10.1071/CH21101_AC
Australian Journal of Chemistry

SUPPLEMENTARY MATERIAL

An investigation of five-component [3+2] self–assembled cage formation using amidinium···carboxylate hydrogen bonds

Chriso M. Thomas,† Émer M. Foyle,† Samuel E. Walker and Nicholas G. White*

†These authors contributed equally to this work

Research School of Chemistry, The Australian National University

137 Sullivan's Creek Road, Canberra, ACT, Australia

Email: nicholas.white@anu.edu.au

URL: www.nwhitegroup.com

NMR spectra of new compounds

Tetraphenyl tris-nitrile 4

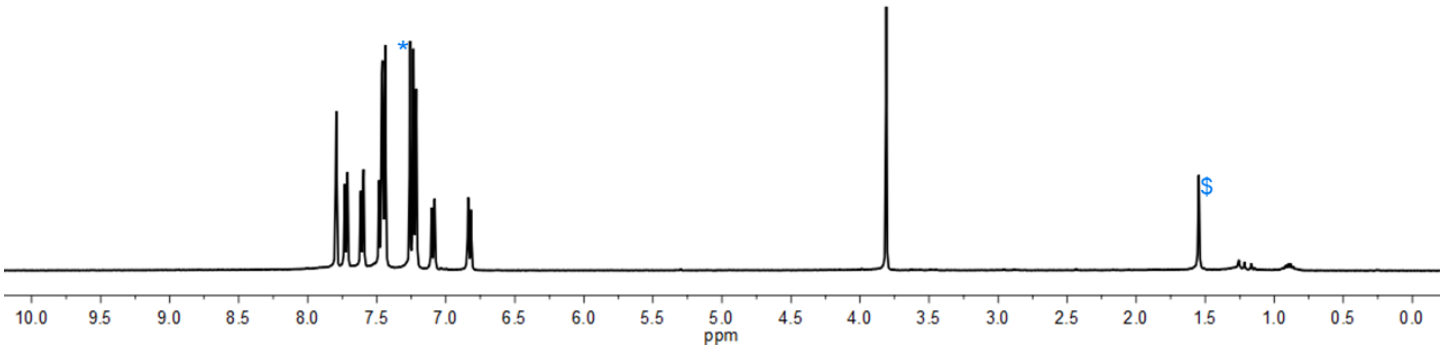

Figure S1. ^{1}H NMR spectrum of 4, peak labelled * results from incompletely deuterated NMR solvent, peak labelled $ results from water ($CDCl_3$, 400 MHz, 298 K).

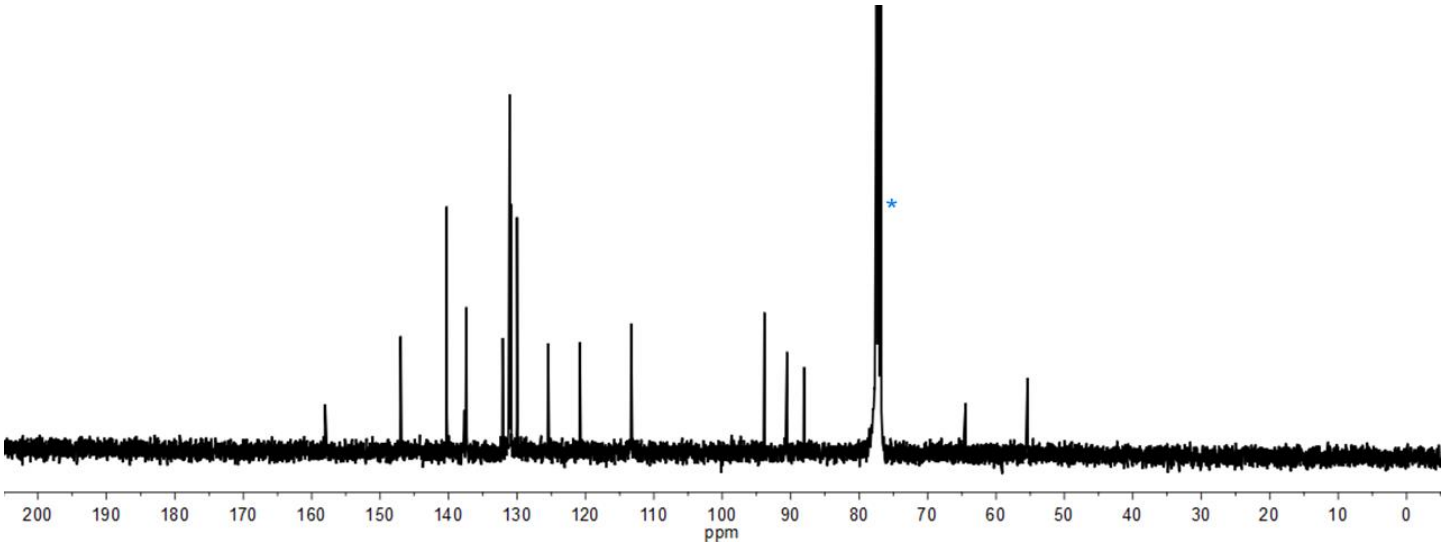

Figure S2. ^{13}C NMR spectrum of 4, peak labelled * results from NMR solvent ($CDCl_3$, 101 MHz, 298 K).

Tetraphenyl tris-amidinium 1·Cl₃

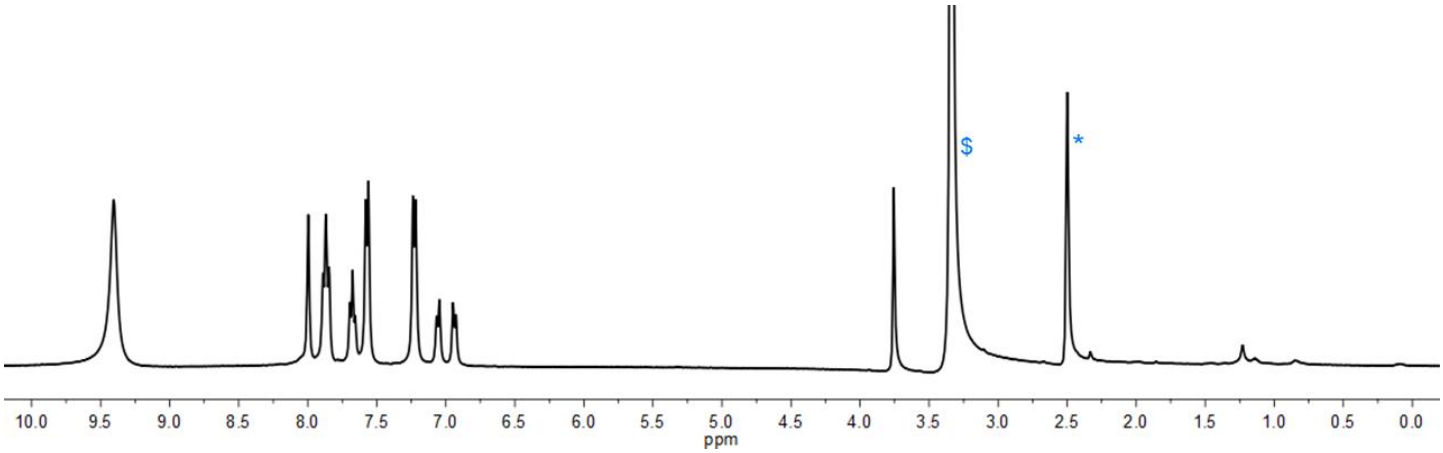

Figure S3. ^{1}H NMR spectrum of **1·Cl₃**, peak labelled * results from incompletely deuterated NMR solvent, peak labelled $ results from water (d_6-DMSO, 400 MHz, 298 K).

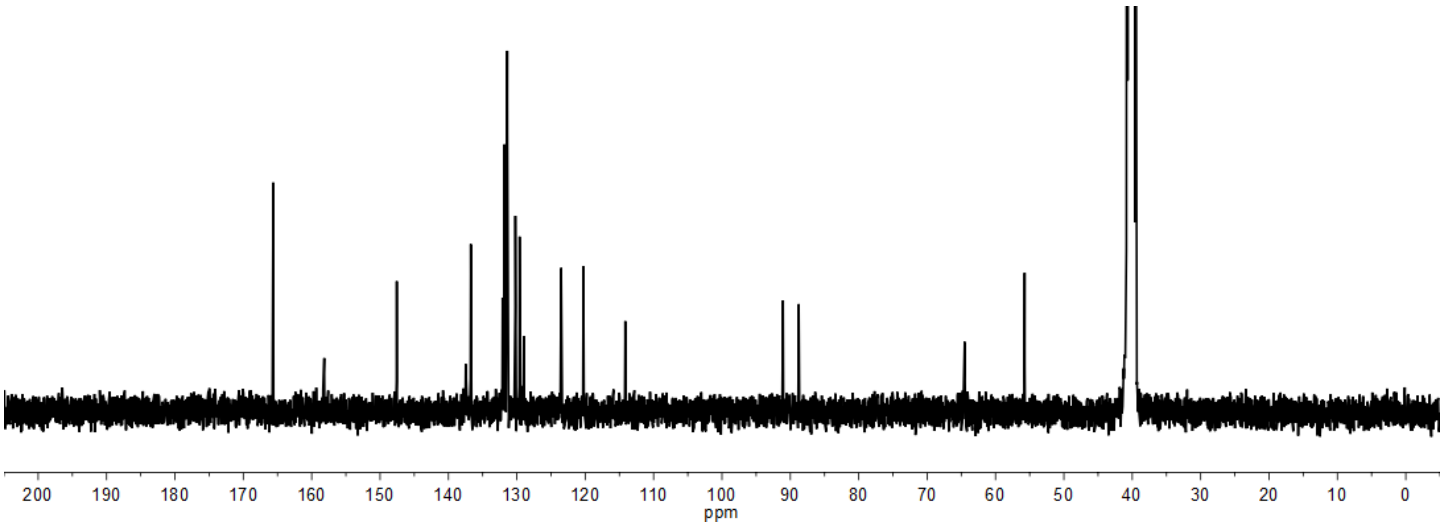

Figure S4. ^{13}C NMR spectrum of **1·Cl₃**, peak labelled * results from NMR solvent (d_6-DMSO, 101 MHz, 298 K).

Tetraphenyl tris-amidinium 1·(BPh$_4$)$_3$

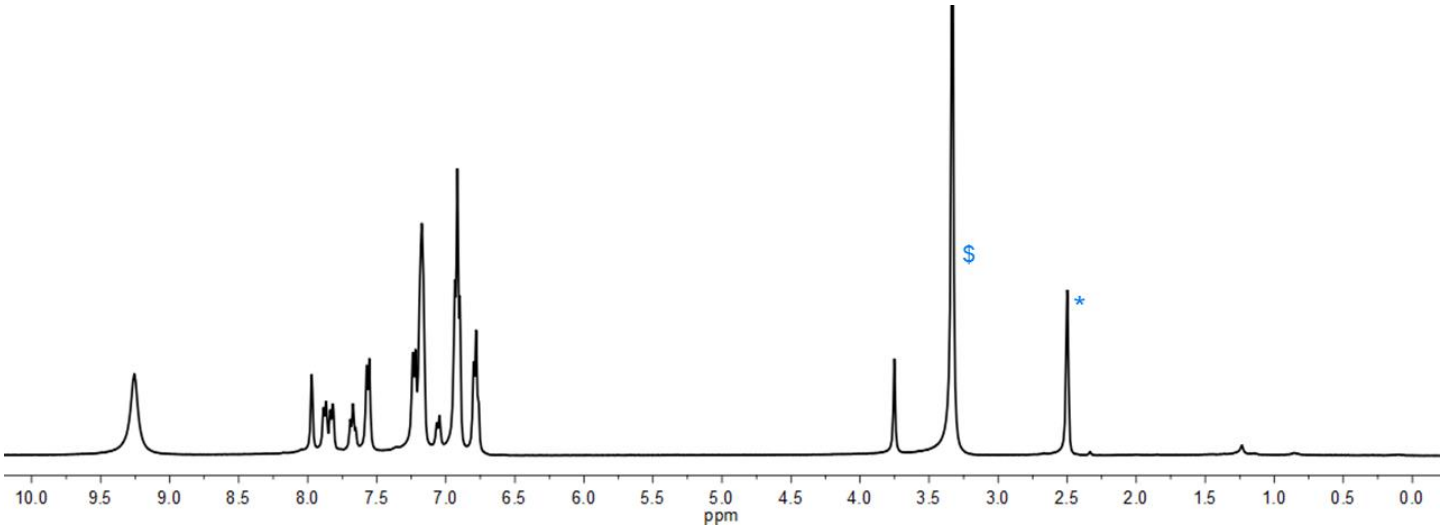

Figure S5. ^{1}H NMR spectrum of **1·(BPh$_4$)$_3$**, peak labelled * results from incompletely deuterated NMR solvent, peak labelled $ results from water (d$_6$-DMSO, 400 MHz, 298 K).

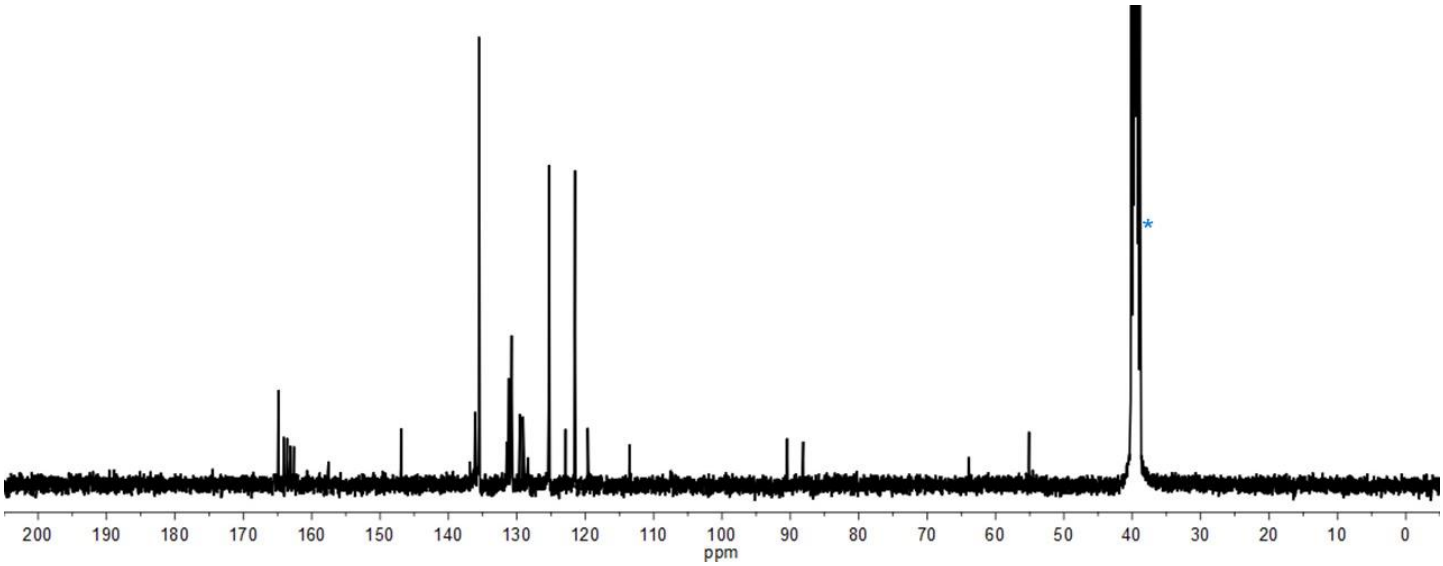

Figure S6. ^{13}C NMR spectrum of **1·(BPh$_4$)$_3$**, peak labelled * results from NMR solvent (d$_6$-DMSO, 101 MHz, 298 K).

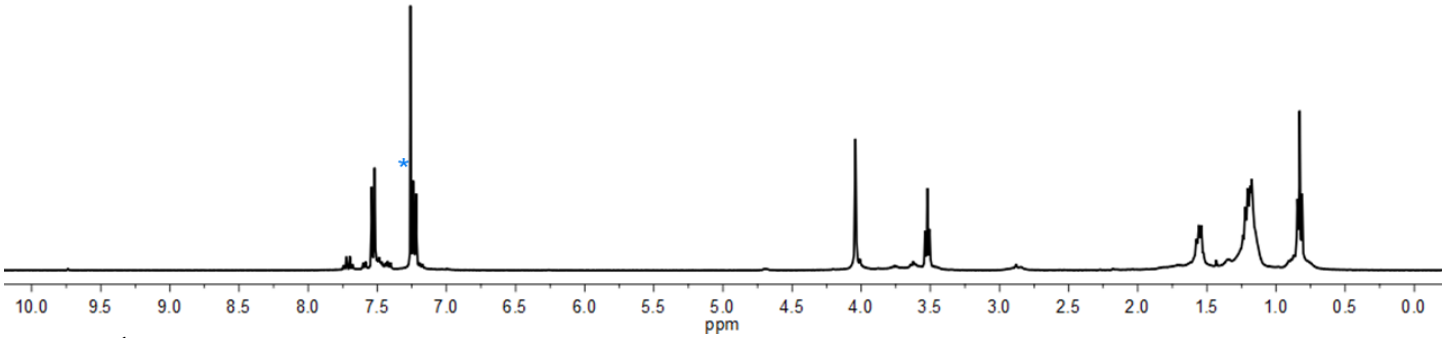

Figure S7. ^{1}H NMR spectrum of **6**, peak labelled * results from incompletely deuterated NMR solvent, peak labelled $ results from water ($CDCl_3$, 400 MHz, 298 K).

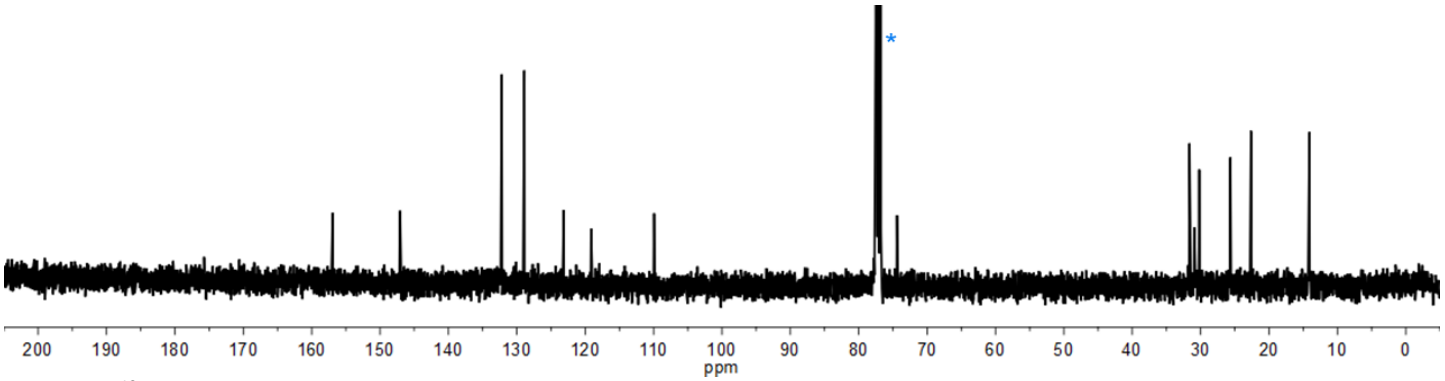

Figure S8. ^{13}C NMR spectrum of **6**, peak labelled * results from NMR solvent ($CDCl_3$, 101 MHz, 298 K).

Tris(hexyloxy)benzene tris-ester 9

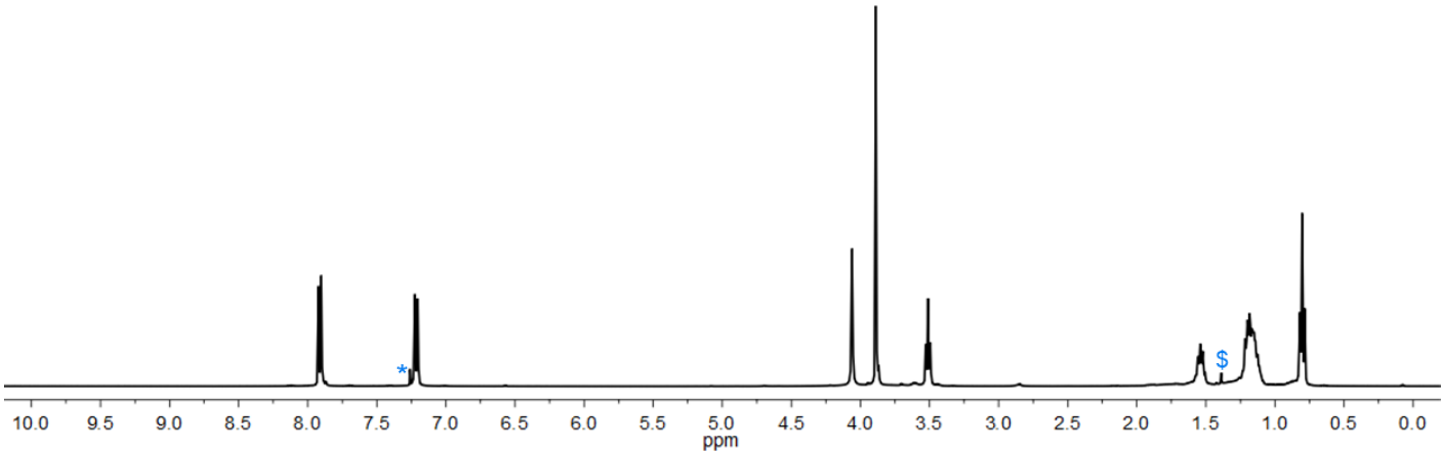

Figure S9. ^{1}H NMR spectrum of **9**, peak labelled * results from incompletely deuterated NMR solvent ($CDCl_3$, 400 MHz, 298 K).

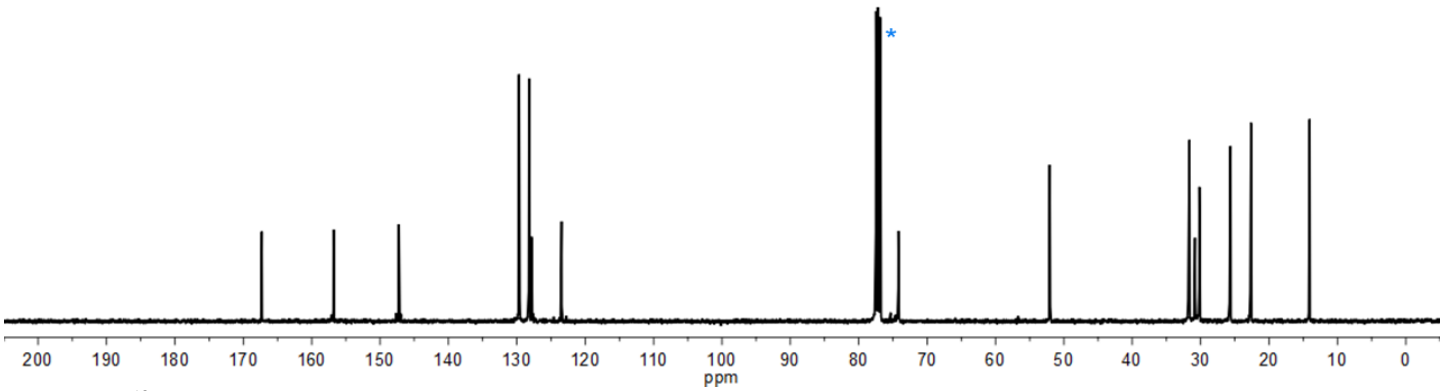

Figure S10. ^{13}C NMR spectrum of **9**, peak labelled * results from NMR solvent ($CDCl_3$, 101 MHz, 298 K).

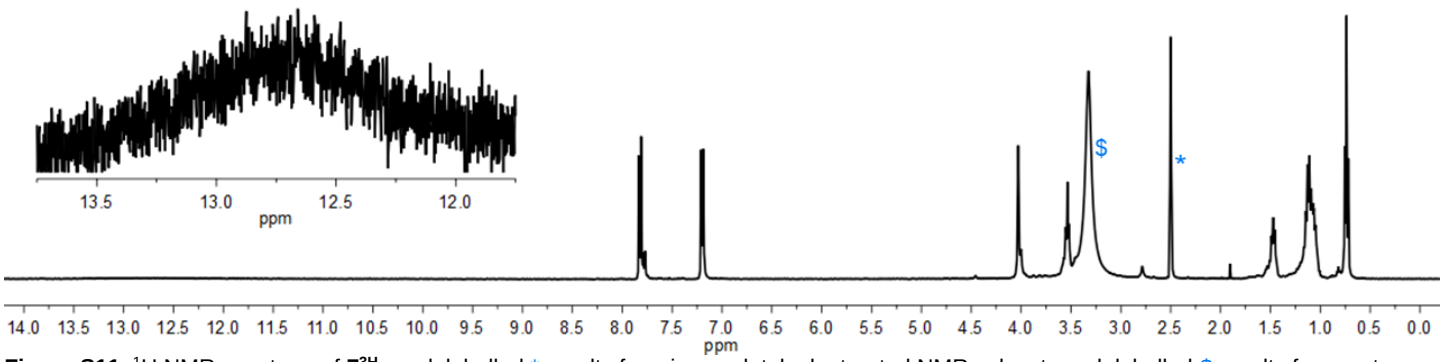

Figure S11. ^{1}H NMR spectrum of **7^{3H}**, peak labelled * results from incompletely deuterated NMR solvent, peak labelled $ results from water (d_6-DMSO, 400 MHz, 298 K).

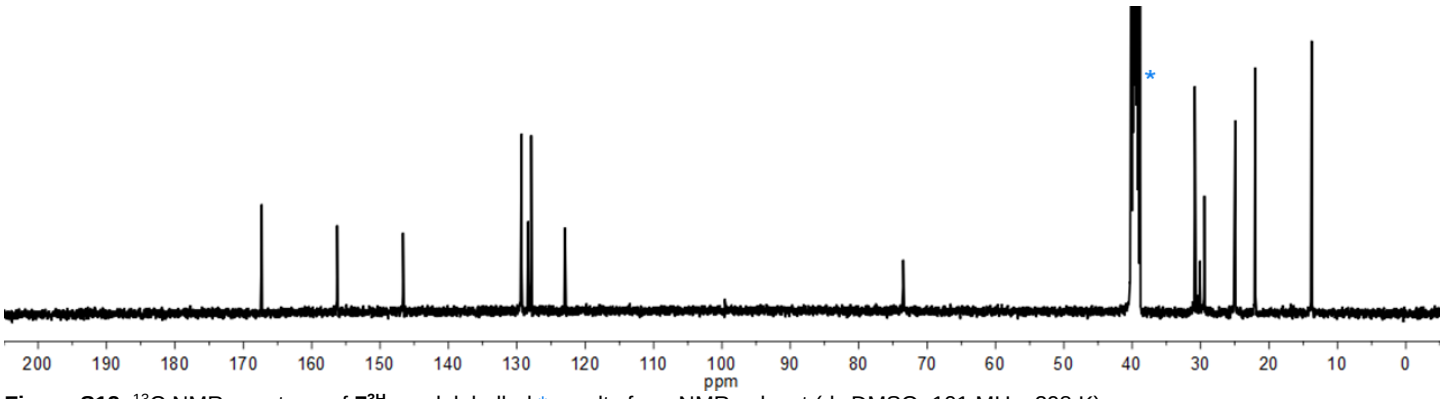

Figure S12. ^{13}C NMR spectrum of **7^{3H}**, peak labelled * results from NMR solvent (d_6-DMSO, 101 MHz, 298 K).

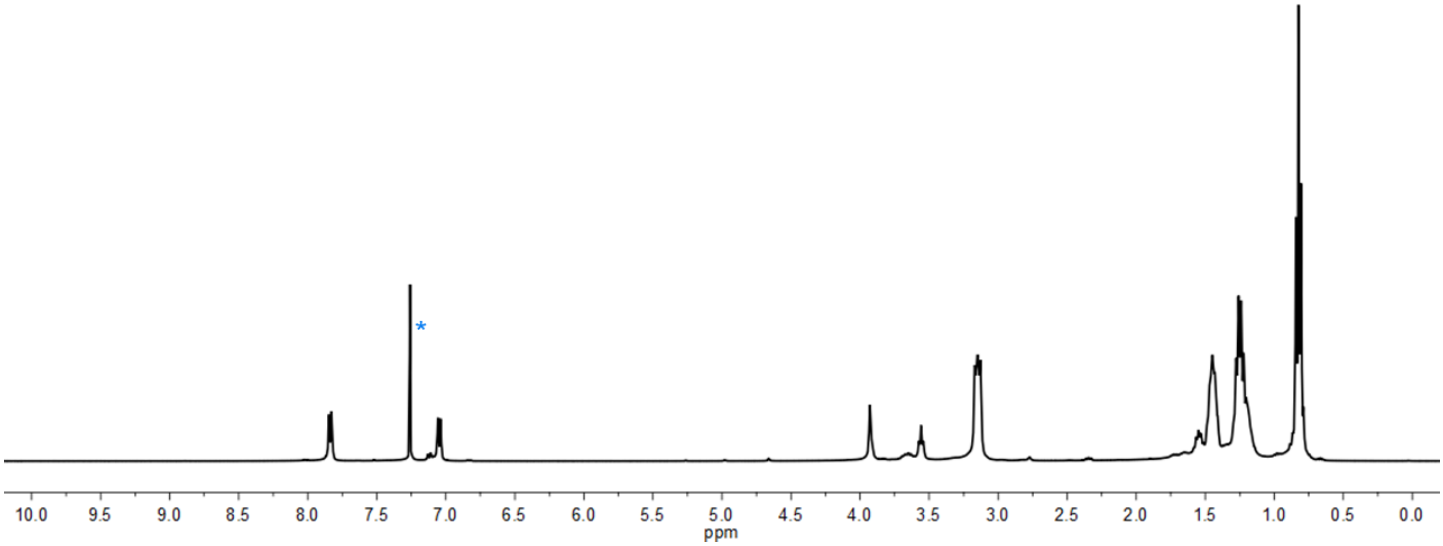

Figure S13. ^{1}H NMR spectrum of **TBA₃·7**, peak labelled * results from incompletely deuterated NMR solvent ($CDCl_3$, 400 MHz, 298 K).

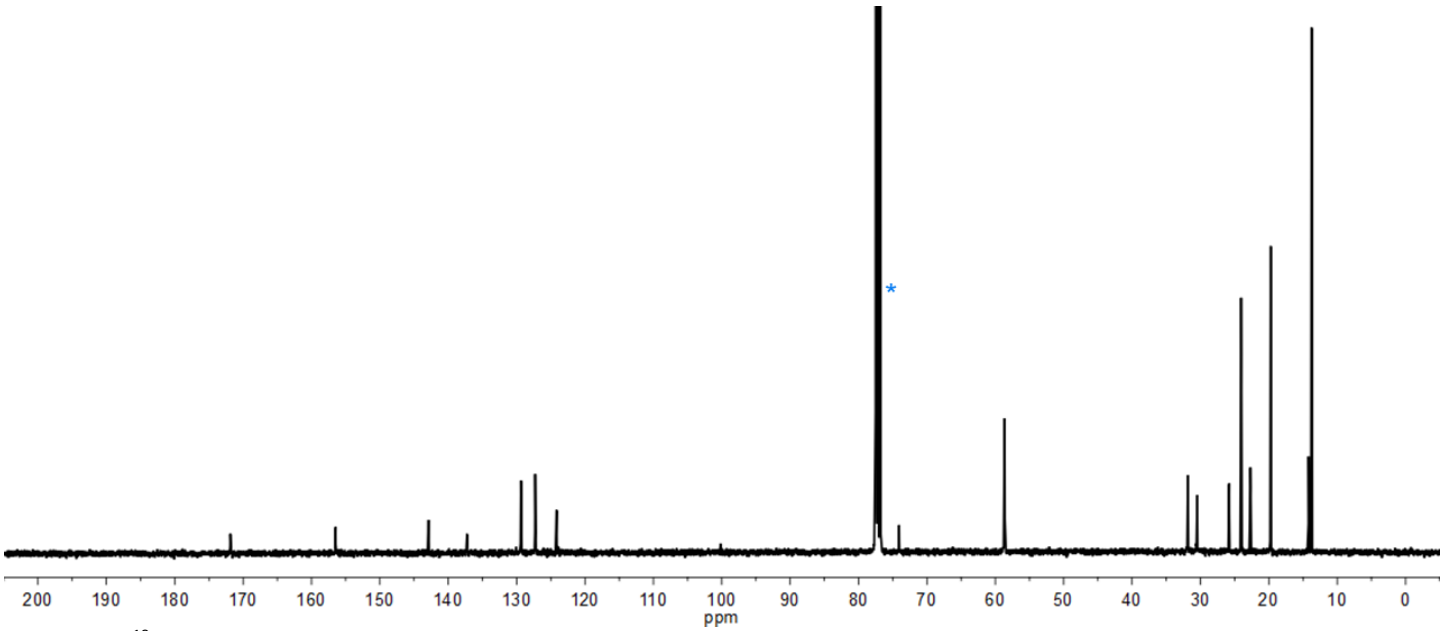

Figure S14. ^{13}C NMR spectrum of **TBA₃·7**, peak labelled * results from NMR solvent ($CDCl_3$, 101 MHz, 298 K).

^{1}H and DOSY NMR spectroscopy of cage self–assembly

General remarks

DOSY NMR spectra were processed in Mestrenova; solvodynamic radii (r_S) were calculated using the Stokes-Einstein equation $D = K_BT/6\pi\eta r_S$. The viscosity of the solutions (η) was estimated by using the viscosity of non-deuterated DMSO (1.987×10^{-3} kg m^{-1} s^{-1}).

Self–assembly of 1$_2$·TP$_3$

The ^{1}H NMR spectra of **1·(BPh$_4$)$_3$** and a 2:3 mixture of **1·(BPh$_4$)$_3$** and **TBA$_2$·TP** are compared in Figure S15. As can be seen, addition of **TBA$_2$·TP** causes only relatively small shifts in peak positions, as well as a slight broadening of the peaks. DOSY NMR (Figure S16) shows that the **TP^{2-}** C–H resonance diffuses at the same rate as the peaks belonging to **1^{3+}**, thus we conclude that the relatively small shifts are due to the C–H peaks of **1^{3+}** being distant from the hydrogen bonding site rather than a lack of interaction. The N–H resonances of **1^{3+}** disappear upon addition of **TP^{2-}**, which we attribute to peak broadening and is common for amidinium···carboxylate interactions in d$_6$-DMSO.[S1,2]

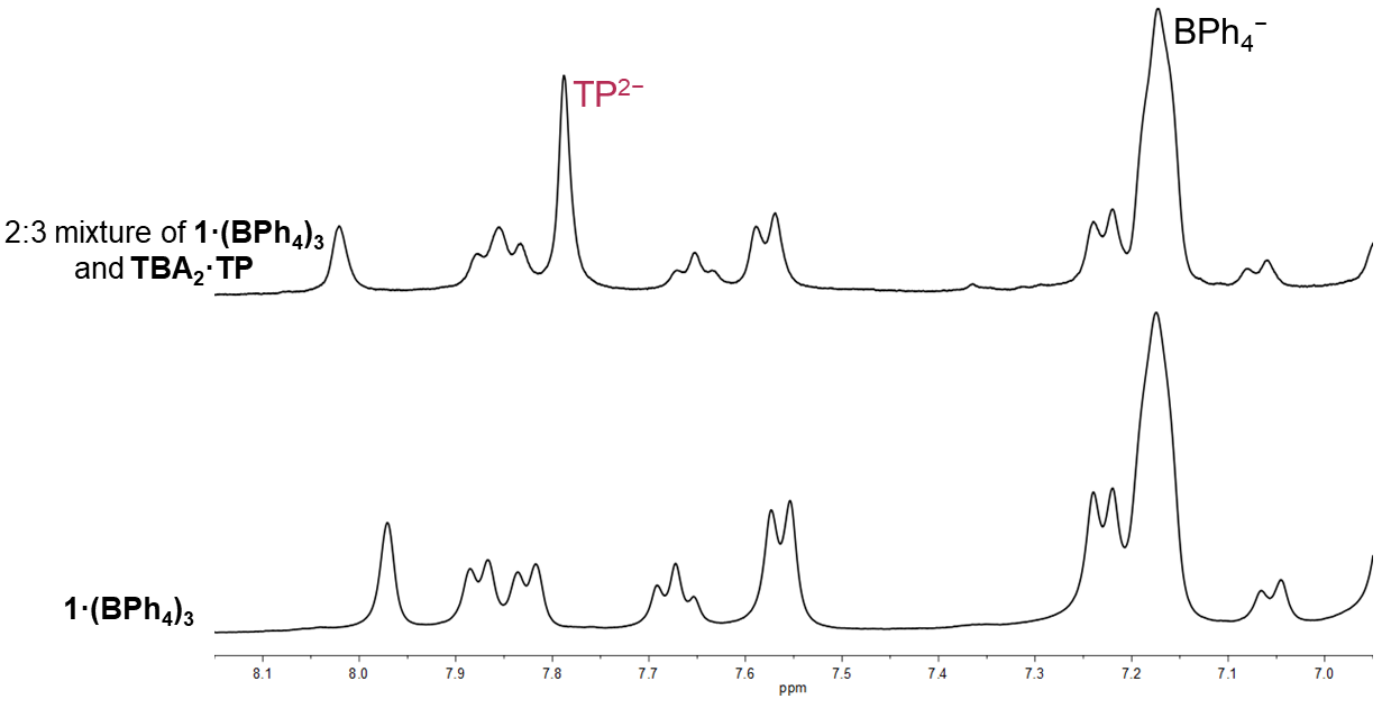

Figure S15. Partial ^{1}H NMR spectrum of a 2:3 mixture of **1·(BPh$_4$)$_3$** and **TBA$_2$·TP** (d$_6$-DMSO, 400 MHz, 298 K).

The DOSY NMR spectrum of a 2:3 mixture of **1·(BPh$_4$)$_3$** and **TBA$_2$·TP** is shown in Figure S16, and compared with the DOSY NMR spectrum of **1·(BPh$_4$)$_3$** (Figure S17).

In addition to using the Stokes-Einstein equation to estimate solvodynamic radii, we estimated these values using the measured *D* value for the BPh_4^- anion from each spectrum as an internal reference. The mixture of $\mathbf{1}^{3+}$ and $\mathbf{TP}^{2-}$ diffuses 3.8 times more slowly than BPh_4^- (0.75 *vs*. 2.9 × 10^{-10} m^2s^{-1}), while $\mathbf{1}^{3+}$ alone diffuses 2.2 times more slowly than BPh_4^- (1.2 *vs.* 2.6 × 10^{-10} m^2s^{-1}), implying that **1$_2$·TP$_3$** has a radius 70% bigger than $\mathbf{1}^{3+}$. This is similar to the difference calculated using the Stokes-Einstein equation (60% bigger).

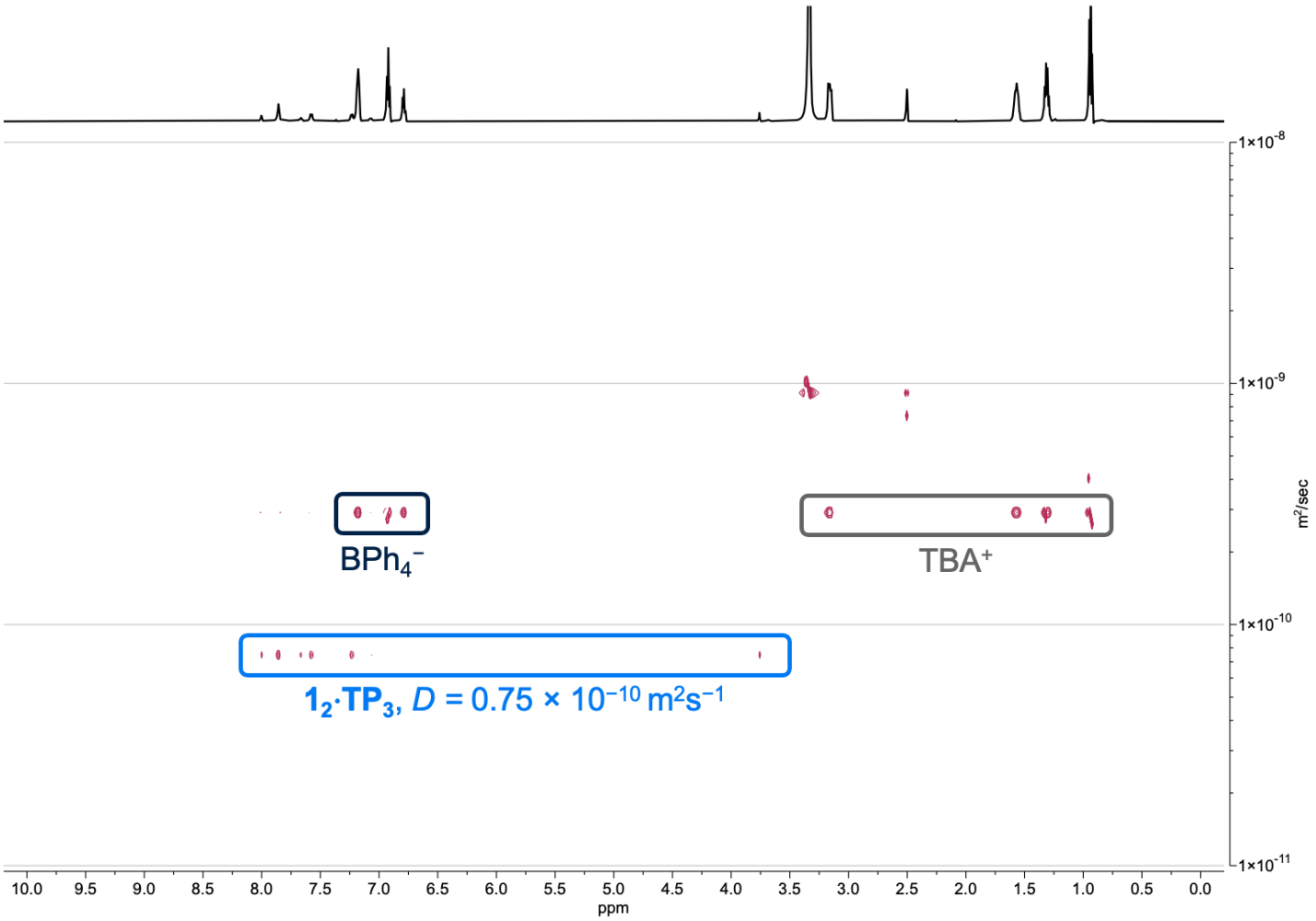

Figure S16. DOSY NMR spectrum of 2:3 mixture of **1·(BPh$_4$)$_3$** and **TBA$_2$·TP** (d_6-DMSO, 600 MHz, 298 K)**.**

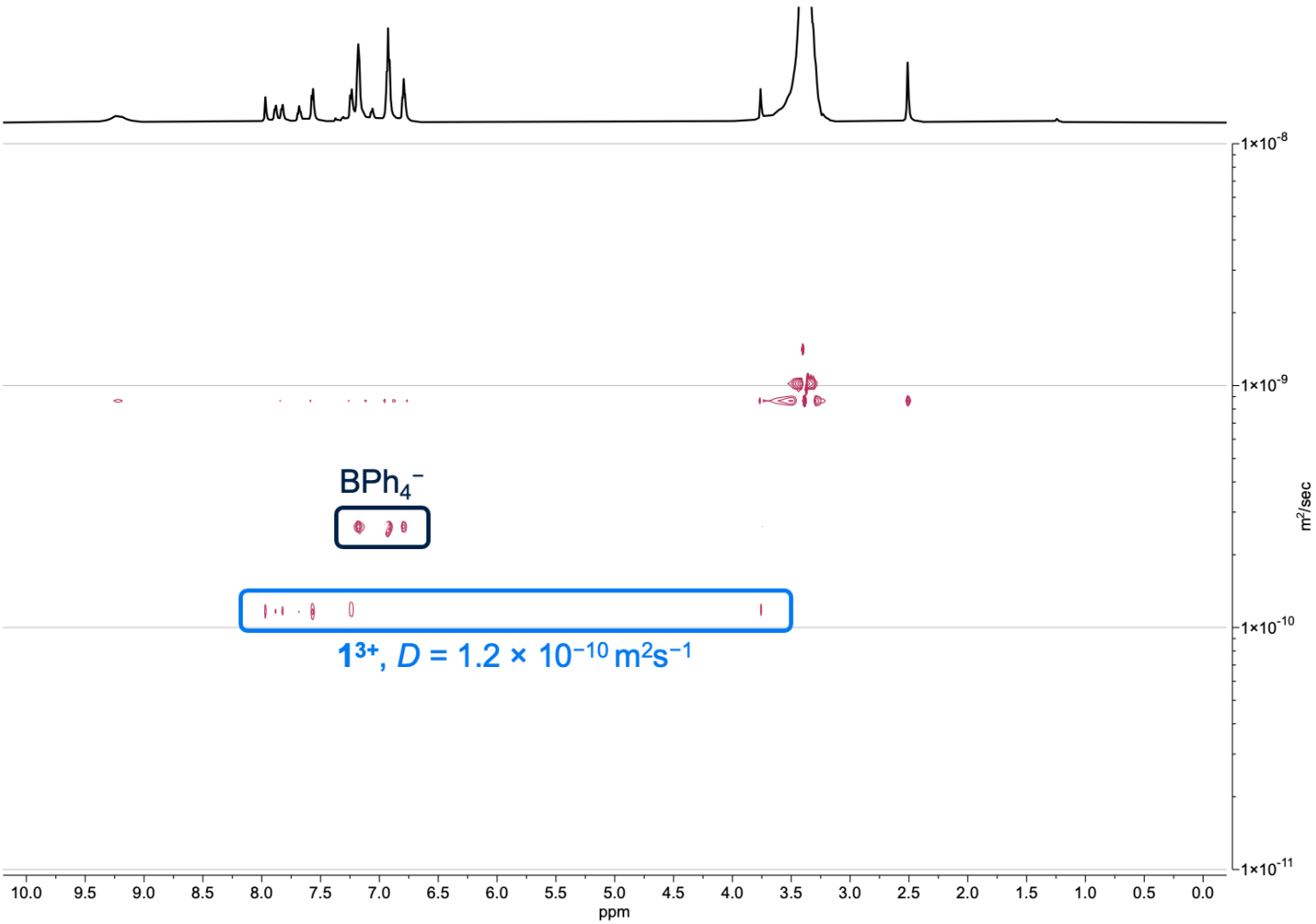

Figure S17. DOSY NMR spectrum of **1·(BPh$_4$)$_3$** (d_6-DMSO, 600 MHz, 298 K).

Self–assembly of 8_3·7_2

The DOSY NMR spectrum of a 2:3 mixture of **TBA_3·7** and **8·$(BPh_4)_2$** is shown in Figure S18, and compared with the DOSY NMR spectrum of **TBA_3·7** (Figure S19).

In addition to using the Stokes-Einstein equation to estimate solvodynamic radii, we estimated these values using the measured *D* value for the TBA^+ cation from each spectrum as an internal reference. The mixture of $\mathbf{7^{3-}}$ and $\mathbf{8^{2+}}$ diffuses 2.9 times more slowly than TBA^+ (1.0 *vs*. 2.9 × 10^{-10} m^2s^{-1}), while $\mathbf{7^{3-}}$ alone diffuses 1.9 times more slowly than TBA^+ (1.5 *vs.* 2.8 × 10^{-10} m^2s^{-1}), implying that **8_3·7_2** has a radius 50% bigger than $\mathbf{7^{3-}}$. This is the same (within error) of the difference calculated using the Stokes-Einstein equation (50% bigger).

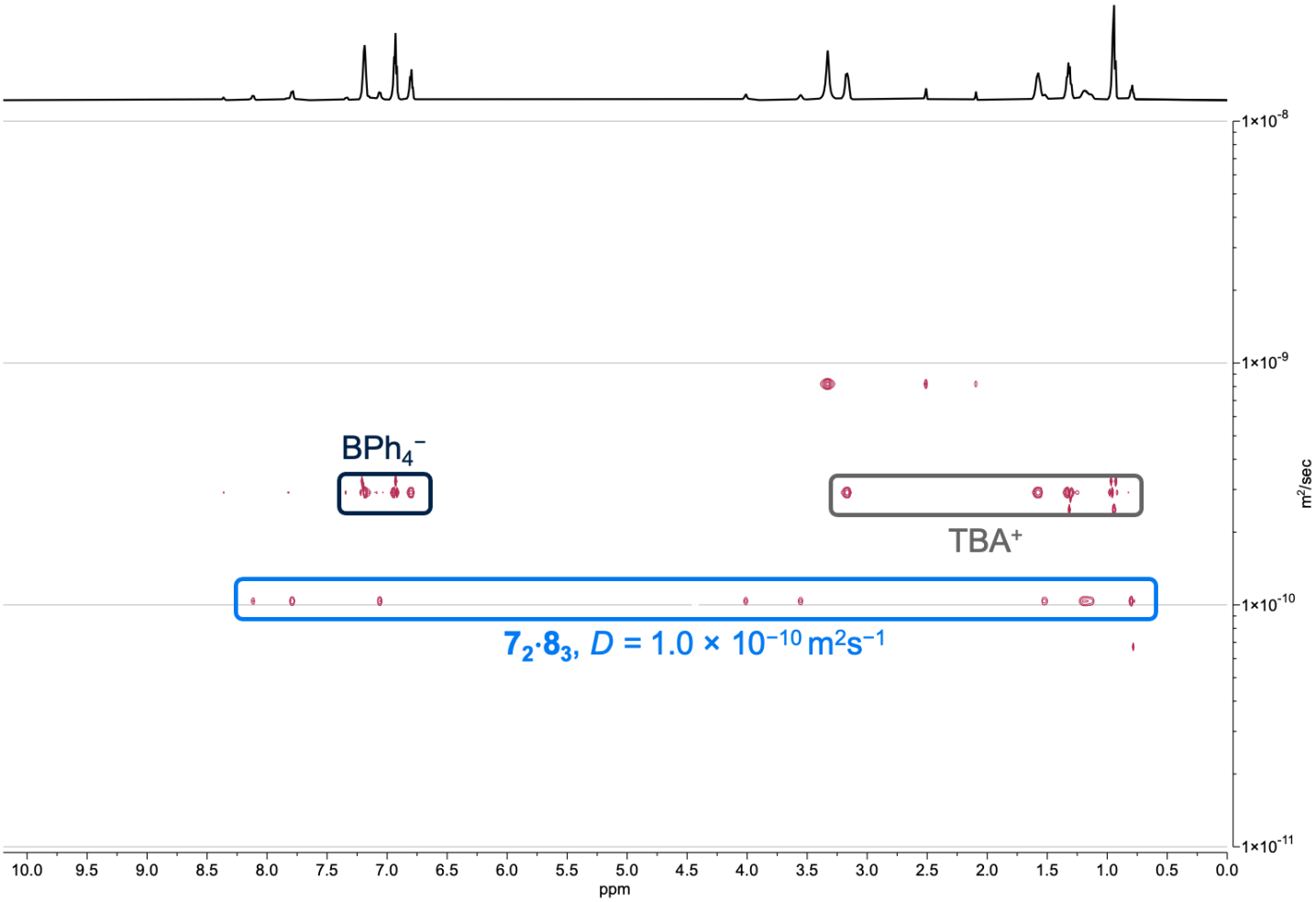

Figure S18. DOSY NMR spectrum 2:3 mixture of **TBA_3·7** and **8·$(BPh_4)_2$** (d_6-DMSO, 600 MHz, 298 K)**.**

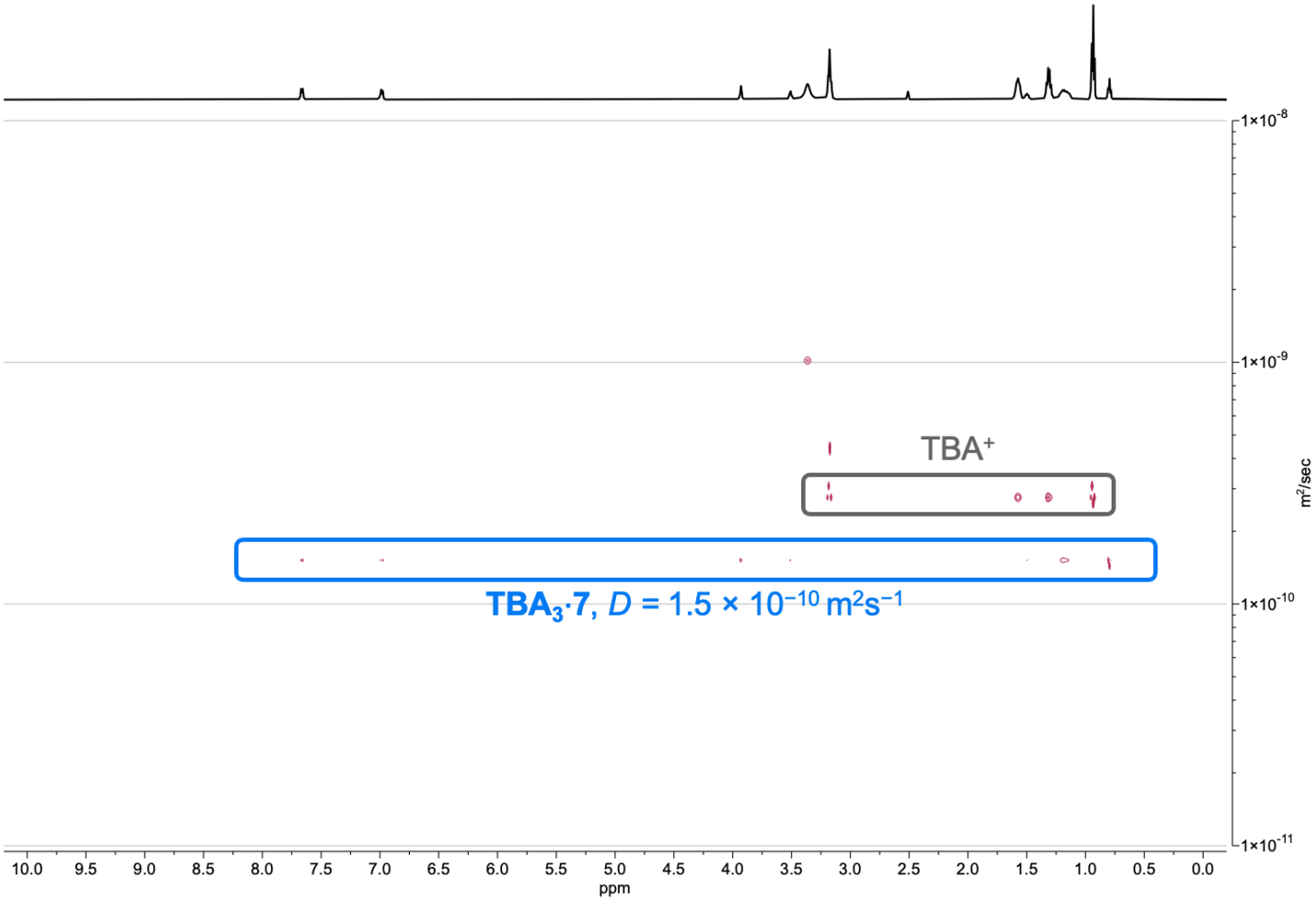

Figure S19. DOSY NMR spectrum of **TBA_3·7** (d_6-DMSO, 600 MHz, 298 K).

X-ray crystallography

Thermal ellipsoid plot

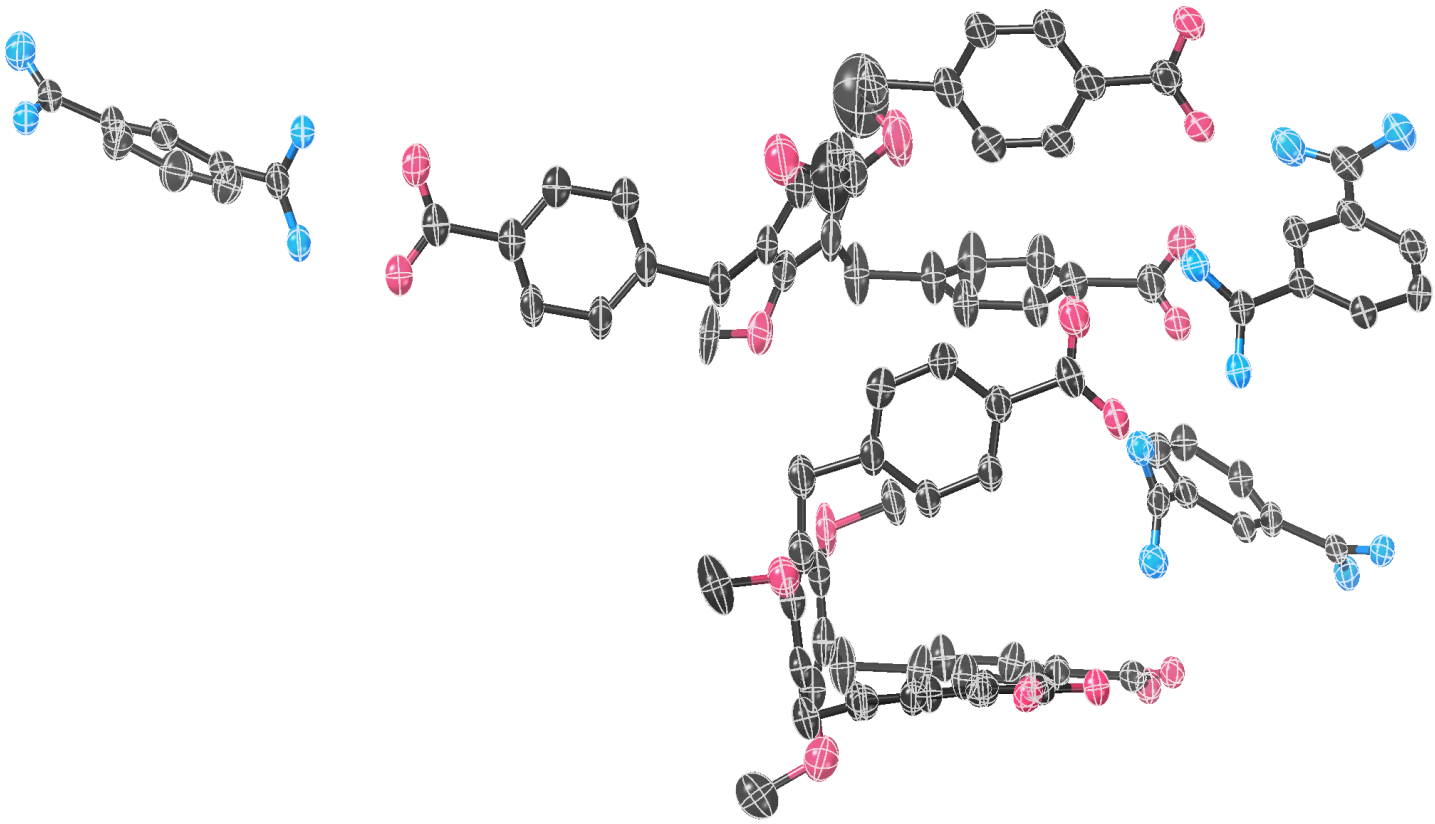

Figure S20. Thermal ellipsoid plot of the asymmetric unit of $\mathbf{8_3 \cdot 7_2}$. Ellipsoids are shown at 50% probability level, hydrogen atoms are omitted for clarity. Note: hexyloxy groups are truncated, and PLATON-SQUEEZE[S3] was used (see main text for further details).

Summary of crystallographic data

Table S1. Selected crystallographic data for **$8_3 \cdot 7_2$**.[a]

Data	Value
Radiation type	synchrotron (λ = 0.71073 Å)
Formula	$C_{90}H_{72}N_{12}O_{18}$[a]
Formula weight	1609.63
a (Å)	15.766(6)
b (Å)	20.057(6)
c (Å)	24.143(7)
α (º)	91.708(10)
β (º)	101.198(10)
γ (º)	105.288(10)
Unit cell volume (Å^3)	7197.6(5)
Crystal system	Triclinic
Space group	*P*–1
Z	2
Reflections (all)	96315
Reflections (unique)	27183
R_{int}	0.037
R_1 [$I > 2\sigma(I)$]	0.166
$wR_2(F^2)$ (all data)	0.288
CCDC number	2080276

[a] PLATON-SQUEEZE used.[S3]

Computational modelling

Modelling of $8_3 \cdot 7_2$

We initially modelled $\mathbf{8_3 \cdot 7_2}$ in the gas phase using a semi-empirical method and PM6 parameters,[S4] as was done for $\mathbf{1_2 \cdot TP_3}$ and $\mathbf{2_2 \cdot IP_3}$ (see main text). As in the simulation of $\mathbf{2_2 \cdot IP_3}$, we replaced the hexyloxy chains with methoxy groups to reduce the size of the system. This level of theory resulted in proton transfer from the amidinium component $\mathbf{8^{2+}}$ to the carboxylate groups of $\mathbf{7^{3-}}$, which we do not observe in solution. We repeated the calculations using the older PM3 parameters[S5] instead, and did not observe this problem (using a higher level of modelling was too computationally expensive). As with the calculations in the main text, this modelling is only intended to gauge geometric viability, and nothing more. As can be seen in Figure S21, the energy minimized structure of $\mathbf{8_3 \cdot 7_2}$ looks geometrically feasible, and quite similar to that of $\mathbf{2_2 \cdot IP_3}$ (main text).

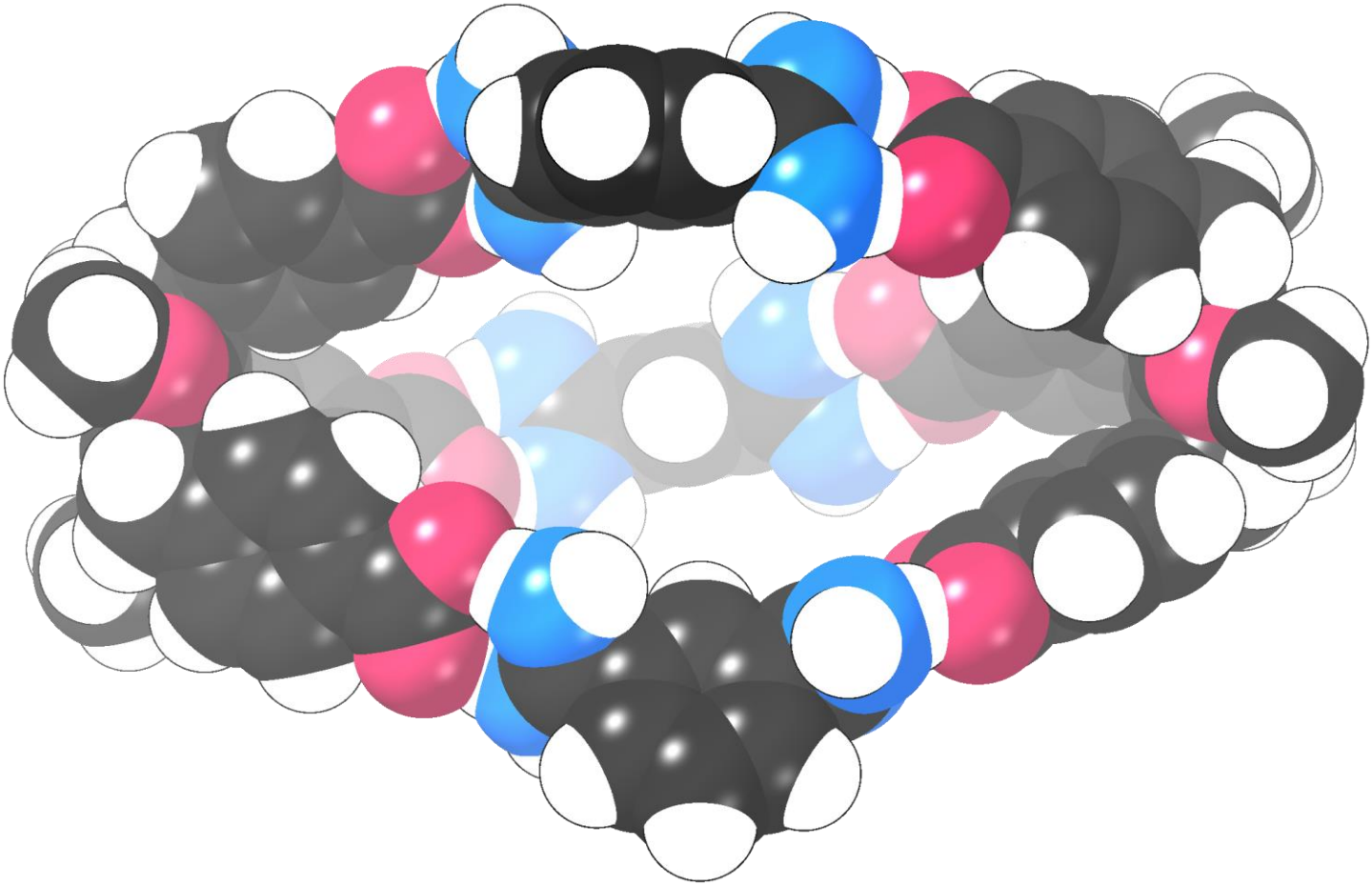

Figure S21. Optimized gas phase geometry of $\mathbf{8_3 \cdot 7_2}$ calculated using semi-empirical calculations with PM3 parameters.[5] The hexyl chains of $\mathbf{7^{3-}}$ were replaced with methyl groups for the calculations.

Atomic coordinates of modelled structures

Table S2. Atomic coordinates for energy minimized structure of $\mathbf{1_2 \cdot TP_3}$.

C	-1.741672	13.95944	1.169217	C	1.892346	10.54181	-9.662849
C	-1.426943	12.49499	0.851085	C	1.644926	9.491583	-8.768917
C	-2.751372	11.80819	1.211116	C	1.273277	9.753518	-7.445042
C	-0.986226	12.26289	-0.599999	C	5.904208	10.27098	5.876344
C	-0.221018	11.94577	1.625897	C	6.961392	9.756841	6.628427
C	-2.241659	14.82293	0.187504	C	7.337086	8.41691	6.496749
C	-2.581588	16.14607	0.488922	C	6.65117	7.59037	5.595829
C	-2.438839	16.58997	1.807375	C	5.592045	8.092199	4.830501
C	-1.971063	15.73197	2.82593	C	0.491287	-14.0821	-0.530646
C	-1.639631	14.42573	2.496915	C	0.69807	-12.57317	-0.372296
C	-0.10998	10.56695	1.8731	C	-0.697725	-12.11604	0.068637
C	1.001631	10.04766	2.534752	C	1.814713	-12.21149	0.616297
C	2.037255	10.90592	2.948651	C	1.197354	-11.88515	-1.650515
C	1.949707	12.2819	2.67106	C	0.616736	-14.93377	0.586361
C	0.833249	12.79022	2.00734	C	0.382549	-16.29712	0.477385
C	-1.314698	11.07349	-1.268711	C	-0.012344	-16.81968	-0.772644
C	-0.868077	10.84151	-2.569412	C	-0.179838	-15.9935	-1.888881
C	-0.068292	11.79795	-3.221766	C	0.064818	-14.62379	-1.749454
C	0.294026	12.97628	-2.543794	C	2.110122	-12.54216	-2.492787
C	-0.155008	13.19602	-1.242394	C	2.625206	-11.90703	-3.621402
C	-2.969728	11.29861	2.500636	C	2.24701	-10.58437	-3.918163
C	-4.203728	10.75222	2.854175	C	1.352308	-9.912293	-3.065806
C	-5.253395	10.72079	1.918834	C	0.841852	-10.55819	-1.939528
C	-5.046608	11.24389	0.628962	C	1.780515	-10.9937	1.314512
C	-3.809325	11.78754	0.286466	C	2.834879	-10.61959	2.147788
C	3.158657	10.3894	3.642378	C	3.954538	-11.45982	2.287339
C	0.370551	11.56519	-4.548409	C	3.998994	-12.67672	1.581832
C	-6.514163	10.18179	2.278303	C	2.9426	-13.03839	0.747205
C	-7.592374	9.729519	2.589756	C	-1.685265	-11.83581	-0.89067
C	0.732277	11.35236	-5.683374	C	-2.983636	-11.50808	-0.50288
C	4.110446	9.949448	4.246211	C	-3.322838	-11.47165	0.862143
C	5.2079	9.437271	4.97896	C	-2.343074	-11.76713	1.826879
C	1.13659	11.08561	-7.01383	C	-1.04646	-12.09244	1.428308
C	-8.854288	9.201503	2.958162	C	2.785386	-9.927714	-5.05154
C	-9.036293	7.808755	3.04003	C	5.050451	-11.07216	3.097525
C	-10.28654	7.301588	3.407988	C	-4.646675	-11.15837	1.26021
C	-11.35557	8.159139	3.697425	C	-5.779428	-10.89997	1.597848
C	-11.16911	9.541975	3.613325	C	6.006469	-10.73811	3.760034
C	-9.928481	10.06657	3.245512	C	3.261455	-9.363555	-6.010444
C	1.385869	12.14195	-7.911575	C	3.837178	-8.688611	-7.113513
C	1.763778	11.86397	-9.226307	C	7.145249	-10.33344	4.497921

C	-7.106269	-10.59949	1.992483	H	6.842004	-8.228486	4.083035
C	-7.495311	-9.261564	2.187007	H	5.066603	7.452683	4.11854
C	-8.809555	-8.980749	2.573557	H	8.153526	8.017616	7.100629
C	-9.739633	-10.00984	2.769345	H	7.494179	10.40288	7.327517
C	-9.346268	-11.33728	2.576459	H	5.610105	11.31632	5.981324
C	-8.038376	-11.63708	2.190405	H	2.757428	12.94897	2.971515
C	7.95878	-11.28831	5.138745	H	1.071859	8.977257	2.729695
C	9.102403	-10.88001	5.826968	H	-0.895063	9.886371	1.538656
C	9.45139	-9.526976	5.882823	H	0.794024	13.85755	1.77999
C	8.638618	-8.577208	5.250564	H	-1.91625	10.31001	-0.771567
C	7.482998	-8.969776	4.564684	H	0.15624	14.10127	-0.718139
C	4.734484	-9.35837	-7.96877	H	0.931347	13.71177	-3.034519
C	5.325486	-8.674761	-9.032856	H	-1.133958	9.915961	-3.080519
C	5.036003	-7.32536	-9.255255	H	-3.672993	12.212	-0.709589
C	4.136551	-6.66188	-8.409269	H	-2.176512	11.33492	3.249047
C	3.528466	-7.335276	-7.343833	H	-4.357747	10.35609	3.85828
H	-7.733096	-12.67392	2.040504	H	-5.85844	11.22931	-0.098259
H	-10.06675	-12.14265	2.729211	H	-2.384042	14.47101	-0.836404
H	-6.77401	-8.456174	2.03374	H	-1.30344	13.7489	3.285367
H	-10.76156	-9.776983	3.072911	H	-1.889408	16.10437	3.844939
H	-3.740384	-11.28759	-1.255748	O	-2.725142	17.85466	2.267032
H	-1.447083	-11.88573	-1.954607	H	-2.954217	16.79794	-0.293636
H	-0.306445	-12.34361	2.190081	H	-8.206501	7.136563	2.813235
H	-2.601415	-11.74969	2.885851	H	-9.785736	11.14656	3.179678
H	0.894767	-14.51993	1.55832	H	-11.99907	10.21433	3.8369
H	0.486118	-16.96507	1.329783	H	-12.32427	7.750813	3.989289
N	-0.204993	-18.1814	-0.744352	H	1.092491	8.935795	-6.743886
H	-0.499747	-16.38926	-2.846718	H	1.279913	13.17415	-7.575788
H	-0.090213	-13.97652	-2.615261	H	1.956204	12.68315	-9.920442
H	0.168522	-10.01105	-1.276556	H	2.175468	10.33074	-10.69565
H	2.435128	-13.55794	-2.259076	C	-9.226306	-7.5613	2.781503
H	3.327438	-12.42962	-4.270258	C	3.838218	-5.215561	-8.63231
H	1.064917	-8.883002	-3.282473	C	1.75852	8.071082	-9.219654
H	4.967615	-10.40972	-7.793504	O	-10.56358	-4.405311	2.230357
H	2.818037	-6.822027	-6.692789	C	-10.09545	-3.800236	3.234912
H	6.021219	-9.195253	-9.693238	O	-9.441434	-4.383771	4.156222
H	5.516822	-6.791061	-10.07652	C	-10.48367	5.82295	3.49174
H	3.009868	-13.97006	0.181705	C	9.002582	-7.128279	5.275966
H	0.930547	-10.31821	1.197936	C	7.038392	6.153389	5.46784
H	2.797439	-9.670913	2.683877	N	-11.12494	5.174961	2.493315
H	4.8663	-13.32967	1.679895	N	0.735819	7.218156	-9.104461
H	7.692119	-12.34467	5.090896	N	8.324983	5.816261	5.21186
H	9.731362	-11.62192	6.321201	N	6.118434	5.181229	5.607259

H	10.35621	-9.216366	6.407484	N	2.922415	7.651975	-9.794677
N	-10.04848	5.133817	4.562631	H	10.03734	1.143142	6.590231
N	-9.968043	-6.935389	1.840579	H	10.5136	-1.324412	6.625314
N	-8.882605	-6.906276	3.905764	H	7.287861	-1.981886	3.843436
N	9.221325	-6.515737	6.473117	H	6.738179	0.469343	3.902283
N	3.41293	-4.788642	-9.845436	H	-11.83139	0.28787	1.760943
N	3.991404	-4.32341	-7.63705	H	-11.57791	-2.217202	1.617608
N	9.154277	-6.433081	4.141983	H	-9.063549	-2.162503	5.113355
C	-3.262881	18.81258	1.323363	H	-9.316431	0.34086	5.257447
C	-0.657144	-18.82645	-1.959531	H	1.388303	2.643035	-7.702778
C	-10.29602	-2.319289	3.349555	H	1.852886	0.185611	-7.440492
C	-10.57505	0.448036	3.507851	H	3.799113	0.143563	-11.28311
C	-9.664509	-1.61498	4.383551	H	3.433371	2.622427	-11.49615
C	-11.08724	-1.646147	2.409147	H	3.712336	-3.211677	-7.790198
C	-11.22711	-0.258924	2.488531	H	4.349178	-4.60454	-6.73659
C	-9.804287	-0.228668	4.462953	H	3.252975	-3.710828	-10.03889
C	-10.67378	1.942945	3.560742	H	3.24729	-5.435129	-10.5988
O	-10.14101	2.539782	4.549432	H	3.043907	6.621655	-10.07431
O	-11.25977	2.551375	2.622323	H	3.749851	8.223926	-9.75971
C	8.921604	-1.788451	5.241936	H	0.880242	6.011082	-9.296171
C	8.355733	0.936417	5.253529	H	-0.15783	7.534831	-8.755308
C	9.702657	-0.922401	6.016699	H	9.027929	6.518386	5.05129
C	7.868769	-1.294388	4.459606	H	8.636549	4.754248	5.198195
C	7.574905	0.069841	4.477361	H	6.404197	4.069387	5.466942
C	9.427704	0.448084	6.01033	H	5.163613	5.399963	5.847277
C	8.017918	2.39688	5.288631	H	-9.581806	5.600906	5.324971
O	8.939979	3.250644	5.369121	H	-10.1401	3.989004	4.602652
O	6.783367	2.705744	5.240702	H	-11.25	4.067819	2.524466
C	9.188889	-3.262702	5.257635	H	-11.42583	5.664097	1.665694
O	9.033615	-3.881942	4.141798	H	9.245941	-5.223205	4.15217
O	9.519285	-3.843438	6.314619	H	9.066276	-6.8905	3.245051
C	2.855266	0.034632	-9.346018	H	9.424689	-5.456192	6.508753
C	2.396698	2.767341	-9.608443	H	8.987824	-6.973875	7.338215
C	2.177647	0.725078	-8.332125	H	-9.162158	-5.802652	4.053866
C	3.29257	0.703808	-10.4956	H	-8.343347	-7.360588	4.626687
C	3.075441	2.078791	-10.62126	H	-10.27203	-5.870638	1.972673
C	1.935445	2.092415	-8.469923	H	-10.20399	-7.393921	0.975601
C	2.173922	4.243916	-9.721482	H	0.094172	-18.72033	-2.747308
O	1.068934	4.689224	-9.229173	H	-1.629995	-18.42876	-2.262719
O	3.028122	4.988766	-10.24505	H	-0.745302	-19.87272	-1.637222
C	3.123518	-1.431062	-9.178047	H	-4.21204	18.45422	0.915035
O	3.18544	-2.175968	-10.19171	H	-3.419416	19.69207	1.961835
O	3.279922	-1.858307	-7.988481	H	-2.531297	19.02297	0.538474

Table S3. Atomic coordinates for energy minimized structure of $\mathbf{2_2 \cdot IP_3}$.

C	-2.081209	-1.616678	10.91932	H	-2.760561	1.500323	-12.68647
C	0.708615	-1.219354	10.86628	C	2.856734	0.115153	-12.47079
C	-1.190896	-2.7043	10.79295	H	2.979364	0.945497	-13.17081
C	-1.524882	-0.330754	11.01064	H	2.036091	-0.549985	-12.77483
C	-0.131953	-0.098265	10.97202	H	3.793996	-0.441763	-12.34517
C	0.201744	-2.536148	10.7744	H	-1.118309	-0.652916	-11.66559
C	1.150427	-3.686336	10.60877	C	-2.592292	3.728215	-8.946567
H	0.804907	-4.561928	11.20616	C	-4.154389	3.061113	-6.716736
H	2.148106	-3.41349	11.02852	C	-3.956529	4.065825	-8.910418
O	-1.779483	-3.952079	10.59184	C	-2.014494	3.069054	-7.849943
C	-3.562141	-1.856231	10.88758	C	-2.791089	2.732966	-6.741118
H	-4.066249	-1.250381	11.6761	C	-4.734039	3.735832	-7.800825
O	-2.325396	0.809611	11.04642	H	-4.414039	4.591791	-9.746469
C	0.376854	1.312453	11.01189	H	-0.953474	2.811833	-7.868106
H	0.96036	1.462197	11.94934	H	-2.337952	2.208204	-5.897772
H	-0.491701	2.018799	11.08767	H	-5.791366	4.006991	-7.776372
O	2.088661	-1.124607	10.73769	C	0.079235	-1.331084	-10.00562
C	2.798659	-0.53811	11.85786	C	0.336291	-2.886479	-7.700819
H	2.653923	-1.153071	12.74923	C	1.289841	-1.986643	-9.732574
H	2.486009	0.497778	12.02674	C	-0.989398	-1.428037	-9.100504
H	3.838385	-0.579227	11.50739	C	-0.863141	-2.205327	-7.948866
C	-1.650591	-4.878699	11.70068	C	1.418208	-2.767597	-8.58463
H	-0.594169	-5.143774	11.85013	H	2.137015	-1.867713	-10.40897
H	-2.230318	-5.740133	11.34523	H	-1.915666	-0.882109	-9.298737
H	-2.088528	-4.451008	12.60614	H	-1.695938	-2.28741	-7.247725
C	-3.060302	1.004274	12.28138	H	2.357604	-3.280857	-8.372812
H	-2.365875	1.109143	13.11853	C	3.63676	3.429299	-9.222094
H	-3.76495	0.176476	12.4426	C	4.526168	3.684257	-6.584842
H	-3.592741	1.943159	12.08256	C	3.873023	4.70176	-8.679915
H	-3.781041	-2.921043	11.14328	C	3.831625	2.285154	-8.430749
C	1.297043	-4.057915	9.155133	C	4.275103	2.410371	-7.114418
C	1.642912	-4.797789	6.484519	C	4.318512	4.830355	-7.363998
C	0.524263	-5.093955	8.608181	H	3.694645	5.594328	-9.277869
C	2.217988	-3.370497	8.348766	H	3.627811	1.297121	-8.853089
C	2.393046	-3.739246	7.014915	H	4.430639	1.521107	-6.500734
C	0.698998	-5.467572	7.275926	H	4.499217	5.820469	-6.941811
H	-0.227228	-5.593662	9.220578	C	5.024865	3.836101	-5.188054
H	2.78829	-2.538455	8.770225	C	0.476351	-3.752863	-6.495994
H	3.114965	-3.211325	6.388663	C	-4.997395	2.676566	-5.549632
H	0.101216	-6.275817	6.85112	N	4.191059	3.635949	-4.142931
C	-4.127996	-1.548128	9.524539	N	-6.074627	1.885108	-5.720685

C	-5.213528	-1.019064	7.004228	N	0.558525	-3.19788	-5.266763
C	-4.944717	-0.423521	9.333353	N	0.517545	-5.093102	-6.627688
C	-3.84254	-2.396969	8.442409	H	0.435773	-5.523186	-7.535291
C	-4.383165	-2.134572	7.184164	H	0.699024	-5.772959	-5.719317
C	-5.488595	-0.159177	8.075842	N	-4.695622	3.124168	-4.309187
H	-5.142966	0.256268	10.16061	H	-3.920127	3.746575	-4.152238
H	-3.188099	-3.260089	8.593232	H	-5.284858	2.787048	-3.428784
H	-4.1649	-2.796125	6.344044	N	6.305673	4.184252	-4.959576
H	-6.121207	0.717331	7.926895	H	6.951532	4.302891	-5.724113
C	1.189331	1.719054	9.810999	H	6.703141	4.317771	-3.887603
C	2.709243	2.538753	7.604221	H	4.550047	3.772602	-3.099004
C	2.241927	2.635915	9.977289	H	3.219151	3.416215	-4.28687
C	0.893843	1.230573	8.528445	H	-6.754145	1.605303	-4.830012
C	1.651152	1.635134	7.429245	H	-6.290319	1.49444	-6.623899
C	2.997447	3.045946	8.879389	H	0.717654	-3.838299	-4.367266
H	2.471587	3.035806	10.96332	H	0.563107	-2.198027	-5.146144
H	0.071567	0.525278	8.392043	H	-9.778416	0.833688	-2.567991
H	1.42337	1.241933	6.436409	C	-9.332022	0.684486	-1.581757
H	3.808626	3.764234	9.013353	C	-8.136653	0.280624	0.913327
C	3.543442	2.951307	6.440592	C	-10.09076	0.185317	-0.519648
C	-5.822758	-0.743769	5.671513	C	-7.977834	0.995353	-1.39153
C	1.848991	-5.230976	5.073113	C	-7.376742	0.803653	-0.141166
N	4.872875	2.731923	6.444645	C	-9.493091	-0.022454	0.726297
N	1.440914	-4.445637	4.052052	H	-11.14242	-0.047445	-0.663511
N	-5.067485	-0.253157	4.664051	H	-6.320356	1.056686	0.012426
N	-7.133825	-0.977984	5.467055	H	-10.0672	-0.422997	1.566345
H	-7.707925	-1.368224	6.197764	C	-7.171108	1.51572	-2.536194
H	-7.620427	-0.765324	4.450454	C	-7.496652	0.02617	2.239289
N	2.45393	-6.405592	4.808747	O	-8.220328	-0.46899	3.162949
H	2.795062	-6.988693	5.55614	O	-6.104842	2.147246	-2.308017
H	2.549489	-6.79512	3.732174	O	-7.605312	1.290325	-3.71412
N	2.97574	3.558965	5.373527	O	-6.274989	0.300934	2.394607
H	1.991818	3.770321	5.355138	C	6.935898	4.381559	-0.180092
H	3.583955	3.814728	4.479468	C	7.99715	4.483661	2.405026
H	5.535928	3.077355	5.563281	C	6.101427	4.144926	0.920125
H	5.31196	2.234499	7.202811	C	8.290403	4.689069	0.012485
H	1.544956	-4.793197	2.996418	C	8.818505	4.745228	1.305117
H	0.946095	-3.585415	4.222205	C	6.640177	4.186574	2.212114
H	-5.526312	-0.014655	3.675056	H	5.037624	3.925422	0.768296
H	-4.092234	-0.041653	4.799556	H	8.919827	4.879165	-0.861108
C	0.202245	0.92088	-11.02866	H	9.868215	4.984238	1.454057
C	0.670488	3.637118	-10.4834	H	8.398229	4.501674	3.421609
C	-0.868531	1.807414	-10.77031	C	5.773064	3.894268	3.392951

C	1.505336	1.439422	-10.99435	C	6.387784	4.283099	-1.566278
C	1.770554	2.799599	-10.72852	O	7.192638	4.468544	-2.536964
C	-0.661934	3.167146	-10.48233	O	4.52236	4.004009	3.287738
C	-1.774083	4.117657	-10.14947	O	5.166426	4.014266	-1.726823
H	-2.42667	4.240475	-11.04463	O	6.350353	3.53857	4.473479
H	-1.345963	5.136413	-9.953017	H	1.908556	-8.6557	-3.525603
O	-2.116747	1.2	-10.72075	C	1.951786	-8.252142	-2.510606
C	-0.0802	-0.531838	-11.27383	C	2.029597	-7.177954	0.06934
H	0.588129	-0.926665	-12.07414	C	2.334279	-9.056402	-1.433555
O	2.622572	0.616237	-11.12951	C	1.614537	-6.907858	-2.297887
C	3.188851	3.283911	-10.65443	C	1.650062	-6.365698	-1.006919
H	3.293205	4.24746	-11.20553	C	2.373974	-8.520443	-0.143392
H	3.864842	2.564096	-11.17664	H	2.598862	-10.09732	-1.599642
O	0.836494	4.973649	-10.12571	H	1.381199	-5.314033	-0.839534
C	1.30535	5.839246	-11.19043	H	2.671199	-9.134327	0.710701
H	0.579986	5.853006	-12.00735	C	1.220641	-6.045007	-3.451245
H	2.297859	5.520335	-11.53775	C	2.059437	-6.606872	1.448596
H	1.357472	6.811856	-10.68506	O	2.520803	-7.333534	2.387338
C	-3.104974	1.682199	-11.66583	O	1.051274	-4.810044	-3.257496
H	-3.330649	2.740475	-11.49899	O	1.078398	-6.597176	-4.590182
H	-3.971263	1.055239	-11.41759	O	1.621597	-5.438085	1.632469

Table S4. Atomic coordinates for energy minimized structure of $\mathbf{8_3 \cdot 7_2}$.

C	-1.945052	-1.421455	10.9842	H	-1.541585	-0.546224	-9.16168
C	0.866477	-1.457881	11.05087	H	1.962112	-2.410307	-10.8434
C	-1.233316	-2.631731	10.90222	H	2.147902	-3.866925	-8.845107
C	-1.207025	-0.227738	11.08544	H	-1.348013	-1.995867	-7.156302
C	0.197804	-0.223101	11.13477	C	3.636076	3.671041	-9.332533
C	0.173101	-2.672683	10.91125	C	4.73886	4.130342	-6.801182
C	0.912731	-3.973515	10.78888	C	3.995612	4.962156	-8.943339
H	0.395703	-4.746729	11.40274	C	3.82322	2.611872	-8.444127
H	1.927347	-3.888874	11.22926	C	4.371345	2.840265	-7.187275
O	-1.963768	-3.808057	10.72352	C	4.544543	5.190438	-7.687993
C	-3.446719	-1.410481	10.99422	H	3.835011	5.803231	-9.627437
H	-3.808272	-0.576136	11.63862	H	3.53352	1.597125	-8.741375
O	-1.865474	1.003626	11.05356	H	4.517324	2.003165	-6.494106
C	0.965694	1.056338	11.29526	H	4.824383	6.207675	-7.389311
H	1.768222	0.89577	12.0533	C	5.319919	4.385287	-5.440775
H	0.321816	1.853556	11.7206	C	0.531652	-3.899254	-6.658885
O	2.262789	-1.487314	11.01975	C	-4.510743	3.040015	-5.292671
C	2.856935	-1.41396	12.29776	H	-8.504049	-0.016272	-3.092138
H	2.529469	-2.225545	12.95751	C	-8.298851	-0.127303	-2.019816
H	2.656889	-0.442863	12.77616	C	-7.774071	-0.432469	0.698372
H	3.922598	-1.510661	12.07643	C	-9.08156	-0.981441	-1.250251
C	-2.10059	-4.581022	11.89601	C	-7.250009	0.576978	-1.42415
H	-1.129918	-4.973431	12.23517	C	-6.982239	0.427873	-0.062834
H	-2.742286	-5.401912	11.56681	C	-8.825265	-1.136917	0.107603
H	-2.579351	-4.027317	12.71131	H	-9.903927	-1.536919	-1.716092
C	-2.384293	1.409402	12.30127	H	-6.155947	0.979228	0.40485
H	-1.609938	1.487851	13.07267	H	-9.450408	-1.80827	0.709601
H	-3.180453	0.730024	12.64091	C	-6.420124	1.481492	-2.252301
H	-2.799905	2.395254	12.07933	C	-7.49012	-0.608255	2.14077
H	-3.825451	-2.331824	11.48428	C	6.41314	5.437835	-0.214792
C	1.04513	-4.435477	9.369997	C	6.869223	5.963284	2.481216
C	1.343803	-5.341503	6.736096	C	5.669784	4.760749	0.752159
C	0.35451	-5.565168	8.929372	C	7.382436	6.370461	0.158316
C	1.887505	-3.762535	8.483989	C	7.606709	6.627812	1.506815
C	2.03484	-4.211233	7.177262	C	5.901969	5.030711	2.100843
C	0.503725	-6.016309	7.622859	H	4.911068	4.025418	0.455351
H	-0.320378	-6.093965	9.612212	H	7.967834	6.897843	-0.604972
H	2.429717	-2.870911	8.819996	H	8.368091	7.359187	1.80316
H	2.695254	-3.673035	6.486409	H	7.046282	6.177624	3.542769
H	-0.041646	-6.905614	7.284586	C	5.122219	4.324207	3.14358
C	-4.050793	-1.291947	9.628396	C	6.162429	5.171275	-1.649966
C	-5.296484	-1.08638	7.127129	H	1.820638	-8.633065	-3.587181

C	-4.368011	-0.040464	9.098291	C	1.765715	-8.283089	-2.548884
C	-4.347574	-2.43925	8.891297	C	1.624527	-7.401085	0.089108
C	-4.963159	-2.336907	7.649945	C	1.967665	-9.17741	-1.502828
C	-4.985465	0.061942	7.856726	C	1.488405	-6.943933	-2.269004
H	-4.1235	0.868334	9.661302	C	1.417467	-6.494096	-0.950556
H	-4.09011	-3.427586	9.290197	C	1.897323	-8.742749	-0.183284
H	-5.193723	-3.243653	7.07834	H	2.18393	-10.23033	-1.719805
H	-5.229505	1.049304	7.446581	H	1.202018	-5.439913	-0.733714
C	1.552274	1.571156	10.01798	H	2.062067	-9.453189	0.636289
C	2.658349	2.618863	7.667742	C	1.269344	-5.993542	-3.383686
C	2.911787	1.882192	9.95498	C	1.555362	-6.935037	1.493228
C	0.750154	1.787531	8.897227	O	4.506549	3.329328	6.284605
C	1.299073	2.307082	7.730776	O	2.20445	-5.168858	4.492652
C	3.460455	2.402915	8.78928	O	-6.411549	-2.024941	5.210165
H	3.55433	1.709307	10.82581	O	-6.155761	0.133321	5.230143
H	-0.317787	1.541972	8.940291	O	0.912091	-6.863038	4.910343
H	0.662323	2.474131	6.853546	O	2.525242	3.478097	5.417312
H	4.529448	2.643009	8.745305	O	-0.334118	-3.852141	-5.733915
C	3.256257	3.163535	6.40322	O	5.555046	5.565986	-5.044667
C	-5.985442	-0.985011	5.796789	O	-3.831046	2.722295	-4.272356
C	1.491351	-5.813173	5.31831	O	-5.771232	3.080173	-5.175043
C	0.241951	0.915251	-11.09328	O	1.494641	-4.709899	-6.522209
C	0.590584	3.64923	-10.52746	O	5.586884	3.431388	-4.651812
C	-0.863459	1.766252	-10.92414	N	-6.971394	2.570451	-2.853872
C	1.528311	1.478318	-11.00306	N	-7.16757	-1.82324	2.632421
C	1.725843	2.844653	-10.73881	N	6.58747	4.024748	-2.226606
C	-0.712633	3.130311	-10.61273	N	5.715241	3.363491	3.907942
C	-1.914018	4.000471	-10.38637	N	3.803296	4.549417	3.296227
H	-2.638485	3.821068	-11.21553	N	5.501705	6.078754	-2.406071
H	-1.64847	5.075385	-10.45513	N	-7.633211	0.425044	3.011117
O	-2.141318	1.204274	-10.98516	N	-5.086023	1.30174	-2.354812
C	0.054197	-0.548198	-11.36828	H	6.348672	3.78606	-3.209868
H	0.78776	-0.869762	-12.14364	H	6.976861	3.336462	-1.63524
O	2.655653	0.659035	-11.09269	H	5.292489	6.951536	-1.994998
C	3.105457	3.433386	-10.71125	H	3.385372	5.225258	2.709992
H	3.092937	4.38577	-11.29173	H	5.262938	3.074585	4.789371
H	3.824139	2.779437	-11.2465	H	6.70212	3.318295	3.859926
O	0.744174	4.979645	-10.13321	H	-6.863275	-1.953489	3.618178
C	0.986199	5.868484	-11.20112	H	-7.096331	-2.570741	1.990879
H	0.17196	5.869019	-11.934	H	-7.758035	1.323033	2.616984
H	1.939249	5.644516	-11.70388	H	-7.959372	2.620131	-2.843386
H	1.046565	6.836196	-10.6976	H	-6.47371	3.023991	-3.642925
C	3.023563	0.338001	-12.41648	H	-4.695476	0.507224	-1.91703

H	3.221207	1.228501	-13.0237	N	0.038472	-5.51196	-3.64575
H	2.256865	-0.283111	-12.90425	N	2.513517	-6.132621	2.000941
H	3.942228	-0.237185	-12.27885	N	0.50273	-7.273065	2.280184
H	-0.941819	-0.738313	-11.81846	N	2.323176	-5.533554	-4.110527
C	-2.572444	3.769625	-9.061636	H	3.184656	-6.001201	-3.983973
C	-3.838538	3.332716	-6.602828	H	-0.158536	-4.904059	-4.469511
C	-3.965793	3.720901	-8.983369	H	-0.705802	-5.827169	-3.078703
C	-1.817803	3.623318	-7.897491	H	-0.118637	-7.957043	1.931069
C	-2.446207	3.403755	-6.67753	H	2.486221	-5.795336	2.98474
C	-4.59479	3.506703	-7.762952	H	3.23399	-5.835389	1.394805
H	-4.569365	3.842947	-9.889614	H	0.50759	-7.059376	3.292821
H	-0.723294	3.670733	-7.951611	H	2.155755	-5.041628	-5.001927
H	-1.846133	3.275496	-5.768248	H	-4.524874	1.830431	-3.048874
H	-5.689503	3.467786	-7.709903	H	-7.243607	0.353174	3.967347
C	0.189951	-1.391944	-10.13786	H	3.26538	4.163138	4.1015
C	0.40936	-3.028796	-7.875199	H	5.37124	5.940162	-3.421843
C	-0.731147	-1.281587	-9.095369	H	-2.237302	1.049242	-13.06693
C	1.22343	-2.324447	-10.03842	C	-2.799101	1.44127	-12.21114
C	1.332044	-3.137716	-8.916475	H	-3.738399	0.895701	-12.09211
C	-0.621686	-2.09254	-7.972353	H	-2.997836	2.514554	-12.35519

References

S1. M. Morshedi, M. Thomas, A. Tarzia, C. J. Doonan and N. G. White, Supramolecular anion recognition in water: synthesis of hydrogen-bonded supramolecular frameworks, *Chem. Sci.*, **2017**, *8*, 3019–3025.

S2. M. Thomas, T. Anglim Lagones, M. Judd, M. Morshedi, M. L. O'Mara and N. G. White, Hydrogen bond-driven self–assembly between amidinium cations and carboxylate anions: A combined molecular dynamics, NMR spectroscopy and single crystal X-ray diffraction study, *Chem. Asian J.*, **2017**, *12*, 1587–1597.

S3. A. L. Spek, *PLATON* SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors, *Acta Crystallogr.*, **2015**, *C71*, 9–18.

S4. J. J. P. Stewart, *J. Mol. Model.*, Optimization of parameters for semiempirical methods V: Modification of NDDO approximations and application to 70 elements, **2007**, *13*, 1173–1213.

S5. J. J. P. Stewart, Optimization of parameters for semiempirical methods II. Applications, *J. Comput. Chem.*, **1989**, *10*, 209–220.