the flask under 40 °C. After complete addition, the reaction mixture was vigorously stirred for 16 h at room temperature. Thereafter, 20 mL of aqueous NH_4OH was added and the product was extracted from the aqueous phase with ethyl acetate in a separatory funnel (3 x 25 mL).

The combined organic layers were dried over $MgSO_4$, the solution was filtered through filter paper and the solvents were then removed under reduced pressure. The crude product was purified by high vacuum distillation to yield 1.3 g (4.5 mmol, 42%) of a yellow oil.

^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 2.28-2.35 (m, 8H), 2.21-2.27 (m, 4H), 2.19 (s, 12H), 2.18 (s, 6H), 1.55-1.66 (m, 4H), 1.36-1.44 (m, 4H). ^{13}C NMR ($CDCl_3$, 100.7 MHz): δ [ppm] = 58.0 (t), 57.8 (t), 55.8 (t), 45.6 (q), 42.3 (q), 25.7 (t), 25.3 (t). IR (film, NaCl): [cm^{-1}] = 2943 (s), 2812 (s), 2762 (s), 1459 (m), 1375 (w), 1303 (w), 1256 (w), 1212 (w), 1154 (w), 1122 (w), 1097 12 (w), 1042 (m), 967 (w), 834(w). MS (EI): m/z (%) = 287.32 (7), 286.31 (41) [M]+, 98.08 (28), 86.08 (44), 85.07 (100), 84.07 (41). HRMS (EI): calc. for [M]+: 286.3097, found: 286.3091.

1.8 Synthesis of 1,1',1''-(Benzene-1,3,5-triyl)tris(N,N-dimethylmethanamine)

The procedure was adapted from a previous literature method.[9] Dimethylamine in THF (30 mL of 2.0 M solution) was mixed with 75 mL dichloromethane cooled to 0 °C. 1,3,5-

Benzenetricarbonyl trichloride (2.334 g, 8.79 mmol) was added dropwise to the stirring solution. The solution evolved a small amount of gas and turned yellow in colour. The solution was slowly warmed to 25 °C and stirred for 18 h.

The solvent was then removed *in vacuo* to leave a green-yellow solid, which was then dissolved in 10 mL of a 1.5 M $KOH_{(aq)}$ solution. Organics were extracted from the alkaline solution by 4 x 30 mL chloroform extractions. The aqueous layer was discarded and the solvents from the combined organic layers were removed under reduced pressure to yield ~2 g of an off-white solid.

The intermediate solid (2.074 g) was dissolved in 200 mL of THF. The solution was cooled to 0 °C and 47 mL of 2.0 M $LiAlH_4$ in THF was added via dropping funnel. After the initial evolution of some gas, the solution was heated to reflux with stirring for 7 h.

After the reaction was complete, the contents were cooled to 0 °C. Excess $LiAlH_4$ was neutralized by slowly adding 3.6 mL H_2O dropwise, followed by 3.6 mL 15% $NaOH_{(aq)}$ dropwise, and finally 10.8 mL H_2O dropwise with vigorous stirring. The solution was then slowly warmed to 25 °C and stirred for 18 h. Precipitated solids were then washed with THF and removed from the solution via vacuum filtration. The organic liquid was dried with $MgSO_4$ and the solvents removed *in vacuo* to yield 1.845 g of a clear brown liquid (84.2 % yield).

^1H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 7.13 (s, 3H), 3.40 (s, 6H), 2.23 (s, 18H). The ^1H NMR shifts matched those reported in the literature.[10] ^{13}C NMR ($CDCl_3$, 100.7 MHz): δ [ppm] = 138.9, 128.8, 64.6, 45.5. (EI): calc. for [M]+: 249.2206, Expected = 249.2205.

1.9 Synthesis of 1,1',1''-(Cyclohexane-1,3,5-triyl)tris(N,N,-dimethylmethanamine)

Parts of this procedure were adapted from previous literature methods.[11,12] 1,3,5-Cyclohexanetricarboxylic acid (mixture of cis/trans) (1.997 g, 9.2 mmol) was taken up in 40 mL dichloromethane to create a suspension. 3.84 g (29.8 mmol) oxalyl chloride and one drop of anhydrous DMF were added to the solution. The solution was refluxed for 3 h, giving a yellow solution with white precipitate. The mixture was cooled to room temperature and the solvent was removed *in vacuo* resulting in 2.509 g of a solid which contained both the desired 1,3,5-cyclohexane tricarbonyl trichloride and unwanted salts. ^1H NMR (400 MHz, $CDCl_3$): δ [ppm] = 2.88 (t, J = 9 Hz, 3H), 2.69 (d, J = 13 Hz, 3H), 1.43 (q, J = 13 Hz, 3H).

The solid mixture (2.509 g) was taken up in 50 mL THF and cooled to 0 °C. A 2.0 M dimethylamine solution in THF (34.5 mL, 69 mmol) was added. The solution was warmed to room temperature and stirred for 18 h. The solvent was then removed *in vacuo* leaving a yellow solid. The solid was taken up in a solution of 2.081 g (37.1 mmol) KOH in 20 mL H_2O. Organic contents were then extracted with 3 x 40 mL chloroform washings. The organic washings were collected and the solvent removed *in vacuo* to yield 1.930 g of a yellow liquid, N,N,N',N',N'',N''-hexamethylcyclohexane-1,3,5-tricarboxamide in 70.2 % yield. ^1H NMR (400 MHz $CDCl_3$): δ [ppm] = 3.06 (s, 9H), 2.92 (s, 9H), 2.65 (q, J = 8 Hz, 3H), 1.86 (t, J = 8 Hz, 6H).

N,N,N',N',N'',N''-hexamethylcyclohexane-1,3,5-tricarboxamide (1.930 g, 6.5 mmol) was dissolved in 80 mL THF and cooled to 0°C. An amount of 2.0 M $LiAlH_4$ in THF solution (42 mL, 84 mmol) was added dropwise to the solution. The solution was refluxed for 6 h and then cooled to 0 °C. The excess $LiAlH_4$ was quenched by addition of 3.2 mL H_2O, 3.2 mL 15% NaOH, and 9.6 mL H_2O. The solution was warmed to room temperature and stirred for 12 h. The precipitate was filtered off and washed with THF. The washings were combined with the original solution and dried with $MgSO_4$. The solvent was removed *in vacuo* to yield 1.285 g of a yellow mixture of liquid and crystalline solids (m.p. 43 °C, uncorrected) resulting in a 54.4 % yield of 1,1',1''- (cyclohexane-1,3,5-triyl)tris(N,N,-dimethylmethanamine).

^{1}H NMR ($CDCl_3$, 400 MHz): δ [ppm] = 2.18 (s, 18H), 2.07 (d, J = 7.0 Hz, 6H), 1.89 (d, J = 12.3 Hz, 3H), 1.52, (m, J= 7.1 Hz, 3H), 0.48 (q, J = 12.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100.7 MHz): δ[ppm] = 67.1 (t), 46.1 (s), 37.1 (m), 35.4 (m). HRMS (EI): calc. for [M]+: 255.2678, Expected = 255.2674.
Elemental Analysis: C = 71.10 %, H = 12.66 %, N = 15.17 % Expected: C = 70.53 %, H = 13.02 %, N = 16.45 %. The structure was confirmed by x-ray crystallography (see Section 2 below)

1.10 Monitoring the Removal of CO_2 from Compounds 13 and 14

This procedure was adapted from our previous publication.[1] The deprotonation of the amine additives (removal of CO_2 from the additive) was monitored using ^{1}H NMR spectroscopy. To establish the chemical shifts of the fully protonated bases, molar equivalents of several strong acids (HCl and HNO_3) were added to solutions of the amines in D_2O. Spectra were acquired for several replicate solutions for each amine. An average value of each chemical shift or each protonated base was calculated along with standard deviations. If the bases when reacted with CO_2 showed chemical shifts within this error range, they were considered to be 100 % protonated within experimental error.

Samples of **13** and **14** at 0.1 molal concentration in fully carbonated D_2O were found to be protonated to their maximum amounts by carbonic acid, as noted in Table 4, with 30 min of CO2 bubbling at 25 °C. They were then deprotonated by sparging the solution with N_2 at a flow rate of 3-5 mL min^{-1} while heating to 75 °C. The percent removal of CO_2 was then calculated via comparison to ^{1}H NMR chemical shifts of fully protonated or completely deprotonated additives.

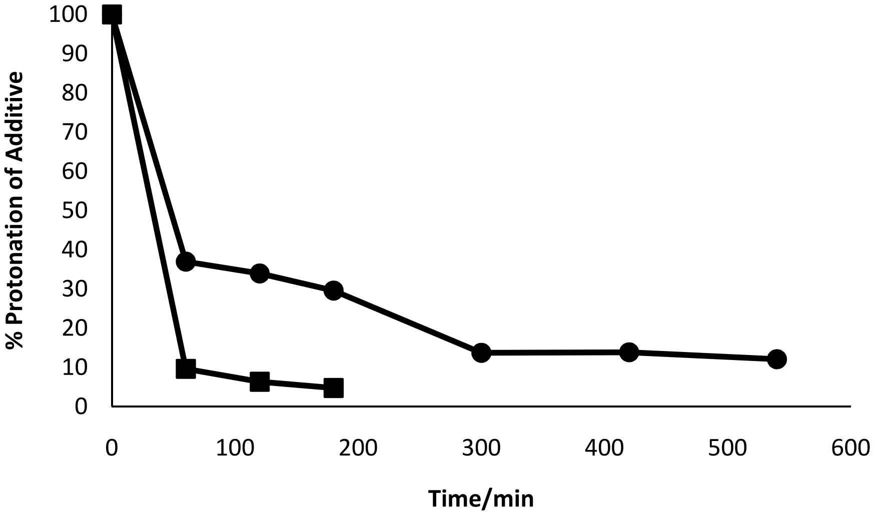
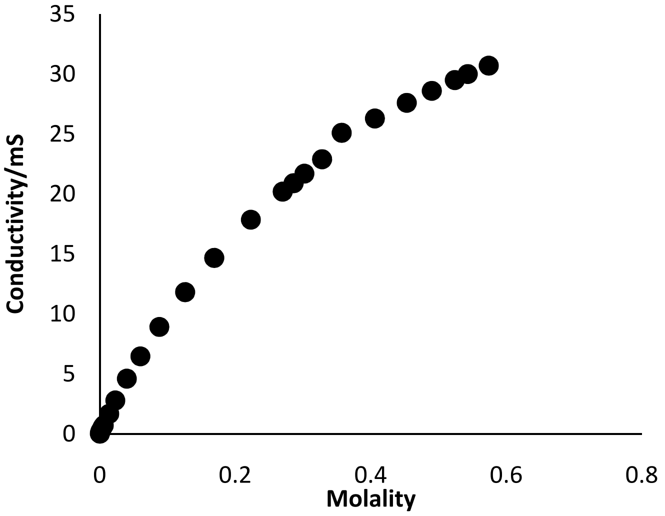


Fig. S1 Removal of CO_2 from or deprotonation of (■) Compound **13** and (●) Compound **14** as monitored by ^{1}H NMR spectroscopy. CO_2 was removed by sparging the D_2O solution with an inert gas at 75 °C.

1.11 Determination of Aggregate Effects on Salting Out Ability of Diamine Dihydrochloride Salts.

To determine if aggregate (micelle) formation assisted in minimizing salting out by higher carbon-spaced additives (Figure 3), attempts to determine the critical micelle concentrations of the 1,6-diaminohexane and 1,8-diaminooctane dihydrochloride salts were performed using conductivity studies. Conductivity was measured using a Jenway 470 conductivity meter (cell constant 1.02 cm^{-1}) at various concentrations of each salt in aqueous solution.

A notable break in the plot or intersection of two separate linear lines suggests a CMC. The plots of both the 1,6-diaminohexane dihydrochloride (Figure S2a) and the 1,8-diaminooctane dihydrochloride (Figure S2b) had no observable breaks in their conductivity curves for the concentration range studied, although the plots are somewhat curved. This suggests that there is no aggregate formation within this concentration range. There is still the possiblilty of aggregates forming at much lower concentrations of the two salts than those studied. However as noted in Table 3, the 1,6-diaminohexane dihydrochloride salt can expel THF from water at 0.3 molal loading while an equimolal loading of the 1,8-diaminooctane salt can not. As these concentrations are both within the range of conductivity studies and no aggregation was observed in that concentration range, any potential aggregation effect is ultimately not dictating whether the higher carbon-spaced salts can effectively salt out THF from water.



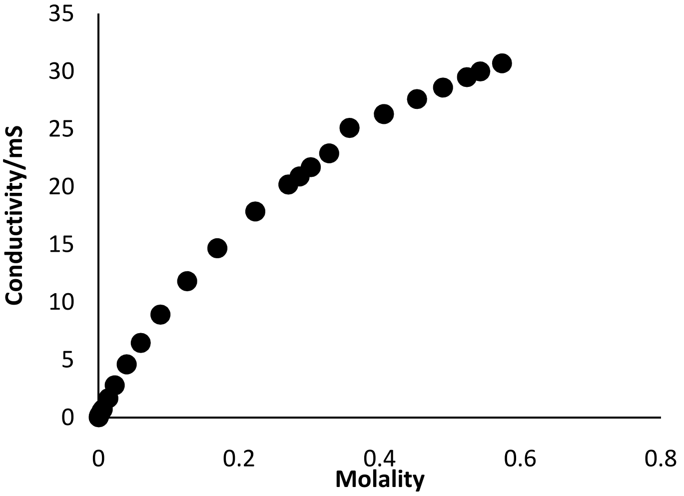


Fig. S2 Conductivity of aqueous solutions of 1,6-diaminohexane dihydrochloride (above) and 1,8-diaminooctane dihydrochloride (below) as a function of the salt concentration.

2. Crystallographic Data

A crystal of the compound (colorless, plate-shaped, size 0.20 x 0.20 x 0.06 mm) was mounted on a glass fiber with grease and cooled to -93 °C in a stream of nitrogen gas controlled with Cryostream Controller 700. Data collection was performed on a Bruker SMART APEX II X-ray diffractometer with graphite-monochromated Mo K$_\alpha$ radiation (λ = 0.71073 Å), operating at 50 kV and 30 mA over 2θ ranges of 5.36 ~ 51.90°. No significant decay was observed during the data collection.

Data were processed on a PC using the Bruker AXS Crystal Structure Analysis Package[13] Data collection: APEX2 (Bruker, 2006); cell refinement: SAINT (Bruker, 2005); data reduction: SAINT (Bruker, 2005); structure solution: XPREP (Bruker, 2005) and SHELXTL (Bruker, 2000); structure refinement: SHELXTL; molecular graphics: SHELXTL; publication materials: SHELXTL. Neutral atom scattering factors were taken from Cromer and Waber.[14] The crystal is hexagonal space group *R*-3, based on the systematic absences, *E* statistics and successful refinement of the structure. The structure was solved by direct methods. Full-matrix least-square refinements minimizing the function $\Sigma w\ (F_o^2 - F_c^2)^2$ were applied to the compound. All nonhydrogen atoms were refined anisotropically. The H atoms on C(1) and C(2) were located from difference Fourier maps, and the rest H atoms were placed in geometrically calculated positions, with C-H = 0.99(CH_2), and 0.98(CH_3) Å, and refined as riding atoms, with Uiso(H) = 1.5UeqC(CH_3) or 1.2 UeqC(other C). In addition, the methyl groups were refined with AFIX 137, which allowed the rotation of the methyl groups whilst keeping the C-H distances and X-C-H angles fixed.

Convergence to final R_1 = 0.0482 and wR_2 = 0.1314 for 974 (I>2σ(I)) independent reflections, and R_1 = 0.0636 and wR_2 = 0.1464 for all 1296 (R(int) = 0.0223) independent reflections, with 67 parameters and 0 restraints, was achieved.[15] The largest residual peak and hole to be 0.193 and – 0.200 e/Å^3, respectively. Crystallographic data, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters, and torsion angles are given in Table 1 to 6. The molecular structure and the cell packing are shown in Figures 1 and 2.

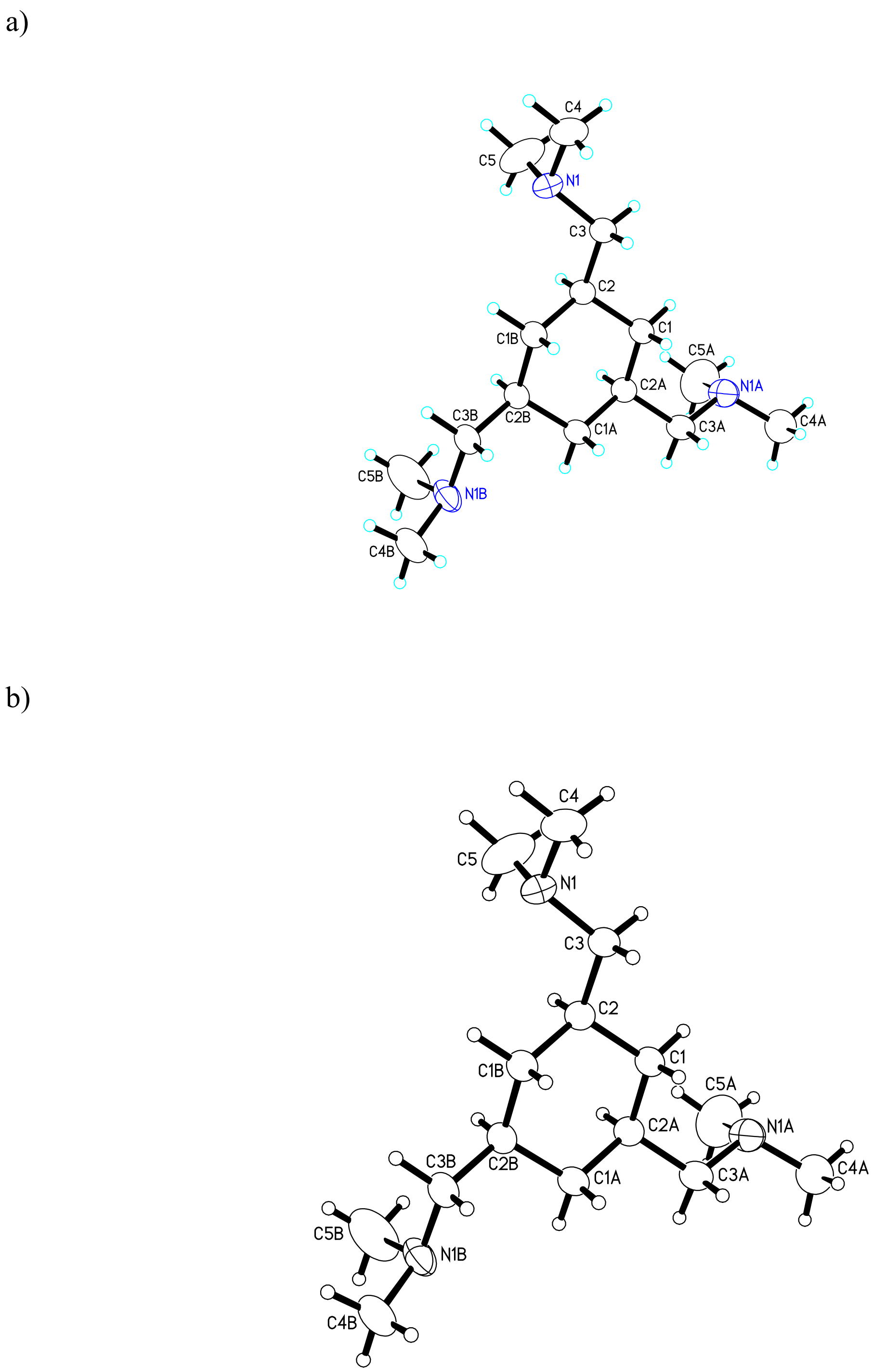


Fig. S3 Molecular Structure (Displacement ellipsoids for non-H atoms are shown at the 50% probability level and H atoms are represented by circles of arbitrary size.)

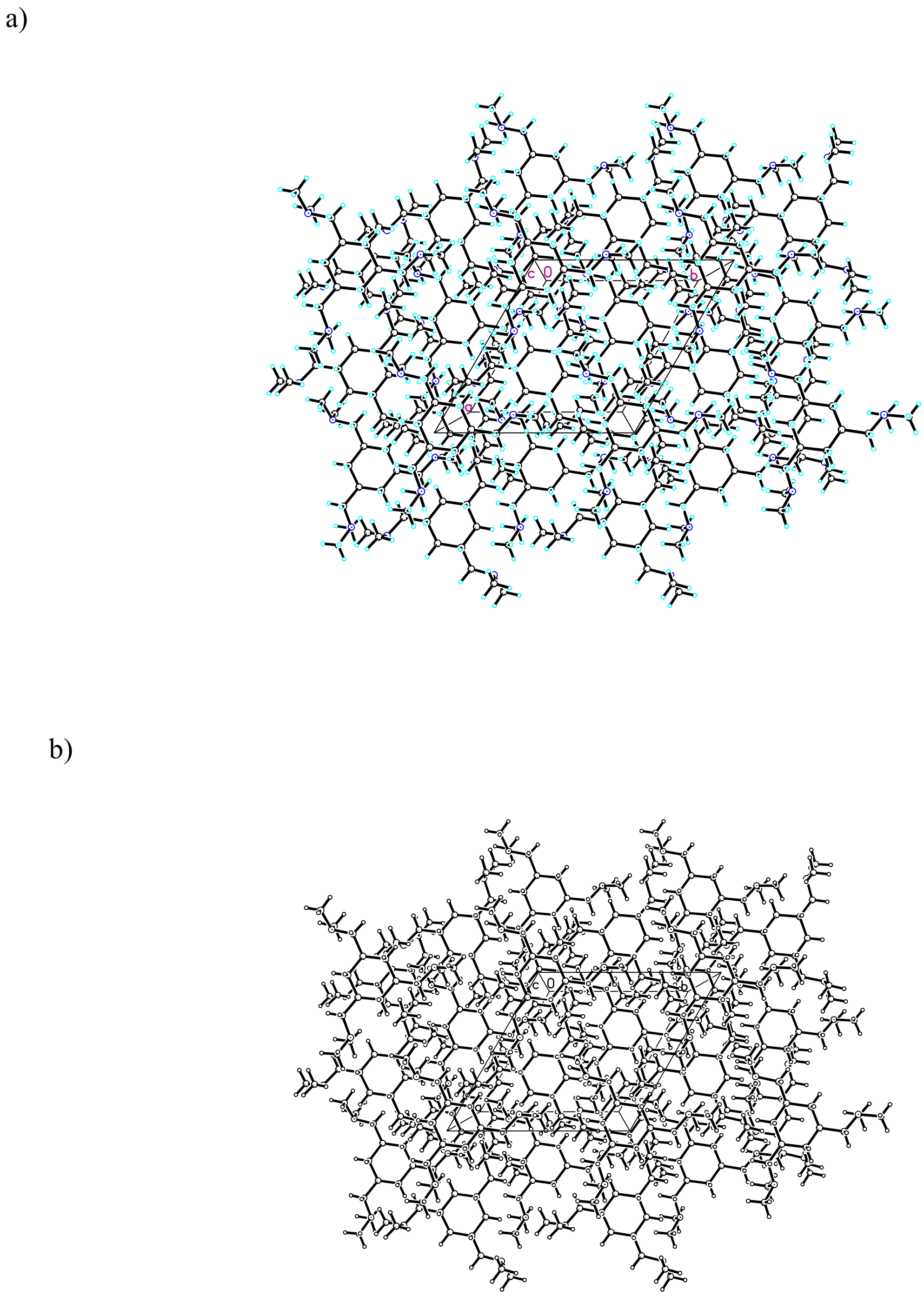


Fig. S4 Unit cell packing

Table S1 Crystal data and structure refinement for 1,1’,1’’-(cyclohexane-1,3,5-triyl)tris(N,N,-dimethylmethanamine)

Identification code	pj35	
Empirical formula	C15 H33 N3	
Formula weight	255.44	
Temperature	180(2) K	
Wavelength	0.71073 Å	
Crystal system	Hexagonal	
Space group	R-3	
Unit cell dimensions	a = 10.3969(4) Å	□= 90°.
	b = 10.3969(4) Å	□= 90°.
	c = 28.4886(15) Å	□ = 120°.
Volume	2666.9(2) Å^3	
Z	6	
Density (calculated)	0.954 Mg/m^3	
Absorption coefficient	0.057 mm^{-1}	
F(000)	864	
Crystal size	0.20 x 0.20 x 0.06 mm^3	
Theta range for data collection	2.68 to 26.95°.	
Index ranges	-12<=h<=13, -13<=k<=9, -32<=l<=36	
Reflections collected	3702	
Independent reflections	1296 [R(int) = 0.0223]	
Completeness to theta = 26.95°	99.5 %	
Absorption correction	Multi-scan	
Max. and min. transmission	0.9966 and 0.9888	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1296 / 0 / 67	
Goodness-of-fit on F^2	1.053	
Final R indices [I>2sigma(I)]	R1 = 0.0482, wR2 = 0.1314	
R indices (all data)	R1 = 0.0636, wR2 = 0.1464	
Largest diff. peak and hole	0.193 and -0.200 e.Å^{-3}	

Table S2 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for 1,1’,1’’-(cyclohexane-1,3,5-triyl)tris(N,N,-dimethylmethanmine). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N(1)	3358(1)	-706(1)	864(1)	44(1)
C(1)	5381(1)	3526(1)	992(1)	34(1)
C(2)	5172(1)	2030(1)	832(1)	32(1)
C(3)	3691(1)	770(1)	1012(1)	37(1)

C(4)	2129(2)	-1839(2)	1138(1)	56(1)
C(5)	3011(2)	-955(2)	371(1)	82(1)

Table S3 Bond lengths [Å] and angles [°] for 1,1’,1’’-(cyclohexane-1,3,5-triyl)tris(N,N,-dimethylmethanmine)

N(1)-C(5)	1.440(2)
N(1)-C(3)	1.4570(15)
N(1)-C(4)	1.4585(18)
C(1)-C(2)#1	1.5228(16)
C(1)-C(2)	1.5274(16)
C(1)-H(1A)	0.981(15)
C(1)-H(1B)	0.988(15)
C(2)-C(1)#2	1.5228(16)
C(2)-C(3)	1.5270(16)
C(2)-H(2A)	1.031(14)
C(3)-H(3A)	0.9900
C(3)-H(3B)	0.9900
C(4)-H(4A)	0.9800
C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800
C(5)-H(5A)	0.9800
C(5)-H(5B)	0.9800
C(5)-H(5C)	0.9800

C(5)-N(1)-C(3)	112.19(13)
C(5)-N(1)-C(4)	109.76(12)
C(3)-N(1)-C(4)	110.24(11)
C(2)#1-C(1)-C(2)	112.50(11)
C(2)#1-C(1)-H(1A)	108.5(8)
C(2)-C(1)-H(1A)	108.3(8)
C(2)#1-C(1)-H(1B)	109.3(8)
C(2)-C(1)-H(1B)	110.6(8)
H(1A)-C(1)-H(1B)	107.5(11)
C(1)#2-C(2)-C(3)	111.88(10)
C(1)#2-C(2)-C(1)	110.48(11)
C(3)-C(2)-C(1)	110.05(9)
C(1)#2-C(2)-H(2A)	107.7(7)
C(3)-C(2)-H(2A)	109.5(7)
C(1)-C(2)-H(2A)	107.1(7)
N(1)-C(3)-C(2)	114.43(10)
N(1)-C(3)-H(3A)	108.7
C(2)-C(3)-H(3A)	108.7
N(1)-C(3)-H(3B)	108.7
C(2)-C(3)-H(3B)	108.7

H(3A)-C(3)-H(3B)	107.6
N(1)-C(4)-H(4A)	109.5
N(1)-C(4)-H(4B)	109.5
H(4A)-C(4)-H(4B)	109.5
N(1)-C(4)-H(4C)	109.5
H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5
N(1)-C(5)-H(5A)	109.5
N(1)-C(5)-H(5B)	109.5
N(1)-C(5)-H(5C)	109.5

Symmetry transformations used to generate equivalent atoms:
#1 -x+y+1,-x+1,z #2 -y+1,x-y,z

Table S4 Anisotropic displacement parameters ($Å^2 x 10^3$) for pj35. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N(1)	32(1)	28(1)	64(1)	-12(1)	-2(1)	10(1)
C(1)	27(1)	28(1)	48(1)	-2(1)	0(1)	15(1)
C(2)	27(1)	28(1)	40(1)	-2(1)	-1(1)	13(1)
C(3)	26(1)	29(1)	54(1)	-6(1)	-1(1)	12(1)
C(4)	39(1)	31(1)	84(1)	-4(1)	-1(1)	7(1)
C(5)	88(2)	54(1)	72(1)	-28(1)	-3(1)	12(1)

Table S5 Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2 x 10^3$) for 1,1’,1’’-(cyclohexane-1,3,5-triyl)tris(N,N,-dimethylmethanmine).

	x	y	z	U(eq)
H(1A)	5348(15)	3528(15)	1336(5)	40
H(1B)	4562(16)	3662(14)	876(5)	40
H(2A)	5168(15)	2034(14)	470(5)	38
H(3A)	3696	802	1359	45
H(3B)	2886	941	901	45
H(4A)	1934	-2825	1041	84
H(4B)	1239	-1761	1085	84
H(4C)	2388	-1692	1472	84
H(5A)	2755	-1971	289	123
H(5B)	3875	-249	187	123
H(5C)	2167	-813	301	123

Table S6 Torsion angles [°] for 1,1',1''-(cyclohexane-1,3,5-triyl)tris(N,N,-dimethylmethanmine)

C(2)#1-C(1)-C(2)-C(1)#2	54.72(17)
C(2)#1-C(1)-C(2)-C(3)	178.77(9)
C(5)-N(1)-C(3)-C(2)	-71.06(16)
C(4)-N(1)-C(3)-C(2)	166.29(11)
C(1)#2-C(2)-C(3)-N(1)	-58.92(15)
C(1)-C(2)-C(3)-N(1)	177.85(10)

Symmetry transformations used to generate equivalent atoms:
#1 -x+y+1,-x+1,z   #2 -y+1,x-y,z

3. References

1. S.M. Mercer, P.G. Jessop, *ChemSusChem*, 2010, **3**, 467–470.
2. D.E. Kiely, A. Vishwanathan, B.P. Jarman, M. Manley-Harris, *J. Carbohydr. Chem.*, 2009, **28**, 348–368.
3. D. Ma, P.Y. Zavalij, L. Isaacs, L. *J. Org. Chem.*, 2010, **75**, 4786–4795.
4. M.W. Scoggins, *J. Chromatogr. Sci.*, 1975, **13**, 146-148.
5. J.R. Harjani, C. Liang, P.G. Jessop, *J. Org. Chem.*, 2011, **76**, 1683–1691.
6. J.J.E. Moreau, B.P. Pichon, C. Bied, M.W.C. Man, *J. Mater. Chem.*, 2005, **15**, 3929–3936.
7. E. Keinan, Frictionless Molecular Rotary Motors. W.O. Patent 2008/096360 A2, August 14, 2008.
8. R.A. da Silva, I.H.S. Estevam, L.W. Bieber, *Tetrahedron Lett.*, 2007, ***48***, 7680–7682.
9. E.G. Knapick, P. Ander, J.A. Hirsch, *Synthesis*, 1985, 58–60.
10. S.A. Young, G.E. Kiefer, L.R. Depalatis, *Targeting Chelants and Chelates*, WO Patent 2006/20779 A2, February 23, 2006.
11. K. Janabusa, A. Kawakami, M. Kimura, H. Shirai, *Chem. Lett.*, 1997, 191–192.
12. I. Tomatsu, C.F.C. Fitié, D. Byelov, W.H. de Jeu, P.C.M.M. Magusin, M. Wübbenhorst, R.P.Sijbesma, *J. Phys. Chem. B*, 2009, **113**, 14158–14164.
13. Bruker AXS Crystal Structure Analysis Package:
    Bruker (2000). SHELXTL. Version 6.14. Bruker AXS Inc., Madison, Wisconsin, USA.
    Bruker (2005). XPREP. Version 2005/2. Bruker AXS Inc., Madison, Wisconsin, USA.
    Bruker (2005). SAINT. Version 7.23A. Bruker AXS Inc., Madison,Wisconsin, USA.
    Bruker (2006). APEX2. Version 2.0-2. Bruker AXS Inc., Madison, Wisconsin, USA.
14. D.T. Cromer, J. T. Waber, *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK, 1974**, 4**, Table 2.2 A.
15. $R_1 = \Sigma \,||Fo| - |Fc|| \,/\, \Sigma\, |Fo|$
    $wR_2 = \{\Sigma\, [w\,(F_o^2 - F_c^2)^2] \,/\, \Sigma\, [w(F_o^2)^2]\}^{1/2}$
    $(w = 1 \,/\, [\sigma_2(F_o^2) + (0.0744P)^2 + 1.186P]$, where $P = [\mathrm{Max}\,(F_o^2, 0) + 2F_c^2] \,/\, 3)$