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1 General Remarks

All reagents and solvents were used without further purification unless otherwise noted. For thin layer chromatography silica gel 60 F254 plates from Merck were used and examined under UV-light irradiation (254 nm and 365 nm). Flash column chromatography was performed on silica gel from Sigma-Aldrich (particle size: 0.04-0.063 mm) using petroleum ether, dichloromethane, chloroform, toluene, methanol, acetone and/or ethyl acetate. Melting points (not corrected) were measured with a Büchi Melting Point B-545. IR-Spectra were recorded on a Bruker Tensor 27 spectrometer on a ZnSe ATR crystal. NMR spectra were taken on a Bruker DRX 300 (300 MHz), Bruker Avance 300 III (300 MHz), Bruker Avance III 400 (400 MHz), Bruker Avance III 500 (500 MHz) and Bruker Avance III 600 (600 MHz) spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) relative to traces of the non-deuterated solvent in the corresponding deuterated solvent. HRMS experiments were carried out on a Fourier Transform Ion Cyclotron Resonance (FTICR) mass spectrometer solariX (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 7.0 T superconducting magnet and interfaced to an Apollo II Dual ESI/MALDI source. MALDI-TOF MS experiments were carried out on a Bruker Daltonik Reflex III, on a Bruker ApexQe or on a Bruker AutoFlex Speed TOF with DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene]malononitrile) as matrix. The surface area and porosity was characterised by nitrogen adsorption and desorption analysis at 77.35 K with an autosorb computer-controlled surface analyser (AUTOSORB-iQ, Quantachrome), typically 10-40 mg were loaded. Powder X-ray diffraction was measured using a Stoe Stadi 611KLS/N 61263 diffractometer.
2 Synthesis and characterization

Synthesis of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (S1): At room temperature, hydrobromic acid (100 mL, 33% in AcOH) was added to 1,3,5-triethylbenzene (10 mL, 53.1 mmol) and paraformaldehyde (17 g, 560 mmol). The suspension was stirred and ZnBr₂ (19.7 g, 88 mmol) was added slowly. After complete addition, the mixture was stirred vigorously at 90 °C for 16 hours. The reaction mixture was cooled to room temperature and the white solid was filtered off, washed with water (300 mL), and dried under vacuum overnight to give 23.2 g (2 mmol, 98%) of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene as a colorless solid. M.p.: 173 °C. ¹H NMR (300 MHz, CDCl₃): δ = 4.58 (s, 6H, -C₃H₂Br), 2.95 (q, J = 7.6 Hz, 6H, -C₃H₂CH₃), 1.34 (t, J = 7.6 Hz, 9H, -C₃H₂CH₃) ppm. The analytical data are consistent with those from literature. [S1]

Synthesis of trimethyl-1,3,5-benzenetricarboxylate (S2): 1,3,5-Benzene-tricarboxylic acid (42 g, 200 mmol) was suspended in a solution of methanol (530 mL) and sulfuric acid (13 mL, 97%). The suspension was refluxed for 24 hours and subsequently cooled to room temperature. A saturated solution of NaHCO₃ (500 mL, in water) was added slowly and the
mixture was filtered. The residue was washed with water (1000 mL) and the filtrate extracted with diethyl ether (500 mL). The residue and the organic layer were combined and the solvent removed under reduced pressure to give 49 g (97%) of trimethyl-1,3,5-benzenetricarboxylate as a colorless solid. M.p.: 144 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.86\) (s, 3H, Ar\(H\)), 3.98 (s, 9H, -COOC\(_2\)H\(_5\)). The analytical data are consistent with those from literature.\(^{[52]}\)

**Synthesis of 1,3,5-tris(hydroxymethyl)benzene (S3):** Under nitrogen atmosphere, a solution of trimethyl-1,3,5-benzenetricarboxylate (5.04 g, 20 mmol) in dry THF (90 mL) was added dropwise through a pressure-equalized addition funnel to LiAlH\(_4\) (3.05 g, mmol) in dry THF (22 mL) at 0 °C. After complete addition, the reaction mixture was refluxed for 24 hours and cooled to room temperature. The reaction was quenched by slow addition of water (50 mL). The reaction mixture was filtered and the residue was extracted first with MeOH (50 mL) then with THF (50 mL). The solvent was removed under reduced pressure to give 3.3 g (95%) of 1,3,5-tris(hydroxymethyl)benzene as a pale yellow solid. M.p.: 76 °C. \(^1\)H NMR (300 MHz, D\(_2\)O): \(\delta = 7.35\) (s, 3H, Ar\(H\)), 4.69 (s, 6H, -CH\(_2\)OH). The analytical data are consistent with those from literature.\(^{[52]}\)

**Synthesis of 1,3,5-tris(bromomethyl)benzene (S4):** 1,3,5-tris(hydroxymethyl)benzene (10 g, 60 mmol) was suspended in a mixture of toluene (150 mL) and HBr (100 mL, 48% in H\(_2\)O) and refluxed for 24 hours. The reaction mixture was cooled to room temperature and the organic layer was separated. The aqueous layer was extracted with diethylether (2 x 100 mL). The organic layers were combined and the solvent was removed under reduced pressure. The crude product was filtered through a short silica pad (elucent: light petroleum ether/toluene 1:1) to give 21.3 g (98%) of 1,3,5-tris(bromomethyl)benzene as a colorless solid. M.p.: 95 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.35\) (s, 3H, Ar\(H\)), 4.46 (s, 6H, -CH\(_2\)Br). The analytical data are consistent with those from literature.\(^{[53]}\)

**Synthesis of 1,3,5-triformylbenzene (2-H):** 1,3,5-Tris(hydroxymethyl)benzene (1.6 g, 10 mmol) was suspended in DCM (100 mL). Pyridinium chlorochromate (PCC, 6.5 g, 30 mmol) and Celite (3 g) were added and the mixture stirred for 6 hours at room temperature. Subsequently the reaction mixture was diluted with ether (80 mL) and was allowed to stir for further 30 minutes. The reaction mixture was filtered and the residue extracted with DCM (200 mL). The extract was concentrated to dryness under reduced pressure and the crude product obtained was purified by column chromatography (DCM, \(R_f = 0.17\)) to give 1.05 g (62%) of 2-H as a colorless solid. M.p.: 92 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 10.21\) (s, 3H, Ar\(H\)), 8.64 (s, 3H, -CHO). The analytical data are consistent with those from literature.\(^{[52]}\)

**Synthesis of 2,4,6-triethylbenzene-1,3,5-tricarbaldehyde (2-Et):** Potassium dichromate (6.6 g, 22.5 mmol) was dissolved in dry DMSO (50 mL). 1,3,5-Tris(bromomethyl)-2,4,6-triethylbenzene (2.2 g, 5 mmol) was added and the reaction mixture heated to 110 °C for 2 hours. The reaction was poured into 200 mL of 10 M NaOH and extracted with DCM (3 x 100 mL). The combined organic layer was washed with brine (100 mL) and water (2 x 100 mL), and dried over MgSO\(_4\). The crude product was purified by column chromatography (toluene/ethyl acetate 10:1, \(R_f = 0.5\)) to give 450 mg (36%) of 2-Et as a colorless waxy solid. M.p.: 50 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 10.60\) (s, 3H, -CHO), 2.99 (q, \(J = 7.5\) Hz, 6H, -CH\(_2\)CH\(_3\)), 1.25 (t, \(J = 7.5\) Hz, 9H, -CH\(_2\)CH\(_3\)) ppm. The analytical data are consistent with those from literature.\(^{[54]}\)

**Synthesis of 2,4,6-triethylbenzene-1,3,5-tricarbaldehyde (2-Et):** Under an argon atmosphere a solution of NaOEt (0.9 g, 13.3 mmol) in absolute ethanol (31 mL) was prepared. To this solution was added 2-nitropropane (1.2 mL, 13.3 mmol) and the mixture was stirred for 5 minutes, followed by the addition of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (1.7 g, 3.9 mmol). The reaction mixture was stirred for 24 hours at room temperature. The solvent was removed in vacuo, the residue was dissolved in toluene (100 mL) and washed with water (75 mL), NaOH\(_{aq}\) (1 M, 75 mL) and again water (75 mL). The organic layer was dried over Na\(_2\)SO\(_4\) and filtered. The solvent was removed in vacuo and the crude product purified by column chromatography (toluene/ethyl acetate 10:1, \(R_f = 0.5\)) to give 850 mg (85%) of 2-Et as a colorless waxy solid.\(^{[5]}\) M.p.: 50 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 10.60\) (s, 3H, -CHO),
2.99 (q, \( J = 7.5 \) Hz, 6H, -CH\(_2\)CH\(_3\)), 1.25 (t, \( J = 7.5 \) Hz, 9H, -CH\(_2\)CH\(_3\)) ppm. The analytical data are consistent with those from literature.\(^{[54]}\)

**Synthesis of 1,3,5-tris(phthalimidomethyl)-2,4,6-triethylbenzene (S5):** A mixture of 1,3,5-tris(bromomethyl)-2,4,6-triethylbenzene (5 g, 11.3 mmol) and potassium phthalimide (8.4 g, 45 mmol) was suspended in dry DMSO (75 mL) and stirred under nitrogen at 85 °C for 8 hours. After the mixture was cooled to room temperature, water (100 mL) was added and the formed precipitate was filtered. The precipitate was suspended in chloroform (200 mL) and the suspension was washed with brine (100 mL) and water (100 mL), and dried over Na\(_2\)SO\(_4\). The crude product was purified by column chromatography (toluene/ethyl acetate 8:1, \( R_f = 0.28 \)) to yield 4.2 g (59%) of 1,3,5-tris(phthalimidomethyl)-2,4,6-triethylbenzene as a white solid. M.p.: 234 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.81 \) (dd, \( J = 5.4\), 3.0 Hz, 6H, ArH), 7.68 (dd, \( J = 5.4\), 3.1 Hz, 6H, ArH), 4.94 (s, 6H, -CH\(_2\)H), 3.10 (q, \( J = 7.6 \) Hz, 6H, -CH\(_2\)CH\(_3\)), 0.97 (t, \( J = 7.5 \) Hz, 9H, -CH\(_2\)CH\(_3\)) ppm. The analytical data are consistent with those from literature.\(^{[51]}\)

**Synthesis of 1,3,5-tris(phthalimidomethyl)-benzene (S6):** A mixture of 1,3,5-tris(bromomethyl)-benzene (5.3 g, 14.8 mmol) and potassium phthalimide (11 g, 60 mmol) was suspended in dry DMSO (90 mL) and stirred under nitrogen at 100 °C for 3 days. After the mixture was cooled to room temperature, water (200 mL) was added and the mixture was extracted with chloroform (3 x 300 mL). The combined organic layer was washed with water (2 x 100 mL) and dried over Na\(_2\)SO\(_4\). The crude product was purified by column chromatography (DCM/acetonitrile 20:1, \( R_f = 0.55 \)) to give 7.6 g (95%) of 1,3,5-tris(phthalimidomethyl)-benzene as a colorless solid. M.p.: 270 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 7.82 \) (dd, \( J = 5.5\), 3.0 Hz, 6H, ArH), 7.70 (dd, \( J = 5.4\), 3.1 Hz, 6H, ArH), 7.35 (s, 3H, ArH), 4.78 (s, 6H, -CH\(_2\)H) ppm. The analytical data are consistent with those from literature.\(^{[56]}\)

**Synthesis of 1,3,5-tris(aminomethyl)-2,4,6-triethylbenzene (1-Et):** 1,3,5-Tris(phthalimidomethyl)-2,4,6-triethylbenzene (3.84 g, 6 mmol) was dissolved in a mixture of dry ethanol and toluene (210 mL, 2:1 v/v) and heated to reflux with hydrazine hydrate (1.74 mL, 36 mmol) for 20 hours. The mixture was cooled to room temperature, an aqueous solution of KOH (40%, 60 mL) was added and the mixture was extracted with CHCl\(_3\) (3 x 100 mL). The combined organic layer was washed with brine (100 mL) and water (100 mL), dried over MgSO\(_4\) and filtered. The solvent was removed in vacuo to give 1.18 g (79%) of 1-Et as a colorless solid. M.p.: 136 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \( \delta = 3.88 \) (s, 6H, -CH\(_2\)NH\(_2\)), 2.83 (q, \( J = 7.5 \) Hz, 6H, -CH\(_2\)CH\(_3\)), 1.39 (s, 6H, -NH\(_2\)), 1.24 (t, \( J = 7.5 \) Hz, 9H, -CH\(_2\)CH\(_3\)) ppm. The analytical data are consistent with those from literature.\(^{[51]}\)

**Synthesis of 1,3,5-tris(aminomethyl)-benzene (1-H):** 1,3,5-Tris(phthalimidomethyl)-benzene (2.5 g, 4.5 mmol) was dissolved in a mixture of dry ethanol and toluene (150 mL, 2:1) and heated to reflux with hydrazine hydrate (1.3 mL, 27 mmol) for 24 hours. The mixture was cooled to room temperature and the ethanol was evaporated. To the mixture CHCl\(_3\) (100 mL) and an aqueous solution of KOH (40%, 75 mL) was added. The organic layer was separated and the aqueous layer was extracted with CHCl\(_3\) (2 x 100 mL). The combined organic layer were washed with water (50 mL), dried over MgSO\(_4\) and filtered. The solvent was removed in vacuo to give 500 mg (66%) of 1-H as a colorless very hygroscopic solid. M.p.: 50 °C. \(^1\)H NMR (300 MHz, DMSO-d\(_6\)): \( \delta = 7.10 \) (s, 3H, ArH), 3.67 (s, 6H, -CH\(_2\)NH\(_2\)), 1.66 (s, 6H, -NH\(_2\)) ppm. The analytical data are consistent with those from literature.\(^{[57]}\)
1,3,5-Triformylbenzene (2-H) (120 mg, 740 µmol) was dissolved in MeCN (15 mL). Within 3 hours a solution of 2,4,6-triethylbenzene-1,3,5-trimethanamine (1-Et) (185 mg, 740 µmol) in MeCN (22 mL) was added dropwise under vigorous stirring at room temperature. The suspension was stirred for 3 days and afterwards the precipitate was filtered and washed with MeCN (20 mL). The solid residue was extracted with DCM (200 mL) and the solvent of the extract removed in vacuo to give 70 mg (27%) of cage compound 3-Et-H as a colorless solid. M.p.: 220 °C (decomp.). $^1$H NMR (400 MHz, CD$_2$Cl$_2$): $\delta = 8.56$ (s, 12H, -CHN-), 7.97 (s, 12H, ArH), 4.76 (s, 24H, -CH$_2$N-), 3.18 (q, $J = 7.5$ Hz, 24H, CH$_2$CH$_3$), 1.28 (t, $J = 7.4$ Hz, 36H, CH$_2$CH$_3$) ppm. $^{13}$C NMR (101 MHz, CD$_2$Cl$_2$): $\delta = 160.8$ (-CHN-), 142.7 (-CCH$_2$CH$_3$), 138.0 (-CCHN-), 133.1 (-CCH$_3$N-), 129.2 (-CH), 58.8 (-CH$_3$N-), 23.7 (-CH$_2$CH$_3$), 16.2 (-CH$_2$CH$_3$) ppm. FT-IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 504 w, 529 m, 543 m, 550 m, 558 m, 565 m, 570 m, 581 m, 595 m, 618 m, 660 m, 687 s, 738 m, 762 m, 817 w, 883 m, 938 s, 961 m, 986 m, 1000 m, 1022 m, 1042 m, 1076 m, 1152 m, 1213 w, 1229 m, 1251 m, 1319 m, 1356 m, 1374 m, 1451 m, 1490 m, 1596 m, 1644 vs, 1702 w, 2868 m, 2927 m, 3272 w, 3294 w, 3366 w, 3439 w. MS (MALDI-TOF, DCTB): $m/z = 1430.817$ [M+H]$^+$, 1452.816 [M+Na]$^+$, 1468.794 [M+K]$^+$, 1646.904 [M+12H$_2$O+H]$^+$ (m/z calculated for C$_{96}$H$_{108}$N$_{12}$ + H$: 1430.893$). Anal. calcd. for C$_{96}$H$_{108}$N$_{12}$·6H$_2$O: C: 74.97, H: 7.86, N: 10.93, O: 6.24; found: C: 74.94, H: 7.66, N: 10.79.
Synthesis of cage compound 3-Et-Et:

2,4,6-Triethylbenzene-1,3,5-tricarbaldehyde (2-Et) (123 mg, 500 µmol) was dissolved in MeCN (6 mL). Within 2 hours a solution of 2,4,6-triethylbenzene-1,3,5-trimethanamine (1-Et) (125 mg, 500 µmol) in MeCN (19 mL) was added dropwise under vigorous stirring at room temperature. The suspension was stirred for 3 d and the precipitate was filtered and washed with MeCN (5 mL). The solid residue was extracted with MeOH (200 mL) and the solvent removed in vacuo to give 103 mg (46%) of cage compound 3-Et-Et as a colorless solid. M.p.: 240 °C (decomp.).

1H NMR (600 MHz, Tol-d8): δ = 8.00 (s, 12H, -C8H6N), 4.90 (s, 24H, -C8H2CH3), 2.68 (q, J = 7.3 Hz, 24H, -C8H2CH3), 2.37 (q, J = 7.3 Hz, 24H, -C8H2CH3), 1.22 (t, J = 7.4 Hz, 36H, -CH2C8H3), 1.14 (t, J = 7.4 Hz, 36H, -CH2C8H3) ppm. 13C NMR (150 MHz, Tol-d8): δ = 160.0 (-CHN), 143.5 (-C8H2CH3), 140.5 (-C8H2CH3), 134.8 (-CCHN), 132.0 (-C8H2N), 56.8 (-C8H2N), 24.6 (-C8H2CH3), 23.4 (-C8H2CH3), 16.4 (-C8H2CH3), 15.7 (-C8H2CH3) ppm. FT-IR (ATR): v (cm⁻¹) = 604 w, 611 w, 627 w, 640 w, 646 w, 675 w, 690 w, 783 s, 839 m, 961 s, 1015 m, 1045 m, 1076 m, 1111 w, 1232 w, 1250 w, 1281 w, 1315 m, 1373 s, 1433 m, 1454 s, 1489 m, 1556 m, 1643 vs, 1691 m, 1767.2725 [M+H]+ (100), 1789.2611 [M+Na]+ (22.2), 884.1389 [M+2H]²⁺ (8.5), 894.6312 [M+H+Na]³⁺ (16.3), 905.6225 [M+2Na]⁴⁺ (8.5) (m/z calculated for C₁₂₀H₁₅₆N₁₂+H+: 1767.2682). Anal. calcd. for C₁₂₀H₁₅₆N₁₂·5 H₂O: C: 77.63, H: 9.01, N: 9.05, O: 4.31; found: C: 77.69, H: 8.93, N: 8.69.

Synthesis of polymer material 3-Et-H:

1,3,5-Triformylbenzene (2-H) (120 mg, 740 µmol) was dissolved in MeCN (15 mL). Within 3 hours a solution of 2,4,6-triethylbenzene-1,3,5-trimethanamine (1-Et) (185 mg, 740 µmol) in MeCN (22 mL) was added dropwise under vigorous stirring at room temperature. The suspension was stirred for 3 days and the precipitate was filtered and washed with MeCN (20 mL). The solid residue was washed with DCM (200 mL) and the residue dried in vacuo to
give 190 mg (68%) of **3-Et-H-Polymer** material as a colorless powder. M.p.: 215 °C (decomp.). 

\[ ^{13}C \text{ CP MAS NMR (125 MHz): } \delta = 164 (-CHN), 147 (-C-Ar), 137 (-C-Ar), 59 (-CH}_2\text{N}), 28 (-CH}_2\text{CH}_3), 20 (-CH}_2\text{CH}_3) \text{ ppm.} \]

\[ \text{FT-IR (ATR): } \tilde{\nu} \text{ (cm}^{-1}) = 663 \text{ m, 689 s, 770 w, 876 w, 941 m, 970 m, 1043 m, 1074 w, 1148 m, 1250 m, 1315 m, 1373 m, 1452 m, 1483 w, 1566 w, 1597 m, 1639 vs, 1701 m, 2870 s, 2930 m, 2964 m.} \]

*Anal. calcd. for 3(C\(_{30}\text{H}_{30}\text{N}_2)_n \cdot n \text{ H}_2\text{O}: } C: 75.56, \text{ H: 7.84, N: 11.01, O: 5.59; found: C: 75.45, H: 7.42, N: 10.81.}*

**Synthesis of polymer material 3-Et-Et:**

\[
\begin{align*}
\text{C} & \text{H}_2\text{Et}_{\text{Ar}} \text{NH}_2 & \rightarrow \text{C} & \text{H}_2\text{Et}_{\text{Ar}} \text{NH}_2 \text{Et} \text{Et} \text{Et} \text{Et} \\
\text{C} & \text{H}_2\text{Et}_{\text{Ar}} & + & \text{C} & \text{H}_2\text{Et}_{\text{Ar}} \text{Et} \text{Et} \text{Et} \text{Et} \\
\text{C} & \text{H}_2\text{Et}_{\text{Ar}} & \rightarrow & \text{C} & \text{H}_2\text{Et}_{\text{Ar}} \text{Et} \text{Et} \text{Et} \text{Et} \\
\text{C} & \text{H}_2\text{Et}_{\text{Ar}} & \rightarrow & \text{C} & \text{H}_2\text{Et}_{\text{Ar}} \text{Et} \text{Et} \text{Et} \text{Et} \\
\end{align*}
\]

2,4,6-Triethylbenzene-1,3,5-tricarbaldehyde (2-Et) (123 mg, 500 μmol) was dissolved in MeCN (6 mL). Within 2 hours a solution of 2,4,6-triethylbenzene-1,3,5-trimethanamine (1-Et) (125 mg, 500 μmol) in MeCN (19 mL) was added dropwise under vigorous stirring at room temperature. The suspension was stirred for 3 d and the precipitate was filtered and washed with MeCN (5 mL). The solid residue was washed with MeOH (200 mL) and the residue dried in vacuo to give 110 mg (49%) of **3-Et-Et-Polymer** material as a colorless powder. M.p.: 245 °C (decomp.). 

\[ ^{13}C \text{ CP MAS NMR (125 MHz): } \delta = 164 (-CHN), 147 (-C-Ar), 137 (-C-Ar), 59 (-CH}_2\text{N}), 28 (-CH}_2\text{CH}_3), 20 (-CH}_2\text{CH}_3) \text{ ppm.} \]

\[ \text{FT-IR (ATR): } \tilde{\nu} \text{ (cm}^{-1}) = 690 \text{ vw, 768 m, 937 m, 959 m, 1013 m, 1043 m, 1074 m, 1232 w, 1250 w, 1313 m, 1371 s, 1452 s, 1556 m, 1639 vs, 1690 m, 2870 s, 2930 s, 2963 vs.} \]

*Anal. calcd. for (C\(_{30}\text{H}_{30}\text{N}_2)_n \cdot n \text{ H}_2\text{O}: } C: 78.39, \text{ H: 8.99, N: 9.14, O: 3.48; found: C: 78.59, H: 8.66, N: 9.07.}*

**Synthesis of polymer material 3-H-Et:**

\[
\begin{align*}
\text{C} & \text{H}_2\text{Et}_{\text{Ar}} \text{NH}_2 & \rightarrow \text{C} & \text{H}_2\text{Et}_{\text{Ar}} \text{NH}_2 \text{Et} \text{Et} \text{Et} \text{Et} \\
\text{C} & \text{H}_2\text{Et}_{\text{Ar}} & + & \text{C} & \text{H}_2\text{Et}_{\text{Ar}} \text{Et} \text{Et} \text{Et} \text{Et} \\
\text{C} & \text{H}_2\text{Et}_{\text{Ar}} & \rightarrow & \text{C} & \text{H}_2\text{Et}_{\text{Ar}} \text{Et} \text{Et} \text{Et} \text{Et} \\
\text{C} & \text{H}_2\text{Et}_{\text{Ar}} & \rightarrow & \text{C} & \text{H}_2\text{Et}_{\text{Ar}} \text{Et} \text{Et} \text{Et} \text{Et} \\
\end{align*}
\]

2,4,6-Triethylbenzene-1,3,5-tricarbaldehyde (2-Et) (82 mg, 330 μmol) was dissolved in MeCN (20 mL). Within 3 hours a solution of 1,3,5-trimethanamine (2-Et) (55 mg, 330 μmol) in MeCN (30 mL) was added dropwise under vigorous stirring at room temperature. The suspension was stirred for 3 days and the precipitate was filtered and washed with MeCN (2x10 mL). The solid residue was dried in vacuo to give 110 mg (95%) of **3-H-Et-Polymer** material as a colorless powder. M.p.: 220 °C (decomp.). 

\[ ^{13}C \text{ CP MAS NMR (125 MHz): } \delta = 166 (-CHN), 145 (-C-Ar), 139 (-C-Ar), 132 (-C-Ar), 71 (-CH}_2\text{N}), 28 (-CH}_2\text{CH}_3), 20 (-CH}_2\text{CH}_3) \text{ ppm.} \]

\[ \text{FT-IR (ATR): } \tilde{\nu} \text{ (cm}^{-1}) = 706 \text{ m, 777 w, 858 m, 999 w, 1043 m, 1074 w, 1155 w, 1319 m, 1367,} \]
1452 m, 1556 m, 1603 m, 1643 vs, 1688 m, 2837 w, 2872 w, 2930 w, 2966 w. Anal. calcd. for (C_{24}H_{27}N_{3})_n·2n H_2O: C: 73.25, H: 7.94, N: 10.68, O: 8.13; found: C: 73.78, H: 7.00, N: 9.87.

**Synthesis of polymer material 3-H-H:**

![](image)

1,3,5-Triformylbenzene (2-H) (49 mg, 300 µmol) was dissolved in MeCN (10 mL). Within 3 hours a solution of 1,3,5-trimethanamine (1-H) (50 mg, 300 µmol) in MeCN (40 mL) was added dropwise under vigorous stirring at room temperature. The suspension was stirred for 3 days and the precipitate was filtered and washed with MeCN (25 mL). The solid residue was dried in vacuo to give 80 mg (97%) of 3-H-H-Polymer material as a colorless powder. M.p.: 210 °C (decomp.). $^{13}$C CP MAS NMR (125 MHz): $\delta = 165$ (-CHN-), 141 (-C-Ar), 133 (C-Ar), 69 (-CH$_3$N-) ppm. FT-IR (ATR): $\tilde{\nu}$ (cm$^{-1}$) = 687 s, 768 w, 793 vw, 858 m, 879 m, 953 w, 995 w, 1040 w, 1146 m, 1225 w, 1252 w, 1288 w, 1319 m, 1366 w, 1443 m, 1601 m, 1639 vs, 1697 m, 2839 w. Anal. calcd. for (C_{18}H_{15}N$_3$)$_n·$2n H$_2$O: C: 69.88, H: 6.19, N: 13.58, O: 10.34; found: C: 70.23, H: 6.16, N: 13.44.
3 Exchange experiments

Mixing 3-Et-H and 3-Et-Et

3-Et-H (4 mg, 3 \( \mu \)mol) and 3-Et-Et (5 mg, 3 \( \mu \)mol) were suspended in 20 mL MeCN. The suspension was stirred at RT for 3 days. The solvent was removed in vacuo and residue analysed via \(^1\)H NMR and MALDI-MS: no exchange of buildings blocks could be detected. Afterwards, 20 mL MeCN and 1 mol\% TFA was added. After 3 hours and 4 days the suspension was analysed via \(^1\)H-NMR spectroscopy. Again, no exchange of buildings blocks could be detected, a slow decomposition of 3-Et-H was observed instead. Adding 10 mol\% of TFA leads to a complete decomposition of 3-Et-H after 2 days, whereby 3-Et-Et is still stable. Adding 1 equivalent of TFA results in an instant decomposition of 3-Et-H and 3-Et-Et. An insoluble precipitate was formed.

Figure S1: \(^1\)H NMR spectra (500 MHz, PhMe-\(d_8\)) of the exchange experiments between compound 3-Et-H and 3-Et-Et.
Scrambled Cages

1,3,5-Triformylbenzene (2-H) (3.2 mg, 20 µmol) and 2,4,6-Triethylbenzene-1,3,5-tricarbaldehyde (2-Et) (5 mg, 20 µmol) were dissolved in MeCN (1 mL). Within 3 hours a solution of 2,4,6-triethylbenzene-1,3,5-trimethanamine (1-Et) (10 mg, 40 µmol) in MeCN (6 mL) was added dropwise under vigorous stirring at room temperature. The suspension was stirred for 3 days and the precipitate was filtered and washed with MeCN (20 mL). The solid residue was extracted with DCM (50 mL) and the solvent of the extract removed in vacuo. The resulting product was analysed by MALDI-MS revealing that mixed cages 3-Et-H, 3-Et-(H,H,H,Et), 3-Et-(H,H,Et,Et), 3-Et-(H,Et,Et,Et) and 3-Et-Et were formed.

Figure S2: MALDI-MS spectra of exchange experiments. (A) MALDI-MS spectrum of 3-Et-H (M₁) and 3-Et-Et (M₅) after stirring in MeCN for 3 days at RT. (B) MALDI-MS spectrum of a mixture of 3-Et-H (M₁), 3-Et-(H,H,H,Et) (M₂), 3-Et-(H,H,Et,Et) (M₃), 3-Et-(H,Et,Et,Et) (M₄) and 3-Et-Et (M₅).
Mixing 1-H and 3-Et-Et

1,3,5-Triformylbenzene (2-H) (1 mg, 6 µmol) and cage 3-Et-Et (4 mg, 2 µmol) were suspended in MeCN (4 mL). The suspension was stirred for 3 days at RT. The solvent was removed in vacuo and the residue analysed by $^1$H NMR spectroscopy.

Figure S3: $^1$H NMR spectra (500 MHz, PhMe-$d_8$) of the exchange experiment between compound 2-H and 3-Et-Et. No exchange of buildings blocks could be detected.
4 MM2 calculations

Figure S4: Rotational energy around the C_{SP2}-C_{SP3}-bond of a methylamine substituent of 1-Et (MM2 calculation).

Figure S5: Rotational energy around the C_{SP2}-C_{SP3}-bond of a methylamine substituent of 1-H (MM2 calculation).
Figure S6: Rotational energy around the $C_{SP^2}$-$C_{SP^3}$ bond of a methylamine substituent of 2-Et (MM2 calculation).

Figure S7: Rotational energy around the $C_{SP^2}$-$C_{SP^3}$ bond of a methylamine substituent of 2-H (MM2 calculation).
5 NMR analytics

Figure S8: $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 1,3,5-triformylbenzene (2-H). * H$_2$O, + DCM.

Figure S9: $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 2,4,6-triethylbenzene-1,3,5-tricarbaldehyde (2-Et).
Figure S10: $^1$H NMR spectrum (300 MHz, CDCl$_3$) of 1,3,5-tris(aminomethyl)-2,4,6-triethylbenzene (1-Et).

Figure S11: $^1$H NMR spectrum (300 MHz, DMSO-$d_6$) of 1,3,5-tris(aminomethyl)-benzene (1-H). * H$_2$O.
Figure S12: $^1$H NMR spectrum (400 MHz, CD$_2$Cl$_2$) of cage compound 3-Et-H. * H$_2$O.

Figure S13: $^{13}$C NMR spectrum (100 MHz, CD$_2$Cl$_2$) of cage compound 3-Et-H.
Figure S14: $^1$H NMR spectrum (600 MHz, PhMe-d$_8$) of cage compound 3-Et-Et. * H-grease from deuterated solvent.

Figure S15: $^{13}$C NMR spectrum (150 MHz, PhMe-d$_8$) of cage compound 3-Et-Et.
Figure S16: $^{13}$C CP MAS NMR spectrum (125 MHz) of 3-Et-Et-Polymer.

Figure S17: $^{13}$C CP MAS NMR spectrum (125 MHz) of 3-Et-H-Polymer.
Figure S18: $^{13}$C CP MAS NMR spectrum (125 MHz) of 3-H-Et-Polymer.

Figure S19: $^{13}$C CP MAS NMR spectrum (125 MHz) of 3-H-H-Polymer.
6 DOSY experiments

DOSY NMR experiments were recorded at 298 K and calibrated using known self-diffusion values for the solvents used (\(D_{solv}\)).\[^{[58]}\] The hydrodynamic radii were estimated using the semi-empirical modification of the Stokes-Einstein relation proposed by Chen and Chen.\[^{[59]}\] This equation was solved for \(r_s\) using values of \(r_{solv}\) and \(\eta\) from the literature.\[^{[510]}\]

\[
D = \frac{k_B T}{6 \left( 1 + 0.695 \left( \frac{r_{solv}}{r_s} \right)^{2.234} \right) \pi \eta r_s}
\]

\(D\) is the measured diffusion coefficient (m\(^2\)·s\(^{-1}\))

\(k_B\) is Boltzmann constant (1.3806485 \(\cdot\) 10\(^{-23}\) m\(^2\)·kg·s\(^{-2}\)·K\(^{-1}\))

\(T\) is the temperature (K)

\(r_{solv}\) is the hydrodynamic radius of the solvent (m)

\(r_s\) is the hydrodynamic radius of the analyte (m)

\(\eta\) is the viscosity of the solvent at temperature \(T\) (kg·m\(^{-1}\)·s\(^{-1}\))

\textbf{Table S1}: Estimation of the hydrodynamic radius of \textbf{3-Et-H-Cage} and \textbf{3-Et-Et-Cage} \((r_h)\) in \(\text{C}_6\text{D}_6\) as solvent using parameters from the literature and diffusion coefficients measured by DOSY NMR.

| Compound      | T [K] | \(D_{solv} \cdot 10^{-9}\) [m\(^2\)·s\(^{-1}\)] | \(r_{solv}\) [nm] | \(\eta \cdot 10^{-3}\) [kg·m\(^{-1}\)·s\(^{-1}\)] | \(D \cdot 10^{-10}\) [m\(^2\)·s\(^{-1}\)] | \(r_h\) [nm] |
|---------------|-------|---------------------------------------------|-------------------|------------------------------------------|----------------------------------------|----------------|
| 3-Et-H-Cage   | 298   | 2.18                                        | 0.270             | 0.603                                    | 4.17                                   | 0.87           |
| 3-Et-Et-Cage  | 298   | 2.18                                        | 0.270             | 0.603                                    | 4.07                                   | 0.89           |
Figure S20: DOSY NMR spectrum (400 MHz, C$_6$D$_6$) of cage compound 3-Et-H.

Figure S21: DOSY NMR spectrum (400 MHz, C$_6$D$_6$) of cage compound 3-Et-Et.
7 Mass spectra

Figure S22: MALDI-TOF MS (DCTB) of compound 3-Et-H.

Figure S23: ESI-MS of compound 3-Et-Et in DCM/MeOH.
8 Infrared spectra

Figure S24: IR spectrum (ATR) of compound 3-Et-H.

Figure S25: IR spectrum (ATR) of compound 3-Et-Et.
Figure S26: IR spectrum (ATR) of compound 3-H-H-Polymer.

Figure S27: IR spectrum (ATR) of compound 3-H-Et-Polymer.
**Figure S28**: IR spectrum (ATR) of compound 3-Et-Et-Polymer.

**Figure S29**: IR spectrum (ATR) of compound 3-Et-H-Polymer.
**Figure S30:** IR spectrum (ATR) of compound 1-Et.

**Figure S31:** IR spectrum (ATR) of compound 1-H.
**Figure S32:** IR spectrum (ATR) of compound 2-Et.

**Figure S33:** IR spectrum (ATR) of compound 2-H.
9 Thermogravimetric analysis

Figure S34: Thermogravimetric analysis (under N₂ atmosphere) of A) 3-Et-Et-Cage B) 3-Et-H-Cage C) 3-Et-Et-Polymer D) 3-Et-H-Polymer E) 3-H-Et-Polymer F) 3-H-H-Polymer.
10 Gas sorption measurements

The samples 3-Et-Et-Cage, 3-Et-Et-Polymer, 3-Et-H-Cage, 3-Et-H-Polymer, 3-H-Et-Polymer and 3-H-H-Polymer were investigated “as synthesized”. Prior to the measurements, the samples were further evacuated at 120 °C under vacuum (10⁻² Pa) overnight.

The samples 3-Et-Et-Cage₆ (α-modification) and 3-Et-H-Cage₆ were investigated in crystalline form and prior to the measurements, the samples were further evacuated at 120 °C under a high vacuum (10⁻² Pa) overnight.

The samples 3-Et-Et-Cageᵦₑthane and 3-Et-H-Cageᵦₑthane were activated by treatment of crystals with n-pentane in an ultrasonic bath for 15 min. The n-pentane was decanted, the procedure was repeated and following the solid dried in vacuo at 40 °C for 15 min. Afterwards the material was cooled to -116 °C and soaked with liquid ethane. The suspension was stirred for 10 min. Subsequently the ethane was decanted, the procedure was repeated and the sample was further evacuated at 40 °C under a high vacuum (10⁻² Pa) overnight.

Table S2: Summarized surface areas (BET, N₂, 77K) of all condensation products.

| Compound                      | SABET [m²g⁻¹] (N₂, 77K) |
|-------------------------------|---------------------------|
| 3-Et-Et-Cageₑthane            | 71                        |
| 3-Et-Et-Cage₆                 | 11                        |
| 3-Et-Et-Cage                 | 5                         |
| 3-Et-Et-Polymer              | 6                         |
| 3-Et-H-Cageₑthane            | 443                       |
| 3-Et-H-Cage₆                 | 27                        |
| 3-Et-H-Cage                  | 10                        |
| 3-Et-H-Polymer               | 26                        |
| 3-H-Et-Polymer               | 16                        |
| 3-H-H-Polymer                | 16                        |
Table S3: Summarized uptakes at 1 bar in wt% of 3-Et-Et-Cage_{ethane} and 3-Et-H-Cage_{ethane}.

| Gas   | 3-Et-Et-Cage_{ethane} | 3-Et-H-Cage_{ethane} |
|-------|------------------------|-----------------------|
|       | 77 K  | 263 K  | 273K | 77 K  | 263 K  | 273K |
| N₂    | 7.22  | -      | 1.30 | 17.15 | -      | 1.59 |
| H₂    | 0.34  | -      | 0.08 | 0.93  | -      | 0.07 |
| CO₂   | -     | 9.54   | 8.26 | -     | 15.71  | 13.82 |
| CH₄   | -     | 1.44   | 1.17 | -     | 2.63   | 2.17 |

Figure S35: Gas-sorption isotherm (77 K, N₂) and pore size distribution (NLDFT, slit/cylindr. pores) for 3-Et-Et-Cage_{ethane}.
Figure S36: N$_2$ (black squares), H$_2$ (red circles), CO$_2$ (blue rhombs) and CH$_4$ (green triangles) sorption isotherms for 3-Et-Et-Cage$_{ethane}$ (A) at 77K (B) 263 K and (C) 273 K. (filled symbols: adsorption; open symbols: desorption).

Figure S37: (A) BET-plot of 3-Et-Et-Cage$_{ethane}$. The selected points are located in the range below $P/P_0 = 0.105$ according to the Rouquerol plot of (B).
Figure S38: (A) Gas-sorption isotherm (77 K, N₂) and (B) BET-plot of for 3-Et-Et-CageΔ.

Figure S39: (A) Gas-sorption isotherm (77 K, N₂) and (B) BET-plot of for 3-Et-Et-Cage.
Figure S40: Gas-sorption isotherm (77 K, N\textsubscript{2}) and pore size distribution (NLDFT, slit/cylindr. pores) for 3-Et-H-Cageethane.
Figure S41: N₂ (black squares), H₂ (red circles), CO₂ (blue rhombus) and CH₄ (green triangles) sorption isotherms for 3-Et-H-Cagethane (A) at 77K (B) 263 K and (C) 273 K. (filled symbols: adsorption; open symbols: desorption).

Figure S42: (A) BET-plot of 3-Et-H-Cageethane. The selected points are located in the range below P/P₀ = 0.020 according to the Rouquerol plot of (B).
Figure S43: (A) Gas-sorption isotherm (77 K, N$_2$) and (B) BET-plot of for 3-Et-H-Cage$_\Delta$.

Figure S44: (A) Gas-sorption isotherm (77 K, N$_2$) and (B) BET-plot of for 3-Et-H-Cage.

Figure S45: (A) Gas-sorption isotherm (77 K, N$_2$) and (B) BET-plot of for 3-H-Et-Polymer.
Figure S46: (A) Gas-sorption isotherm (77 K, N₂) and (B) BET-plot of for 3-H-H-Polymer.

Figure S47: (A) Gas-sorption isotherm (77 K, N₂) and (B) BET-plot of for 3-Et-H-Polymer.

Figure S48: (A) Gas-sorption isotherm (77 K, N₂) and (B) BET-plot of for 3-Et-Et-Polymer.
11 Electron micrographs

Figure S49: Electron micrographs of crystalline 3-Et-Et-Cage (α-modification). (A), (B), (C) and (D) were captured before activation with liquid ethane, whereas (E) and (F) afterwards. Pictures (A), (C), (E) and (F) are secondary electron images, while (B) and (D) are the corresponding backscattered electron images.
Figure S50: Electron micrographs of 3-H-H-Polymer. (A) and (C) are secondary electron images, while (B) and (D) are the corresponding backscattered electron images.

Figure S51: Electron Micrographs of 3-H-Et-Polymer. (A) and (C) are secondary electron images, while (B) and (D) are the corresponding backscattered electron images.
Figure S52: Electron micrographs of crystalline 3-Et-H-Cage. (A), (B), (C) and (D) were captured before activation with liquid ethane, whereas (E) and (F) afterwards. Pictures (A), (C), (E) and (F) are secondary electron images, while (B) and (D) are the corresponding backscattered electron images.
Figure S53: Electron micrographs of 3-Et-H-Polymer. (A) und (C) are the secondary electron images, while (B) and (D) are the corresponding backscattered electron images.

Figure S54: Electron micrographs of 3-Et-Et-Polymer. (A) und (C) are secondary electron images, while (B) and (D) are the corresponding backscattered electron images.
12 Powder X-ray diffractograms

Figure S55: Powder X-ray diffraction profile of 3-Et-Et-Cage$_{\Delta}$.

Figure S56: Powder X-ray diffraction profile of 3-Et-Et-Cage$_{\text{ethane}}$.
Figure S57: Powder X-ray diffraction profile of 3-Et-H-CageΔ.

Figure S58: Powder X-ray diffraction profile of 3-Et-H-Cageethane.
Figure S59: Powder X-ray diffraction profile of 3-Et-H-Polymer.

Figure S60: Powder X-ray diffraction profile of 3-Et-Et-Polymer.
Figure S61: Powder X-ray diffraction profile of 3-H-Et-Polymer.

Figure S62: Powder X-ray diffraction profile of 3-H-H-Polymer.
Figure S63: Powder X-ray diffraction profiles comparison between (A) 3-Et-H-Cage$_{\Delta}$, (B) 3-Et-H-Cage$_{\text{calc}}$ and (C) 3-Et-H-Cage$_{\text{ethane}}$. 3-Et-H-Cage$_{\text{calc}}$ (B) is a simulated powder X-ray diffraction profile received from single-crystal X-ray diffraction data.
13 Single-crystal X-ray diffraction data

General remarks
All crystals were obtained in closed flat bottom tubes (35 x 7.8 mm) by very slow evaporation of the appropriate solvent through a PE-plug (1-4 weeks). The crystallisation batches were protected from light. All obtained crystals of cages are extremely sensitive to the loss of solvent, and needed to be kept under a solvent atmosphere all the time or cooled down to – 78 °C.

Crystal structure of compound 1-Et
CCDC-number : 1588271
Solvent : CHCl₃

Table 1: Crystal data and structure refinement for.

| Property                              | Value                  |
|---------------------------------------|------------------------|
| Empirical formula                    | C₁₅H₂₇N₃               |
| Formula weight                       | 249.39                 |
| Temperature                          | 200(2) K               |
| Wavelength                           | 0.71073 Å              |
| Crystal system                       | monoclinic             |
| Space group                          | P2₁/c                  |
| Z                                     | 4                      |
| Unit cell dimensions                 | a = 9.1876(6) Å        |
|                                      | b = 15.9379(10) Å      |
|                                      | c = 10.0928(7) Å       |
|                                      | α = 90 deg.            |
|                                      | β = 102.9749(19) deg.  |
|                                      | γ = 90 deg.            |
| Volume                               | 1440.17(16) Å³        |
| Density (calculated)                 | 1.15 g/cm³             |
| Absorption coefficient               | 0.07 mm⁻¹              |
| Crystal shape                        | polyhedron             |
| Crystal size                         | 0.080 x 0.060 x 0.050 mm³ |
| Crystal colour                       | colourless             |
| Theta range for data collection      | 2.3 to 25.0 deg.       |
| Index ranges                         | -10≤h≤10, -18≤k≤18, -12≤l≤12 |
| Reflections collected                | 9063                   |
| Independent reflections              | 2533 (R(int) = 0.0368) |
| Observed reflections                 | 1727 (I > 2σ(I))       |
| Absorption correction                | Semi-empirical from equivalents |
| Max. and min. transmission           | 0.96 and 0.89          |
| Refinement method                    | Full-matrix least-squares on F² |
| Data/restraints/parameters           | 2533 / 0 / 190         |
| Goodness-of-fit on F²                | 1.05                   |
| Final R indices (I>2sigma(I))        | R1 = 0.049, wR2 = 0.122 |
| Largest diff. peak and hole          | 0.19 and -0.17 eÅ⁻³    |
Figure S64: Molecular structure of 1-Et as determined by X-ray diffraction. Atoms of carbon are depicted in white and nitrogen in blue.

**Crystal structure of compound 3-Et-Et-α**

| Identification code | jol1sq |
|---------------------|--------|
| Empirical formula   | C_{120}H_{156}N_{12} |
| Formula weight      | 1766.56 |
| Temperature         | 100(2) K |
| Wavelength          | 1.54178 Å |
| Crystal system      | trigonal |
| Space group         | R3 |
| Z                   | 3 |
| Unit cell dimensions | a = 25.004(3) Å  $\alpha = 90$ deg.  
b = 25.004(3) Å  $\beta = 90$ deg.  
c = 20.623(5) Å  $\gamma = 120$ deg. |
| Volume              | 11166(4) Å³ |
| Density (calculated) | 0.79 g/cm³ |
| Absorption coefficient | 0.35 mm⁻¹ |
| Crystal shape       | plate |
| Crystal size        | 0.150 x 0.100 x 0.004 mm³ |
| Crystal colour      | colourless |
| Theta range for data collection | 4.8 to 47.2 deg. |
| Index ranges        | -13≤h≤23, -20≤k≤23, -19≤l≤19 |
Reflections collected 4324
Independent reflections 2695 (R(int) = 0.1161)
Observed reflections 1454 (I > 2σ(I))
Absorption correction Semi-empirical from equivalents
Max. and min. transmission 1.96 and 0.44
Refinement method Full-matrix least-squares on F²
Data/restraints/parameters 2695 / 442 / 373
Goodness-of-fit on F² 1.13
Final R indices (I>2sigma(I)) R1 = 0.114, wR2 = 0.292
Absolute structure parameter 4.1(10)
Largest diff. peak and hole 0.26 and -0.27 eÅ⁻³

Figure S65: Molecular structure of 3aa-α as determined by X-ray diffraction. Atoms of carbon are depicted in white and nitrogen in blue.

Crystal structure of compound 3-Et-Et-β

CCDC-number : 1588272
Solvent : Toluene

Table 2: Crystal data and structure refinement.

| Identification code | jol5sq |
|---------------------|--------|
| Empirical formula   | C₁₂₀H₁₅₆N₁₂ |
| Formula weight      | 1766.56 |
| Temperature         | 100(2) K |
| Wavelength          | 1.54178 Å |
| Crystal system      | tetragonal |
| Property                     | Value                                      |
|------------------------------|--------------------------------------------|
| Space group                  | P4;2;2                                     |
| Z                            | 4                                          |
| Unit cell dimensions         | a = 15.7284(1) Å, α = 90 deg.             |
|                              | b = 15.7284(1) Å, β = 90 deg.             |
|                              | c = 55.3968(12) Å, γ = 90 deg.            |
| Volume                       | 13704.2(4) Å³                             |
| Density (calculated)         | 0.86 g/cm³                                 |
| Absorption coefficient       | 0.38 mm⁻¹                                  |
| Crystal shape                | irregular                                  |
| Crystal size                 | 0.200 x 0.100 x 0.070 mm³                 |
| Crystal colour               | colourless                                 |
| Theta range for data collection | 3.2 to 47.2 deg.                         |
| Index ranges                 | -14 ≤ h ≤ 13, -14 ≤ k ≤ 14, -52 ≤ l ≤ 51 |
| Reflections collected        | 32702                                      |
| Independent reflections      | 6162 (R(int) = 0.0475)                     |
| Observed reflections         | 4237 (I > 2σ(I))                          |
| Absorption correction        | Semi-empirical from equivalents           |
| Max. and min. transmission   | 1.61 and 0.65                             |
| Refinement method            | Full-matrix least-squares on F²            |
| Data/restraints/parameters   | 6162 / 1155 / 595                         |
| Goodness-of-fit on F²        | 1.03                                       |
| Final R indices (I>2sigma(I))| R1 = 0.089, wR2 = 0.245                    |
| Absolute structure parameter | 0.4(3)                                     |
| Largest diff. peak and hole  | 0.38 and -0.26 eÅ⁻³                        |

**Figure S66:** Molecular structure of 3-Et-Et-β as determined by X-ray diffraction. Atoms of carbon are depicted in white and nitrogen in blue.
Table 2: Crystal data and structure refinement for jol8.

| Property                                      | Value                                      |
|-----------------------------------------------|--------------------------------------------|
| Identification code                           | jol8                                       |
| Empirical formula                             | C_{107}H_{130}Cl_{22}N_{12}               |
| Formula weight                                | 2364.12                                    |
| Temperature                                   | 100(2) K                                   |
| Wavelength                                    | 1.54178 Å                                  |
| Crystal system                                | monoclinic                                 |
| Space group                                   | P2\_1/n                                    |
| \( Z \)                                       | 4                                          |
| Unit cell dimensions                          | \( a = 16.0211(8) \text{ Å} \) \( \alpha = 90 \text{ deg.} \) |
|                                              | \( b = 41.134(2) \text{ Å} \) \( \beta = 110.782(4) \text{ deg.} \) |
|                                              | \( c = 19.4840(10) \text{ Å} \) \( \gamma = 90 \text{ deg.} \) |
| Volume                                        | 12004.8(11) Å\(^3\)                       |
| Density (calculated)                          | 1.31 g/cm\(^3\)                           |
| Absorption coefficient                        | 4.97 mm\(^{-1}\)                          |
| Crystal shape                                 | plate                                      |
| Crystal size                                  | 0.180 x 0.12 x 0.040 mm\(^3\)             |
| Crystal colour                                | colourless                                 |
| Theta range for data collection               | 3.1 to 44.5 deg.                          |
| Index ranges                                  | -13 \leq h \leq 14, -37 \leq k \leq 37, -17 \leq l \leq 17 |
| Reflections collected                         | 36874                                      |
| Independent reflections                       | 9224 (R(int) = 0.1379)                     |
| Observed reflections                          | 5738 (I > 2\( \sigma(I) \))               |
| Absorption correction                         | Semi-empirical from equivalents            |
| Max. and min. transmission                    | 2.48 and 0.45                              |
| Refinement method                             | Full-matrix least-squares on F\(^2\)      |
| Data/restraints/parameters                    | 9224 / 4470 / 1315                         |
| Goodness-of-fit on F\(^2\)                    | 2.12                                       |
| Final R indices (I>2\( \sigma(I) \))         | R1 = 0.200, wR2 = 0.505                    |
| Largest diff. peak and hole                   | 1.73 and -0.76 eÅ\(^3\)                   |
**Figure S67:** Molecular structure of 3-Et-H as determined by X-ray diffraction. Atoms of carbon are depicted in white and nitrogen in blue.
14 Reference

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