Supplementary Material (ESI) for Chemical Communications

Supporting information

for the publication

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Two diamino-substituted lithiocarbanions in one molecule – identification of reaction paths in the charge density of isolated intermediates

Syntheses

Synthesis of 1 and bis(2-deuterio-3-methyl-1,3-diazacyclohex-1-yl)methane:

A solution of bis(3-methyl-1,3-diazacyclohex-1-yl)methane (3.62 g, 17.1 mmol) in pentane (20 mL) was added dropwise to a pentane solution of *t*BuLi (1.7 M, 10.1 mL, 17.1 mmol) with rigorous stirring at -78 °C. The reaction mixture was stirred for 10 h and allowed to reach ambient temperature. A white product precipitated. The mixture was filtered, the solid was washed with pentane (3x10 mL) and dried under vacuum. The product was crystallised from the clear filtrate at 4 °C. Colourless crystals were obtained, yield 3.23 g, 84%; ^{1}H NMR (600 MHz, d_8-tol): δ = 1.26 (s, 2H, LiC*H*), 1.18 (m, 2H, NC*H*(ax)$_2$CH$_2$), 2.76 (m, 2H, NC*H*(eq)$_2$CH$_2$), 1.35 (m, 2H, NC*H*(ax)$_2$CH$_2$), 3.02 (m, 2H, NC*H*(eq)$_2$CH$_2$), 1.45 (m, 2H, CH$_2$C*H*(ax)$_2$CH$_2$), 2.03 (m, 2H, CH$_2$C*H*(ax)$_2$CH$_2$), 2.27 (s, 6H, NC*H*$_3$), 2.61 (s, 2H, NC*H*$_2$N); ^{13}C{H} NMR (150 MHz, d_8-tol): δ = 26.3 (CH$_2$*C*H$_2$CH$_2$), 46.0 (N*C*H$_3$), 55.2 and 58.6 (N*C*H$_2$CH$_2$), 85.3 (N*C*H$_2$N), 91.8 (br, Li*C*H). ^{7}Li NMR (194 MHz, d_8-tol): δ = 0.98. Found: C, 59.09; H, 9.64; N, 24.87. Calc. for $C_{11}H_{22}Li_2N_4$ (224.21): C, 58.93; H, 9.89, N, 24.99%.

In another experiment the crude reaction mixture was concentrated under vacuum and hydrolysed with D_2O, extracted with ether, distilled and characterised by NMR spectroscopy.

^{1}H NMR (500 MHz, CDCl$_3$): δ 1.64 (br, 4H, CH$_2$C*H*$_2$CH$_2$), 2.17 (s, 6H, NC*H*$_3$), 2.48 (br, 8H, NC*H*$_2$CH$_2$), 3.11 (s, 2H, C*H*D), 3.68 (s, 2H, NC*H*$_2$N); ^{13}C{H} NMR (125 MHz, CDCl$_3$): δ 23.4 (CH$_2$*C*H$_2$CH$_2$), 43.0 (N*C*H$_3$), 49.7 and 55.1 (N*C*H$_2$CH$_2$), 74.7 (N*C*H$_2$N), 75.6 (t, *C*HD, $^{1}J_{C,D}$ = 21.7 Hz).

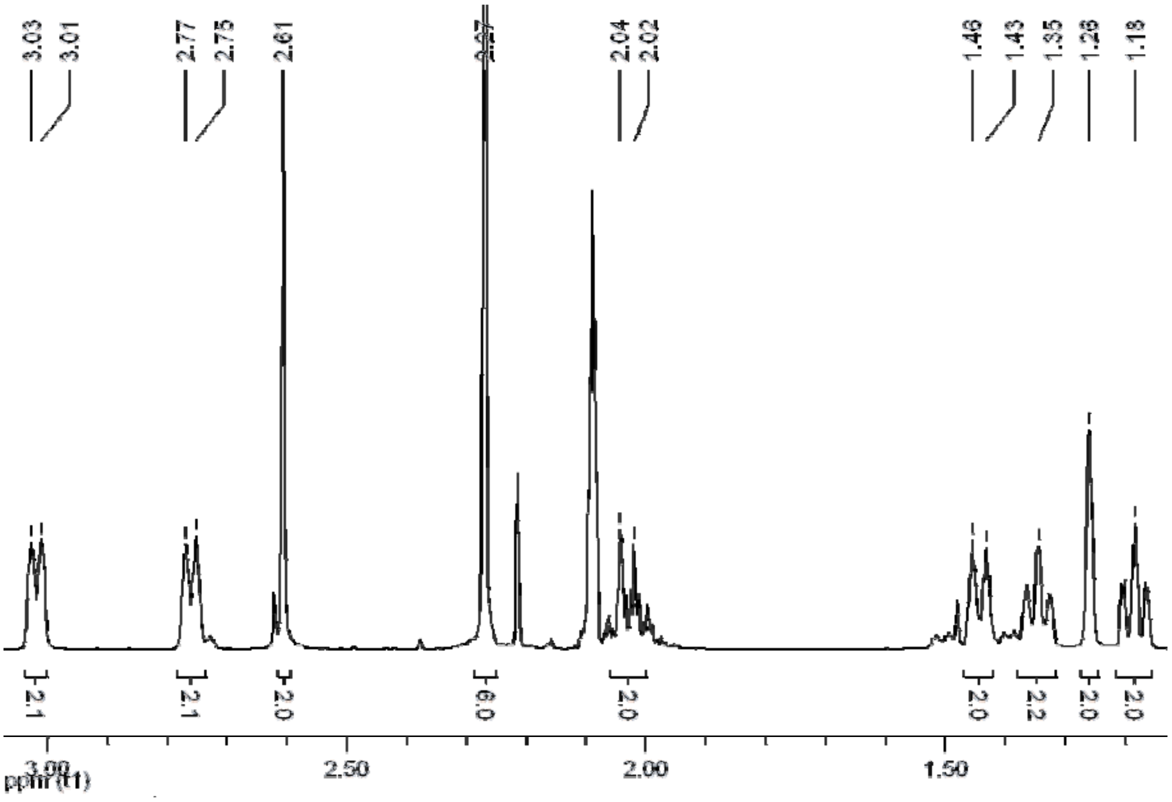


Fig. S1 ^{1}H NMR (600 MHz, d$_8$-tol) spectrum of **1**.

Synthesis of 2 and bis(2-deuterio-3-methyl-1,3-diazacyclopent-1-yl)methane:

A solution of bis(3-methyl-1,3-diazacyclopent-1-yl)methane (2.76 g, 15.0 mmol) in pentane (20 mL) was added dropwise to a pentane solution of *t*BuLi (1.7 M, 8.8 mL, 15.0 mmol) with rigorous stirring at -78 °C. The reaction mixture was stirred for 10 h and allowed to reach ambient temperature. A white product precipitated. The mixture was filtered, the solid was washed with pentane (3x10 mL) and dried under vacuum.

In another experiment the crude reaction mixture was concentrated under vacuum and hydrolysed with D_2O, extracted with ether and characterised by NMR spectroscopy.

^{1}H NMR (500 MHz, C_6D_6): δ = 2.16 (s, 6H, NCH_3), 2.48 (t, 2H, C*H*D, $^2J_{H,D}$ = 3.8 Hz), 2.49/2.80 (t, 8H, CH_2CH_2, $^3J_{H,H}$ = 6.5 Hz), 3.11 (s, 2H,), 3.68 (s, 2H, NCH_2N); ^{13}C{H} NMR (125 MHz, C_6DC_6): δ = 43.0 (N*C*H_3), 49.7 and 55.1 (*C*H_2*C*H_2), 76.3 (t, *C*HD, $^1J_{C,D}$ = 22.3 Hz), 76.7 (N*C*H_2N).

Synthesis of 3:

A solution of *t*BuLi (1.7 M in pentane, 11.8 mL, 20.0 mmol) was added dropwise to a solution of bis(3-methyl-1,3-diazacyclohex-1-yl)methane (4.25 g, 20.0 mmol) in hexane (30 mL) with rigorous stirring at -90 °C. During the addition a white solid precipitated directly. The reaction mixture was allowed to warm to ambient temperature until the precipitate was dissolved again. After slowly cooling first to -100 °C, the product crystallised at -78 °C after one day. Colourless crystals were obtained, yield 4.32 g, 43%; ^{1}H NMR (500 MHz, d$_8$-THF): δ = 0.91/0.93 (s, 2H, LiC*H*), 1.40 - 1.59 (m, 8H, $CH_2C\mathit{H}_2CH_2$), 2.13 (s, 9H, *t*BuLi), 2.20 (s, 12H, $NC\mathit{H}_3$), 2.41/2.60/2.69/3.00 (br, 4H, $NC\mathit{H}_2CH_2$), 3.16 (br, 4H, $NC\mathit{H}_2N$), 3.23 (s, 4H, $NC\mathit{H}_2NCH_3$); ^{13}C{H} NMR (125 MHz, d$_8$-THF): δ = 22.5 ($Me_3\mathit{C}Li$), 22.6/27.6 ($CH_2\mathit{C}H_2CH_2$), 42.2 ($\mathit{C}H_3CLi$), 47.3 ($N\mathit{C}H_3$), 49.3/52.6 and 55.3/59.1 ($N\mathit{C}H_2CH_2$), 73.6 ($N\mathit{C}H_2N$), 75.5 ($N\mathit{C}H_2NCH_3$), 93.1 (br, Li*C*H); ^{7}Li NMR (194 MHz, d$_8$-THF): δ = 1.01.

Electron density topology analyses

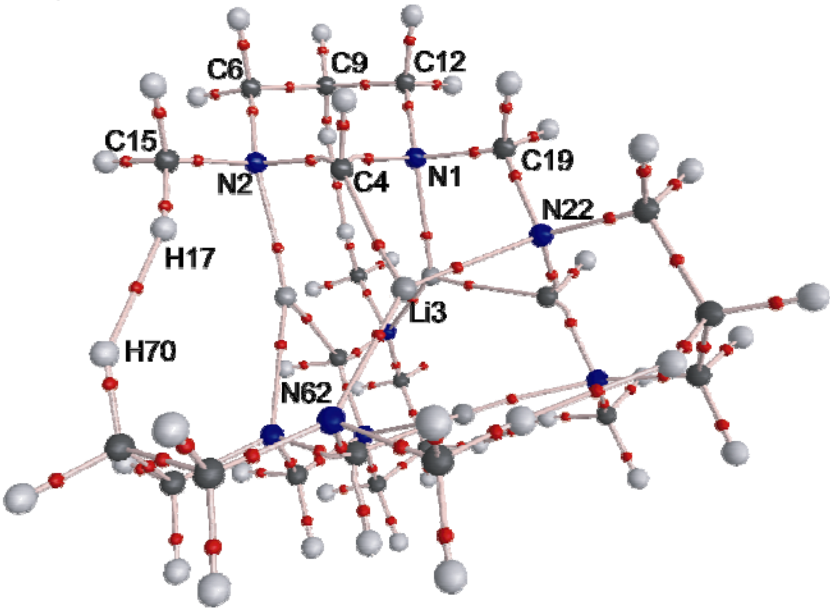


Fig. S2 Molecular graph obtained by a topologic al analysis of the electron density of **1** at B3LYP/TZVPP level of theory. Note that the labels are different from those used in the crystal structure and main manuscript (for symmetry reasons).

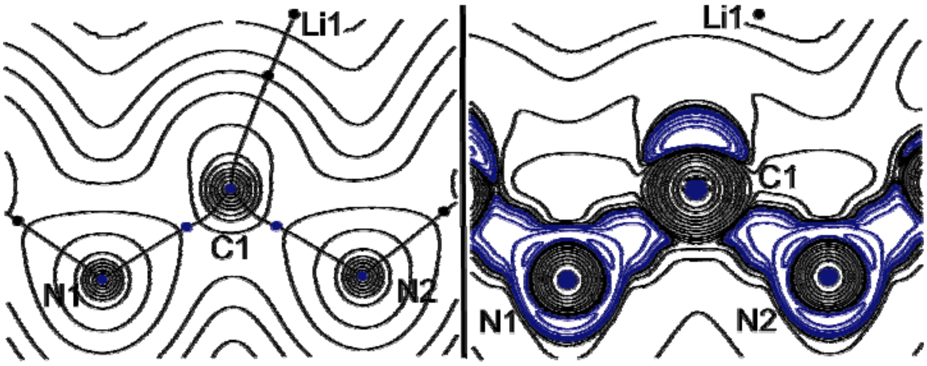


Fig. S3 Map of the electron density (left) and Laplacian (right) in the NCN plane of **1**. The labelling is adapted to the crystal structure notation.

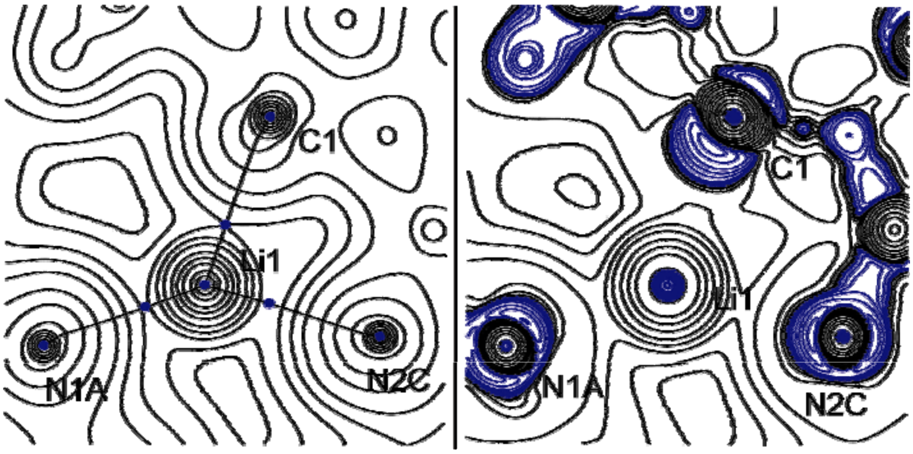


Fig. S4 Map of the electron density (left) and Laplacian (right) in the C1–Li1–N1 plane of **1**. The labelling is adapted to the crystal structure notation.

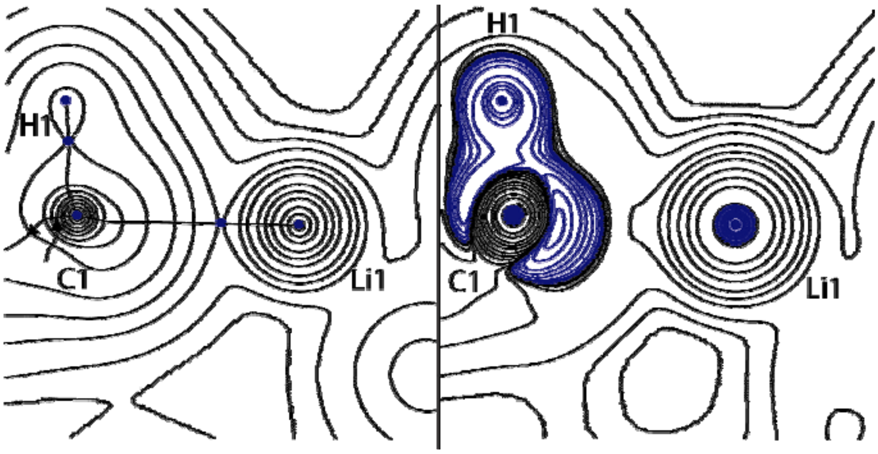


Fig. S5 Map of the electron density (left) and Laplacian (right) in the HCLi plane of **1**. The elctron density map shows the curved bond paths C–H and also C–N (out of plane) about the carbanions. The Laplacian map shows the orientation of the carbanion pair of electrons, which is not exactly towards the lithium cation, but trying to realise an almost tetrahedral surrounding of charge concentrations about this carbanion. The labelling is adapted to the crystal structure notation.

Table S1 Electron density topology parameters for selected bonds in **1** in the calculated ground state as obtained at the B3LYP/TZVPP level of theory. The values given are the distances of the bond critical points (bcp) to the nuclear positions along the bond paths (in Å), the electron densities ρ(rBCP) (in e Å^{-3}) and the values of the Laplacians $\nabla^2\rho$(rBCP) (in e Å^{-5}), the ellipticities of the interaction at the BCP's and energy criterions in atomic units. Labels are provided for the crystallography labelling (manuscript) and calculations (Fig. S2).

A···B crystallogr. label	A···B calculation label	$d_{\text{A-bcp}}$	$d_{\text{B-bcp}}$	ρ_{bcp}	$\nabla^2\rho_{\text{bcp}}$	ε	G_{bcp}	K_{bcp}	V_{bcp}
Li(1)–N(1A)	Li3–N22	0.797	1.400	0.096	2.959	0.086	0.024	-0.007	0.017
Li(1)–N(2C)	Li3–N62	0.759	1.304	0.139	4.270	0.562	0.035	-0.009	0.027
Li(1)–C(1)	Li3–C4	0.762	1.403	0.144	3.663	0.025	0.031	-0.007	0.023
C(1)–N(1)	C4–N1	0.571	0.940	1.292	-2.516	0.214	0.145	0.171	0.316
C(1)–N(2)	C4–N2	0.562	0.938	1.315	-2.660	0.227	0.152	0.180	0.333
N(1)–C(6)	N1–C19	0.989	0.476	1.296	0.443	0.575	0.219	0.215	0.434
N(1)–C(4)	N1–C12	0.983	0.493	1.303	-1.330	0.092	0.200	0.214	0.414
C(2)–C(3)	C8–C9	0.751	0.767	1.462	-10.526	0.035	0.057	0.166	0.223
H(15A)···H(15C)	H17···H70	0.951	0.971	0.114	0.829	0.025	0.009	0.000	0.009

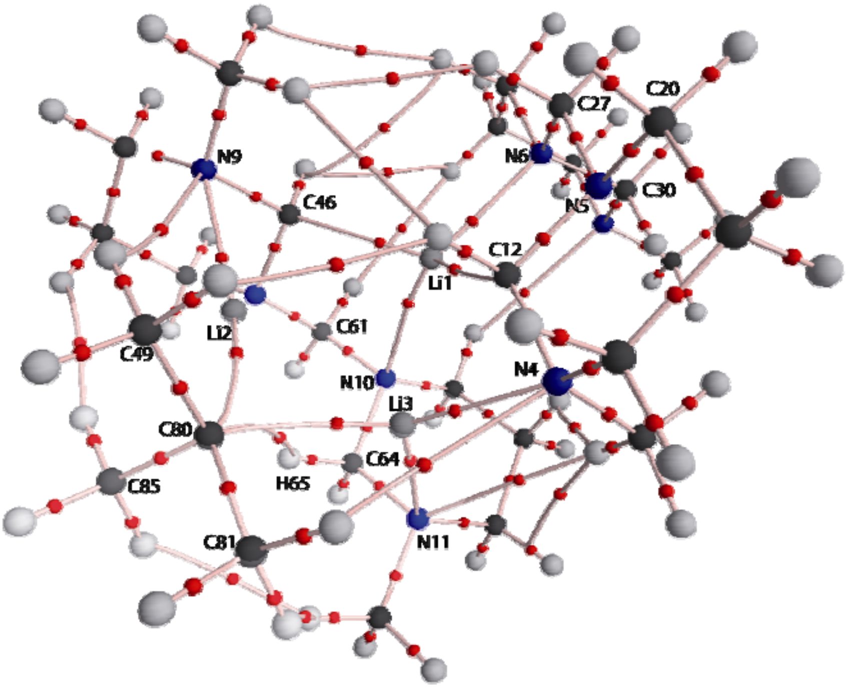


Fig. S6 Molecular graph obtained by a topologic al analysis of the electron density of **3** at B3LYP/TZVPP level of theory. Note that labels here are different from those used for crystallography.

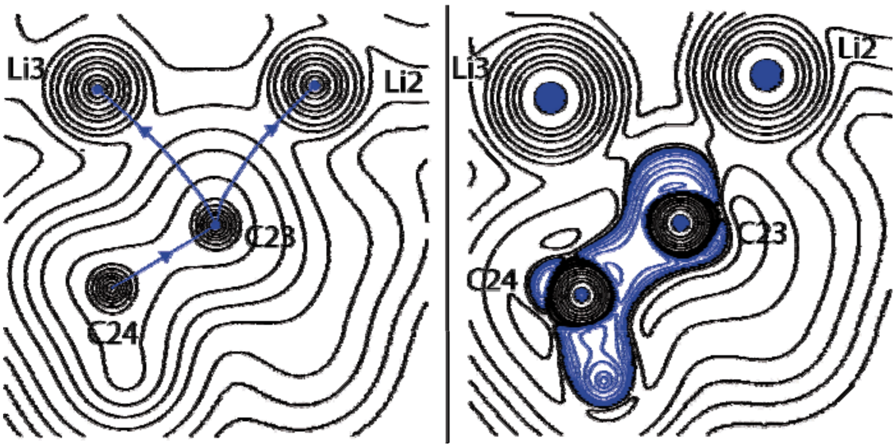


Fig. S7 Map of the electron density (left) and Laplacian (right) in the C23–Li2–Li3plane of **3** showing the interaction of the *tert*-butyl carbanion with two lithium atoms. Note the bonding situation of the carbanion of the *tert*-butyl anion C(23), which shows two curved bond paths to the lithium atoms Li(2) and Li(3) (Figure 5), with its localised charge density (lone pair) oriented towards the centre of these two positively charged atoms.

Table S2 Electron density topology parameters for selected bonds in **3** in the calculated ground state as obtained at the B3LYP/TZVPP level of theory. The values given are the distances of the bond critical points (bcp) to the nuclear positions along the bond paths (in Å), the electron densities ρ(rBCP) (in e Å^{-3}) and the values of the Laplacians $\nabla^2\rho$(rBCP) (in e Å^{-5}), the ellipticities of the interaction at the BCP's and energy criterions in atomic units. Labels are provided for the crystallography labelling (manuscript) and calculations (Fig. S3).

A···B	A···B	$d_{\text{A-bcp}}$	$d_{\text{B-bcp}}$	ρ_{bcp}	$\nabla^2\rho_{\text{bcp}}$	ε	G_{bcp}	K_{bcp}	V_{bcp}
crystallogr. label	calculation label								
Li(2)–C(23)	Li2–C80	0.776	1.400	0.175	2.738	0.044	0.027	–0.002	0.025
Li(3)–C(23)	Li3–C80	0.793	1.486	0.156	2.227	0.185	0.022	–0.001	0.020
C(23)–H(18a)	C80–H65	1.957	1.180	0.046	0.347	0.181	0.003	0.000	0.003
C(23)–C(24)	C80–C81	0.738	0.799	1.609	–13.389	0.086	0.063	0.202	0.265
Li(2)–N(6)	Li2–N9	0.749	1.291	0.189	4.212	0.418	0.038	–0.005	0.033
Li(3)–N(1)	Li3–N4	0.747	1.289	0.188	4.174	0.036	0.038	–0.005	0.032
Li(3)–N(8)	Li3–N11	0.900	1.637	0.056	1.089	0.102	0.009	–0.002	0.006
Li(1)–C(12)	Li1–C46	0.778	1.464	0.171	2.564	0.040	0.025	–0.002	0.023
Li(1)–C(1)	Li1–C12	0.777	1.452	0.171	2.593	0.041	0.025	–0.002	0.023
Li(1)–N(3)	Li1–N6	0.792	1.399	0.131	2.709	0.132	0.023	–0.004	0.019
Li(1)–N(7)	Li1–N10	0.873	1.569	0.075	1.417	0.756	0.012	–0.003	0.009
C(1)-N(2)	C12-N5	1.393	0.889	1.667	–13.331	0.146	0.113	0.252	0.364
C(6)–N(2)	C27–N5	0.605	0.833	1.964	–19.231	0.098	0.112	0.311	0.423
C(4)–N(2)	C20–N5	0.616	0.848	1.820	–15.867	0.041	0.106	0.271	0.378
C(6)–N(3)	C27–N6	0.617	0.857	1.751	–14.613	0.099	0.102	0.253	0.355

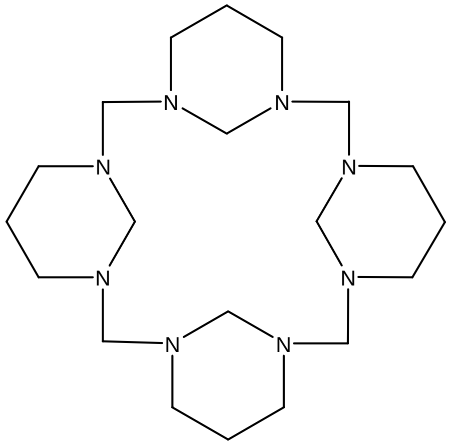
Diffusion coefficient determination for 1 by NMR spectroscopy

Diffusion coefficient determination in dry d_8-toluene at 295.3 K.

NMR diffusion measurements were performed on a Bruker Avance 600 MHz FT-NMR spectrometer. The diffusion experiments were performed using an LED pulse sequence with bipolar gradients as delivered by the manufacturer. The gradient length (δ) was set to 4000 ms and was varied linearly from 5 to 95%. The diffusion delay (Δ) was set to 85 ms. 16 data points per diffusion experiment were collected and 32 scans were applied per increment. Prior to the measurements the heater and the airflow were switched off. and the sample was left in the magnet for an additional 4 h in order to have constant temperature conditions (296 K). Compounds **4** and **5** (see below) were used as a reference for molecular size to determine the grade of aggregation of **1**.

Table S3 Diffusion coefficients of **1**, **4** and **5** as determined by NMR spectroscopy

System	D/m^{2}s^{-1}	Aggregation
1	9.047×10^{-10}	dimer
4	9.05×10^{-10}	monomer
5	1.251×10^{-9}	monomer



4