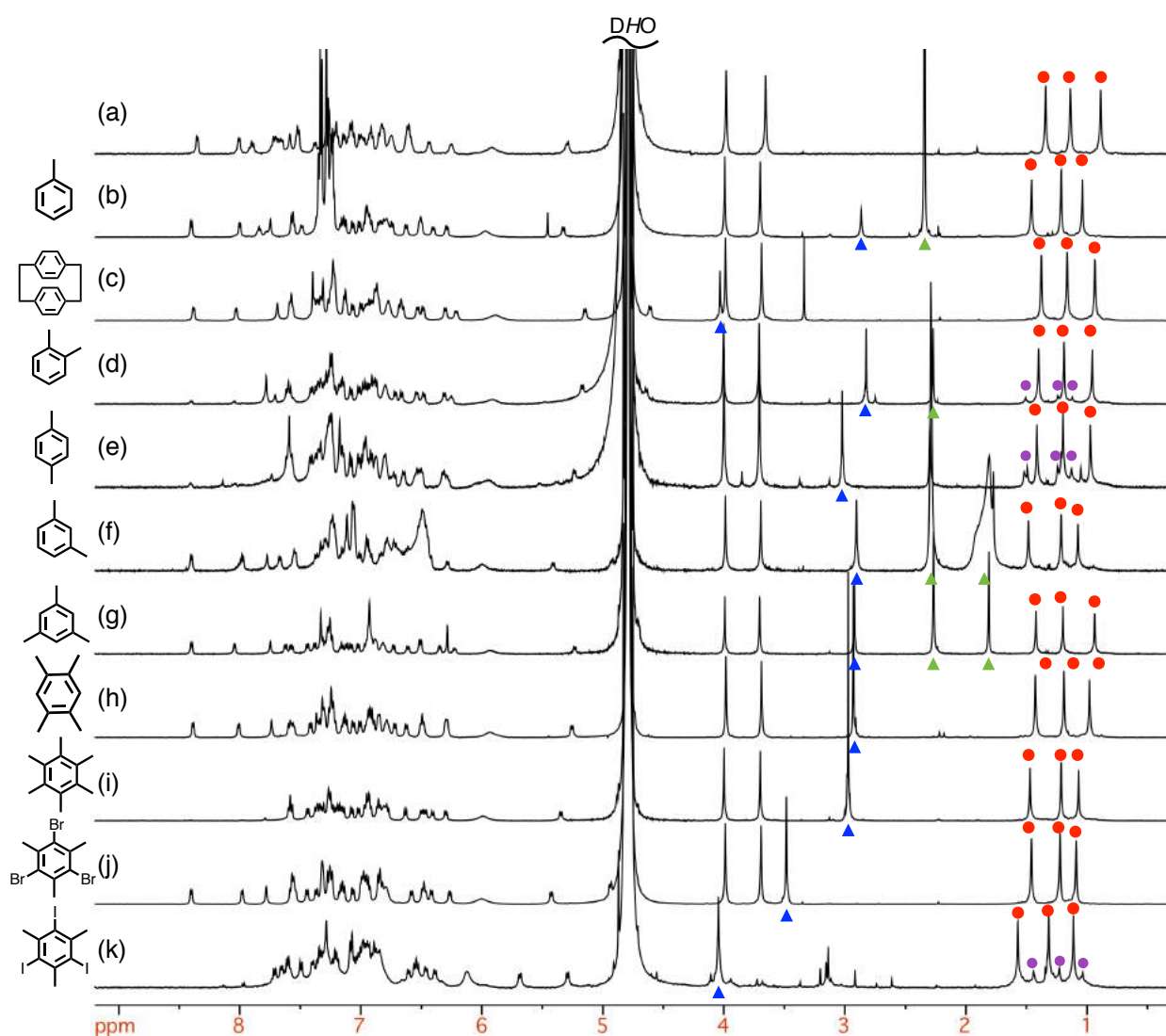
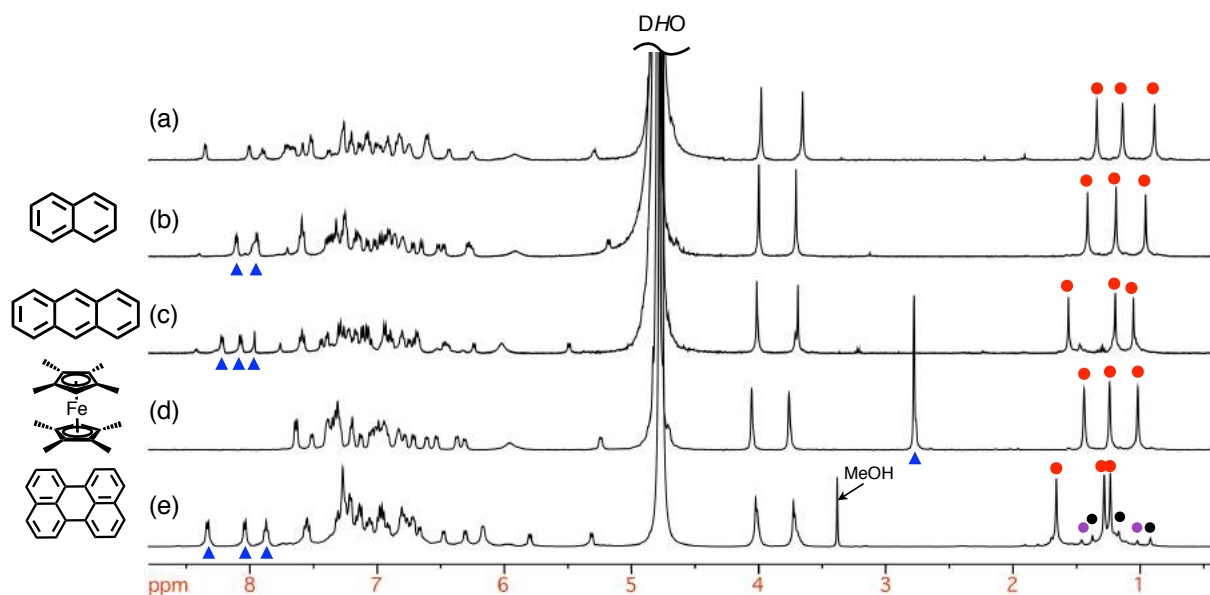


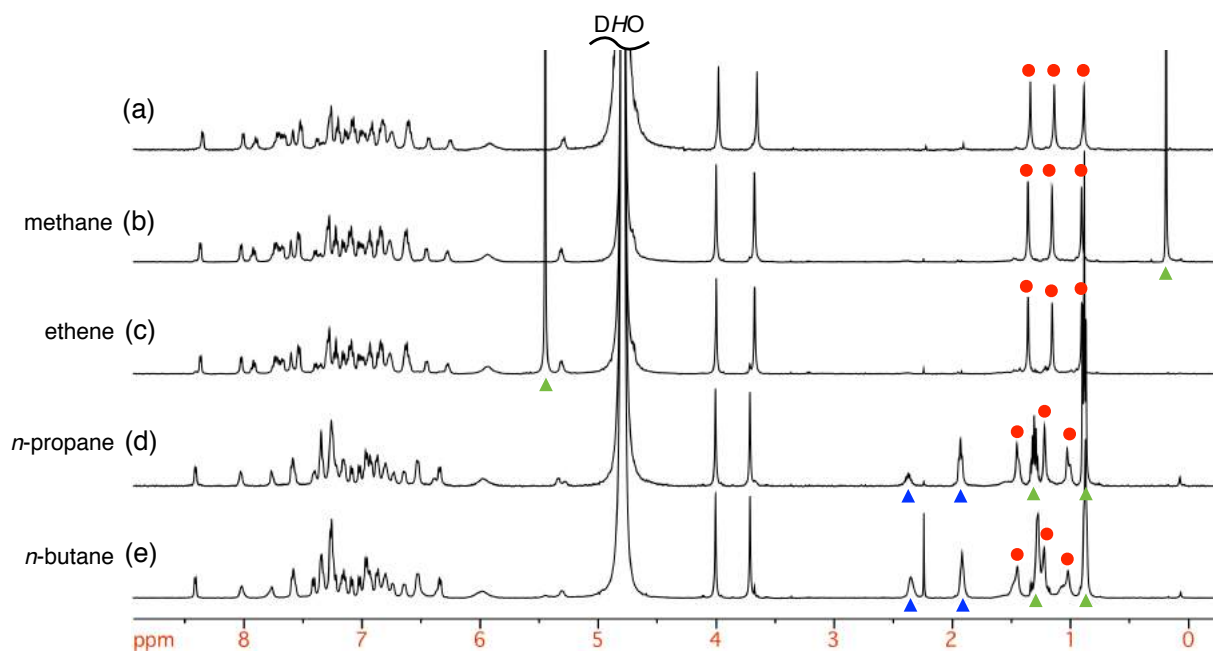
Supplementary Figures



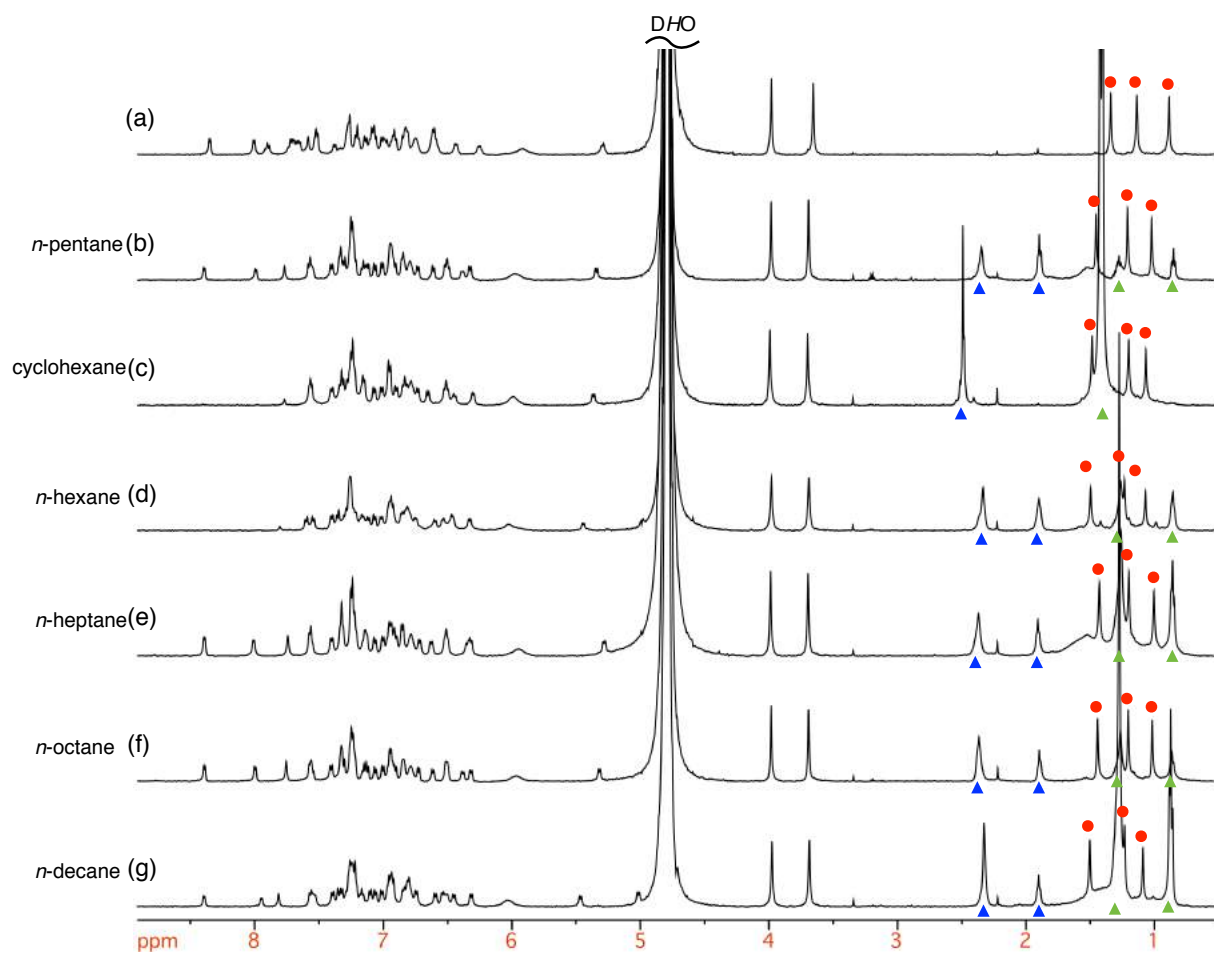
Supplementary Figure 1. ^1H NMR spectra of the host-guest complexes between $\mathbf{1}_6$ and aromatic guest molecules (500 MHz, 298 K, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0$ mM). (a) $\mathbf{1}_6$. (b) toluene $_3$ @ $\mathbf{1}_6$. (c) PC@ $\mathbf{1}_6$, PC indicates [2.2]paracyclophane. (d) *o*-xylene $_2$ @ $\mathbf{1}_6$, a trace amount of *o*-xylene $_3$ @ $\mathbf{1}_6$ is indicated by violet solid circles. (e) *p*-xylene $_2$ @ $\mathbf{1}_6$, a trace amount of *p*-xylene $_3$ @ $\mathbf{1}_6$ is indicated by violet solid circles. (f) *m*-xylene $_3$ @ $\mathbf{1}_6$. (g) mesitylene $_2$ @ $\mathbf{1}_6$. (h) durene $_2$ @ $\mathbf{1}_6$. (i) hexamethylbenzene $_2$ @ $\mathbf{1}_6$. (j) TBM $_2$ @ $\mathbf{1}_6$, TBM indicates 1,3,5-tribromomesitylene. (k) 1,3,5-triodomesitylene $_2$ @ $\mathbf{1}_6$, a trace amount of 1,3,5-triodomesitylene@ $\mathbf{1}_6$ is indicated by violet solid circles. Red solid circles indicate the methyl signals of the *p*-tolyl methyl groups in $\mathbf{1}_6$. Blue and green solid triangles indicate the signals of encapsulated and free guests, respectively. Two signals were observed for liquid free guest, mesitylene and *m*-xylene, that derived from the water-soluble molecules and the undissolved bulky molecules.



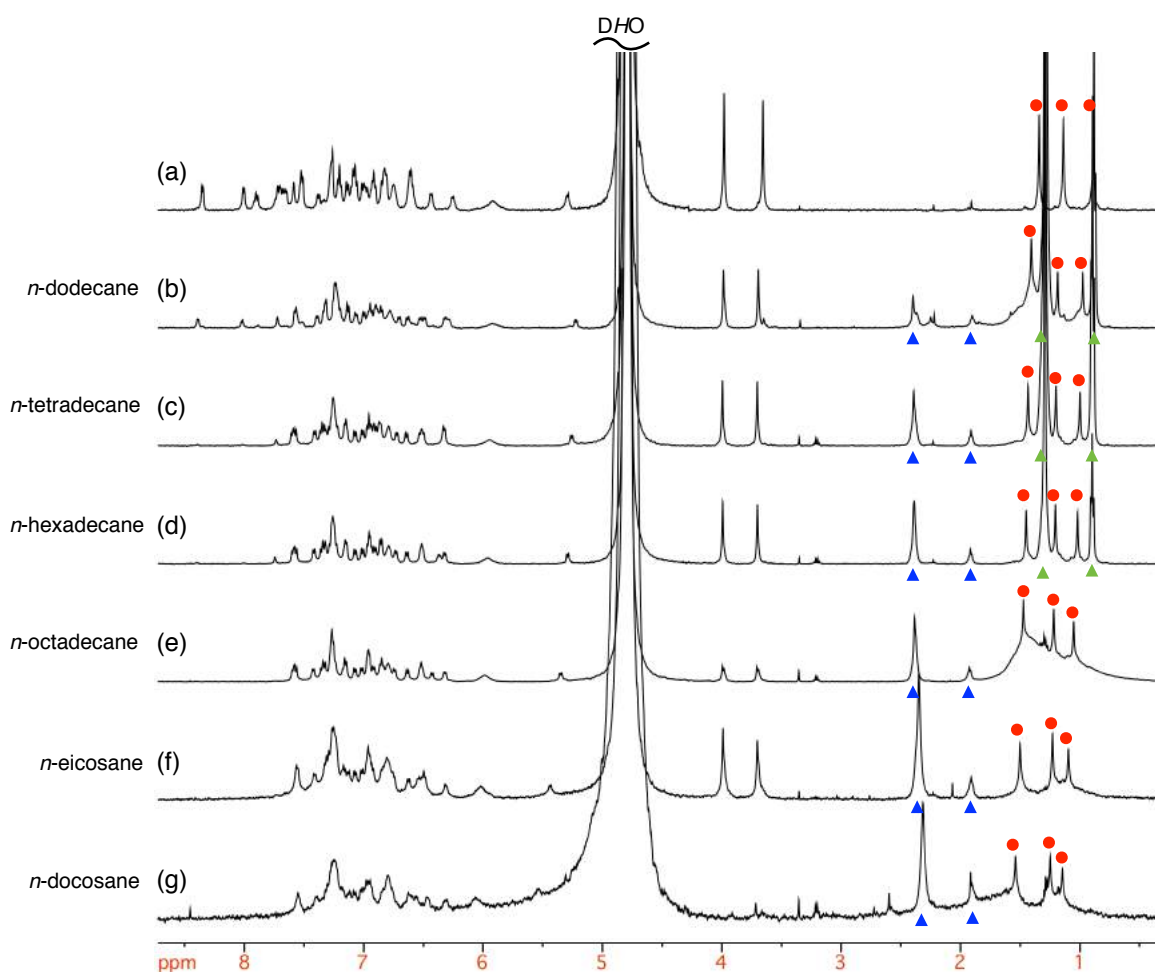
Supplementary Figure 2. ^1H NMR spectra of the host-guest complexes between $\mathbf{1}_6$ and large aromatic molecules (500 MHz, 298 K, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0$ mM). (a) $\mathbf{1}_6$. (b) naphthalene $_2$ @ $\mathbf{1}_6$. (c) anthracene $_2$ @ $\mathbf{1}_6$. (d) DF@ $\mathbf{1}_6$, DF indicates decamethylferrocene. (e) perylene $_2$ @ $\mathbf{1}_6$, a trace amount of $\mathbf{1}_6$ and perylene@ $\mathbf{1}_6$ are indicated by black and violet solid circles, respectively. Red solid circles indicate the *p*-tolyl methyl groups of $\mathbf{1}_6$. Blue solid triangles indicate the signals of encapsulated guests.



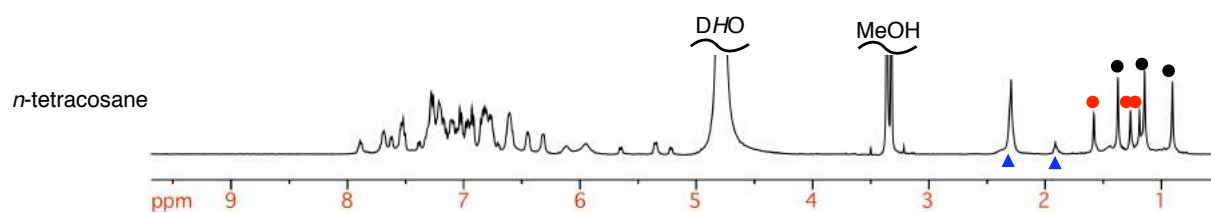
Supplementary Figure 3. ^1H NMR spectra of the host-guest complexes between $\mathbf{1}_6$ and C1 – C4 hydrocarbons (500 MHz, 298 K, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0$ mM). (a) $\mathbf{1}_6$. (b) $\mathbf{1}_6$ in the presence of methane. (c) $\mathbf{1}_6$ in the presence of ethene. (d) *n*-propane $_3$ @ $\mathbf{1}_6$. (e) *n*-butane $_3$ @ $\mathbf{1}_6$. Red solid circles indicate the *p*-tolyl methyl groups of $\mathbf{1}_6$. Blue and green solid triangles indicate the signals of encapsulated and free guests, respectively.



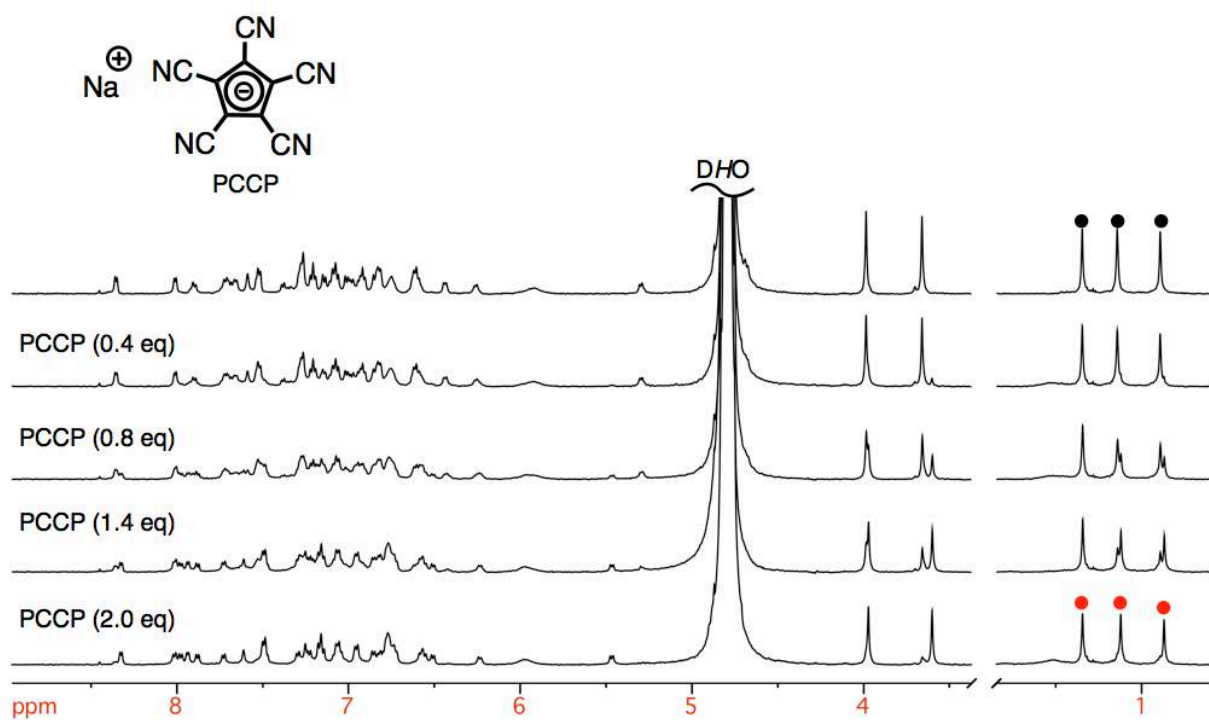
Supplementary Figure 4. ^1H NMR spectra of the host-guest complexes between $\mathbf{1}_6$ and C5 – C10 alkanes (500 MHz, 298 K, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0 \text{ mM}$). (a) $\mathbf{1}_6$. (b) $n\text{-pentane}_3@1_6$. (c) $\text{cyclohexane}_3@1_6$. (d) $n\text{-hexane}_3@1_6$. (e) $n\text{-heptane}_2@1_6$. (f) $n\text{-octane}_2@1_6$. (g) $n\text{-decane}_2@1_6$. Red solid circles indicate the *p*-tolyl methyl groups of $\mathbf{1}_6$. Blue and green solid triangles indicate the signals of encapsulated and free guests, respectively.



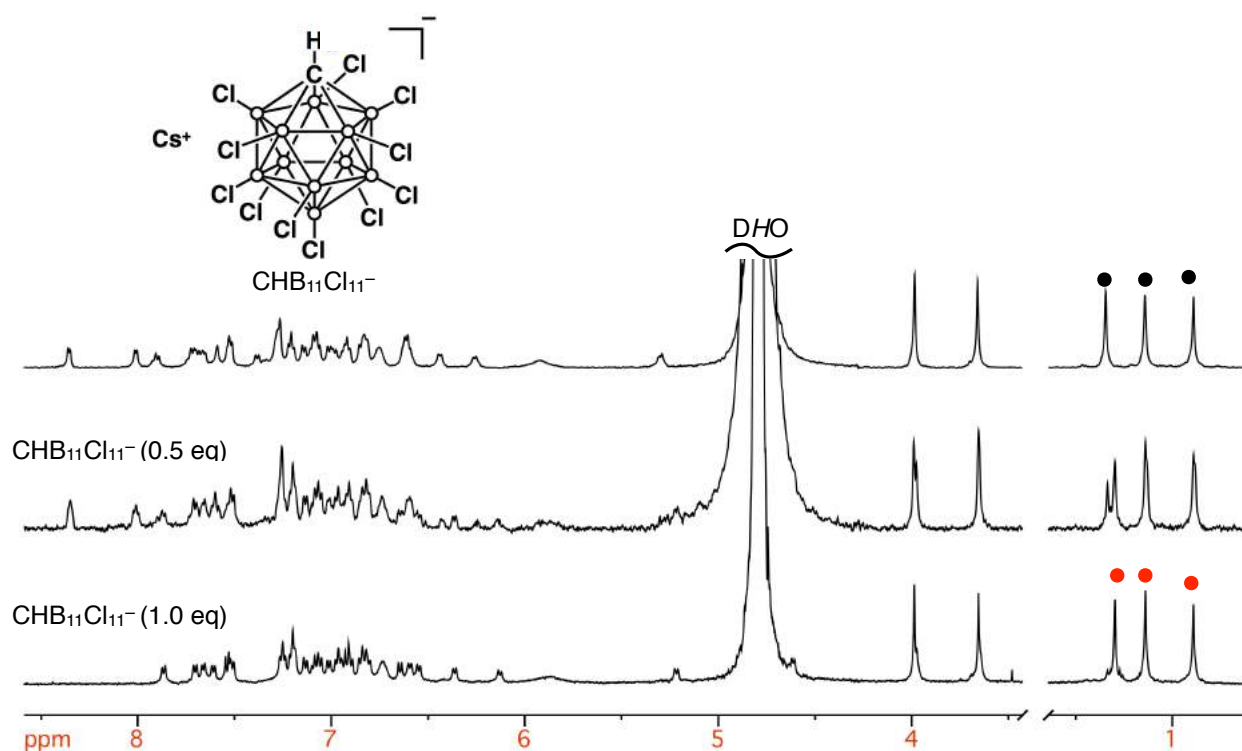
Supplementary Figure 5. ^1H NMR spectra of the host-guest complexes between $\mathbf{1}_6$ and C12 – C22 alkanes (500 MHz, 298 K, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0$ mM). (a) $\mathbf{1}_6$. (b) n -dodecane@ $\mathbf{1}_6$. (c) n -tetradecane@ $\mathbf{1}_6$. (d) n -hexadecane@ $\mathbf{1}_6$. (e) n -octadecane@ $\mathbf{1}_6$. (f) n -eicosane@ $\mathbf{1}_6$. (g) n -docosane@ $\mathbf{1}_6$. Red solid circles indicate the p -tolyl methyl groups of $\mathbf{1}_6$. Blue and green solid triangles indicate the signals of encapsulated and free guests, respectively.



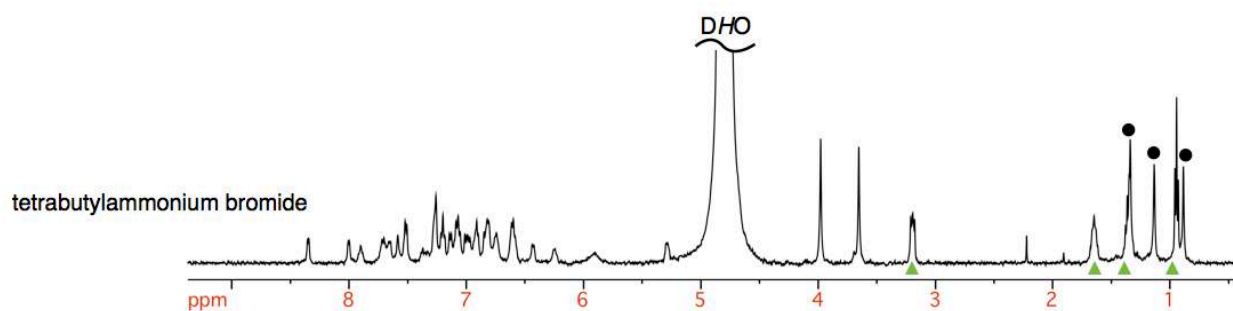
Supplementary Figure 6. ^1H NMR spectra of the host-guest complexation between $\mathbf{1}_6$ and n -tetracosane (500 MHz, 298 K, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0$ mM). Red and black solid circles indicate the signals of the p -tolyl methyl groups of n -tetracosane@ $\mathbf{1}_6$ and $\mathbf{1}_6$, respectively. Blue solid triangles indicate the signals of the encapsulated n -tetracosane.



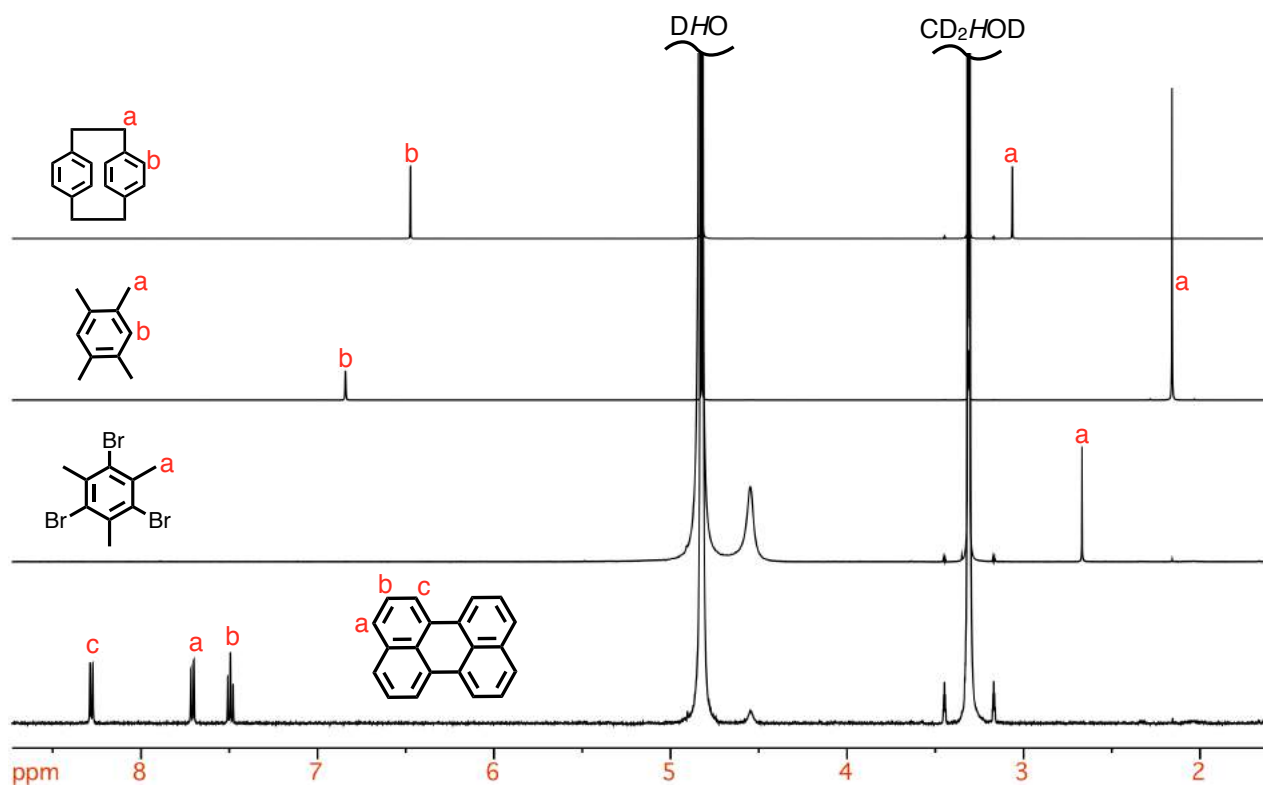
Supplementary Figure 7. ¹H NMR titration experiments of PCCP against **1**₆ (500 MHz, 298 K, D₂O, [**1**]_{total} = 1.0 mM, PCCP indicates pentacyanocyclopentadienide). Red and black solid circles indicate the signals of the *p*-tolyl methyl signals of PCCP₂@**1**₆ and **1**₆, respectively.



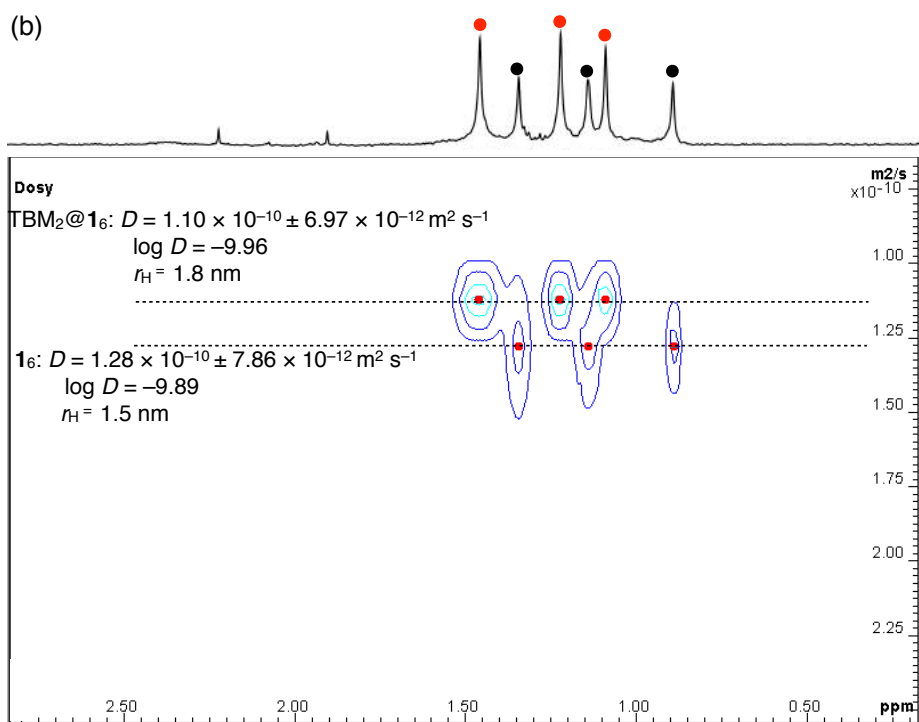
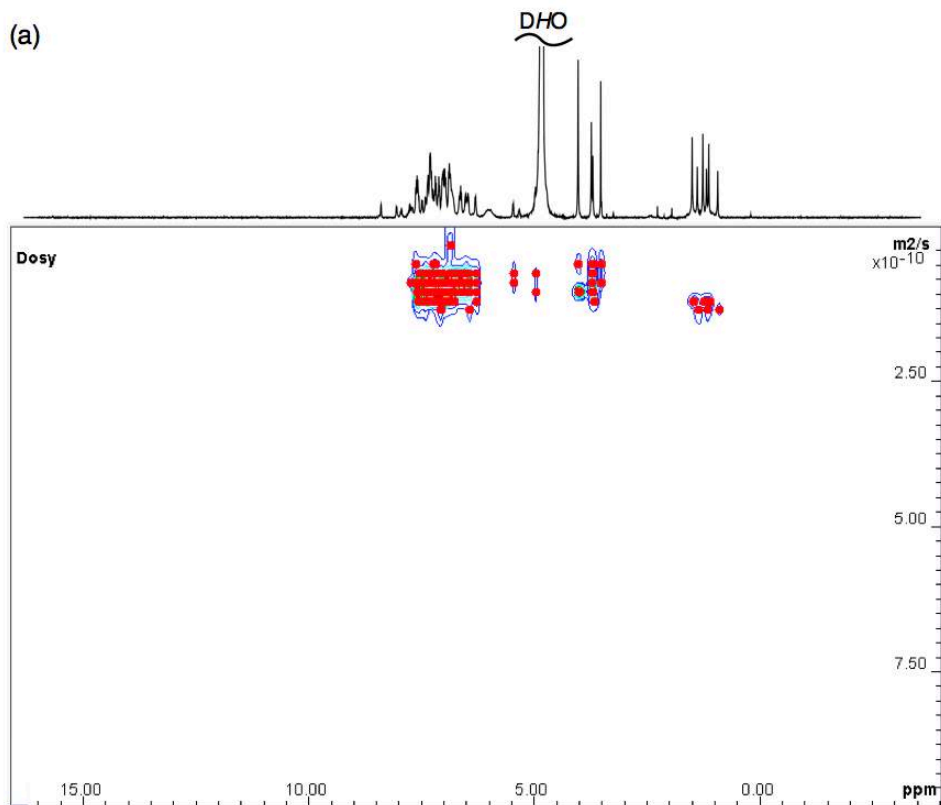
Supplementary Figure 8. ¹H NMR titration experiments of CHB₁₁Cl₁₁⁻ (CB) against **1**₆ (500 MHz, 298 K, D₂O, [**1**]_{total} = 1.0 mM). Red and black solid circles indicate the *p*-tolyl methyl signals of CHB₁₁Cl₁₁⁻@**1**₆ and **1**₆, respectively.



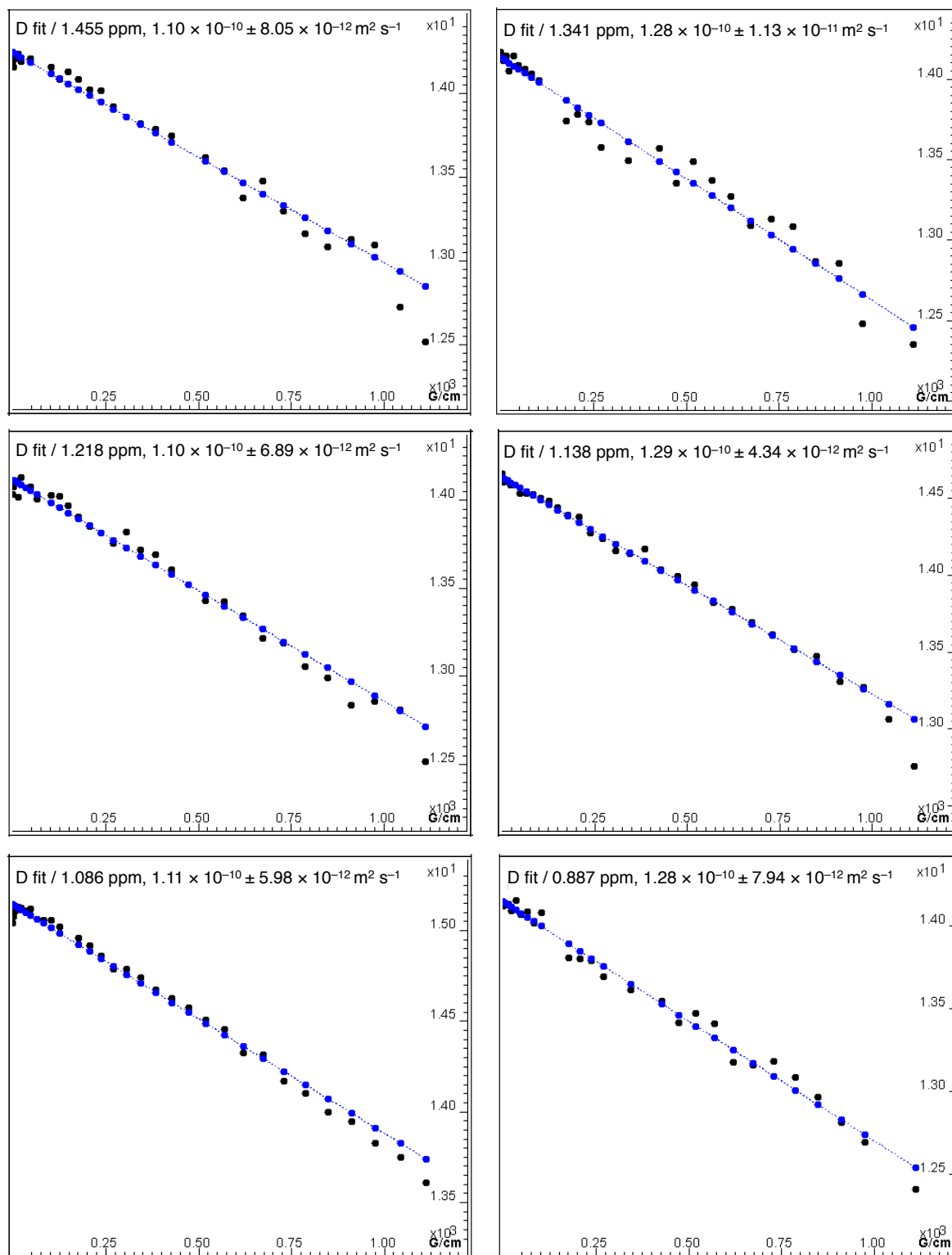
Supplementary Figure 9. ^1H NMR spectra of the mixture of **1**₆ and tetra-*n*-butylammonium (TBA) bromide (500 MHz, 298 K, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0$ mM). Black and green solid circles indicate the signals of the *p*-tolyl methyl groups of free **1**₆ and TBA, respectively.



Supplementary Figure 10. ^1H NMR spectra of selected guest molecules (500 MHz, 298 K, CD_3OD).

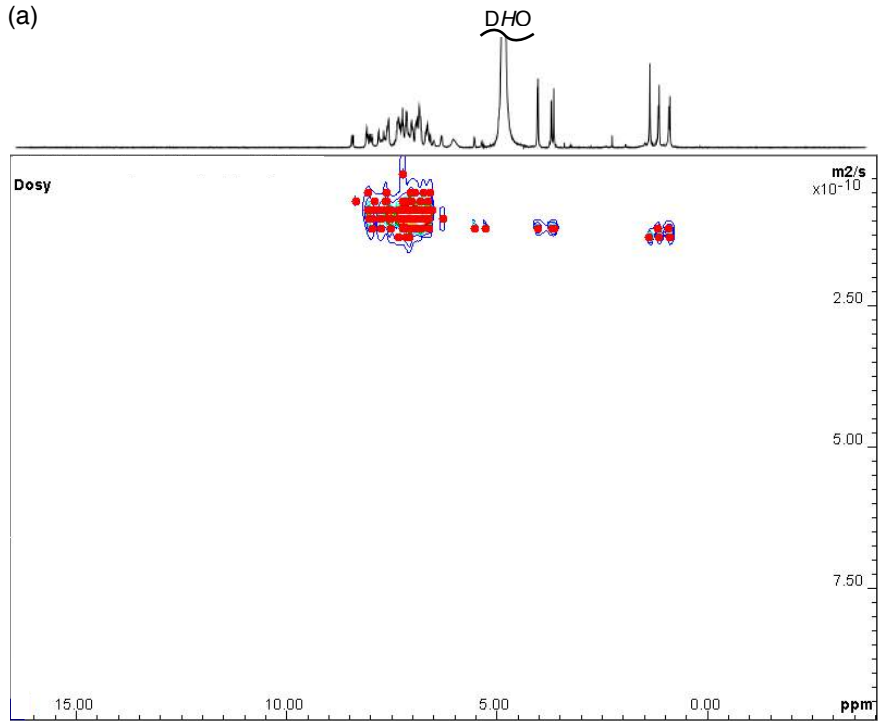


(c)

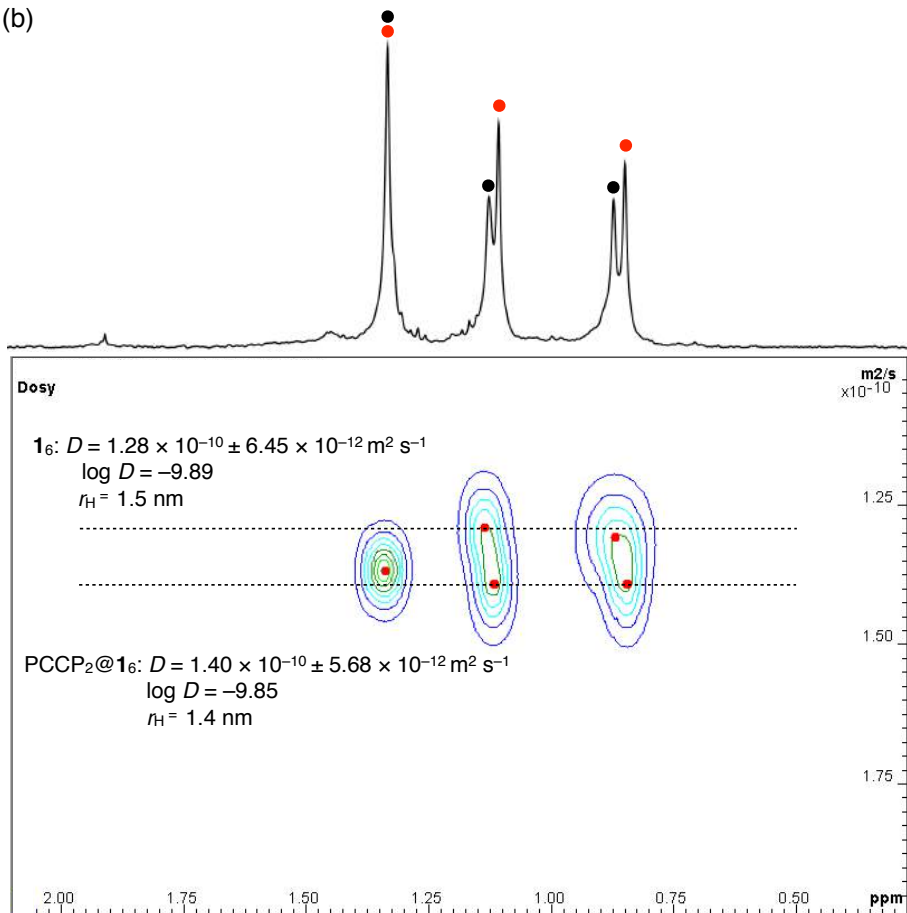


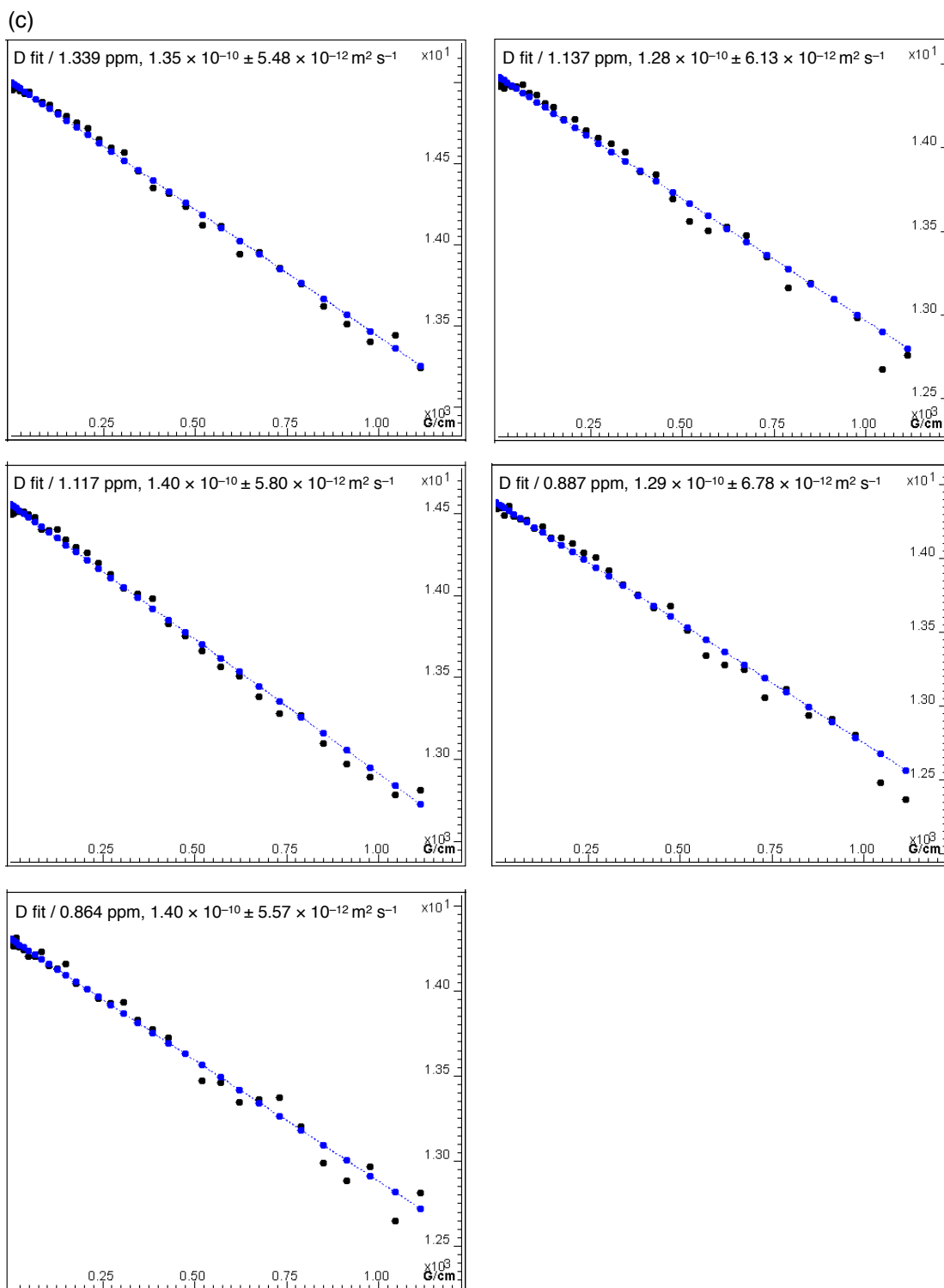
Supplementary Figure 11. ^1H DOSY spectra of a mixture of the $\mathbf{1}_6$ and $\text{TBM}_2@1_6$ (500 MHz, 298 K, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0 \text{ mM}$). (a) A full spectrum. (b) Aliphatic region from 0 to 3 ppm. TBM indicates 1,3,5-tribromomesitylene. Red and black solid circles indicate the *p*-tolyl methyl signals of $\text{TBM}_2@1_6$ and $\mathbf{1}_6$, respectively. The diffusion coefficient of $\text{TBM}_2@1_6$ and $\mathbf{1}_6$ was determined by the average D value of the three *p*-tolyl methyl groups of $\text{TBM}_2@1_6$ and $\mathbf{1}_6$, respectively. r_{H} indicates hydrodynamic radius, which was determined by using the Stokes-Einstein equation, $D = kT/6\pi\eta r_{\text{H}}$, where k is the Boltzmann constant, T is the temperature, and η is the viscosity of the solution. (c) The fitting curves of the *p*-tolyl methyl groups of $\text{TBM}_2@1_6$ and $\mathbf{1}_6$.

(a)

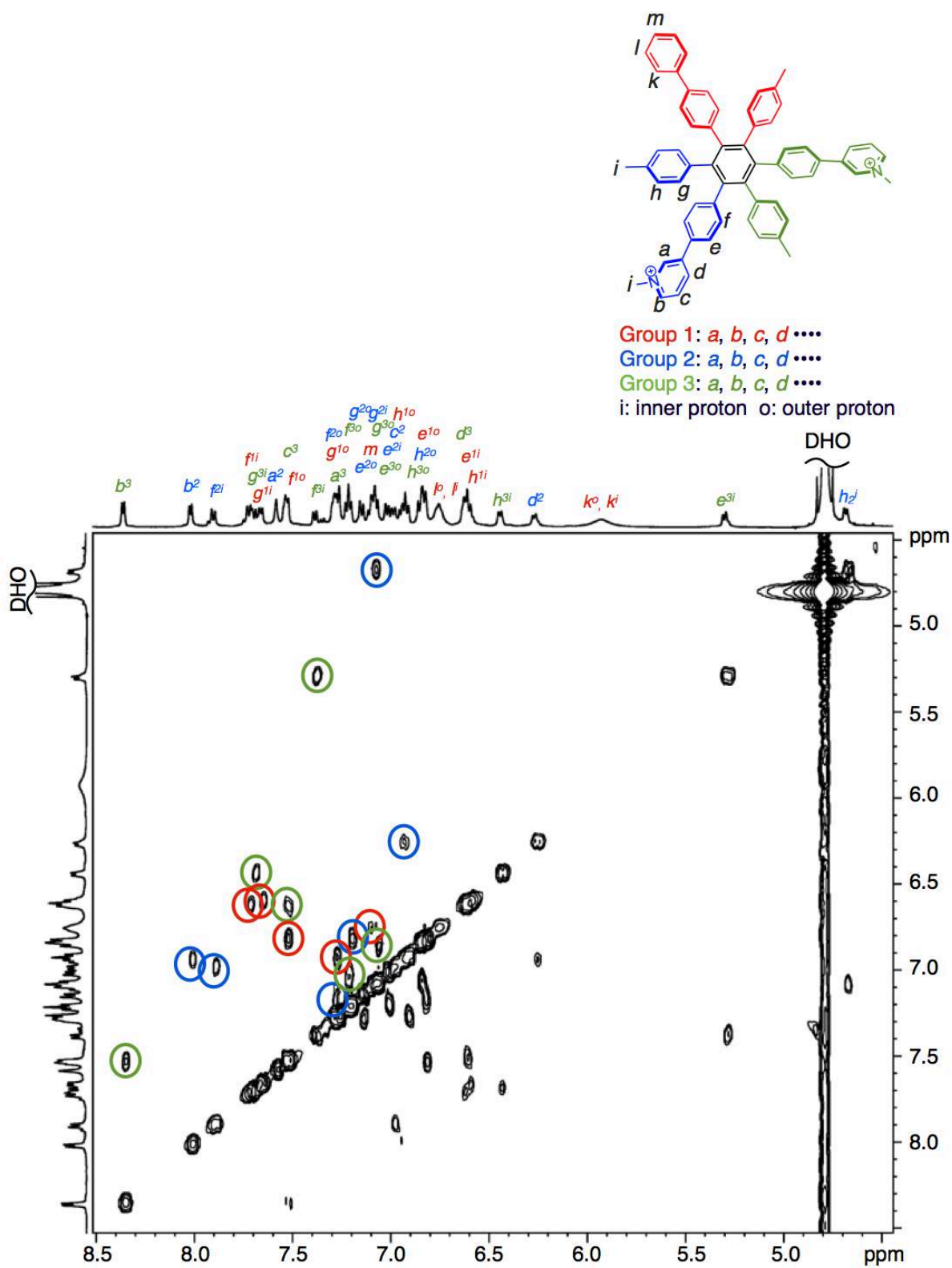


(b)

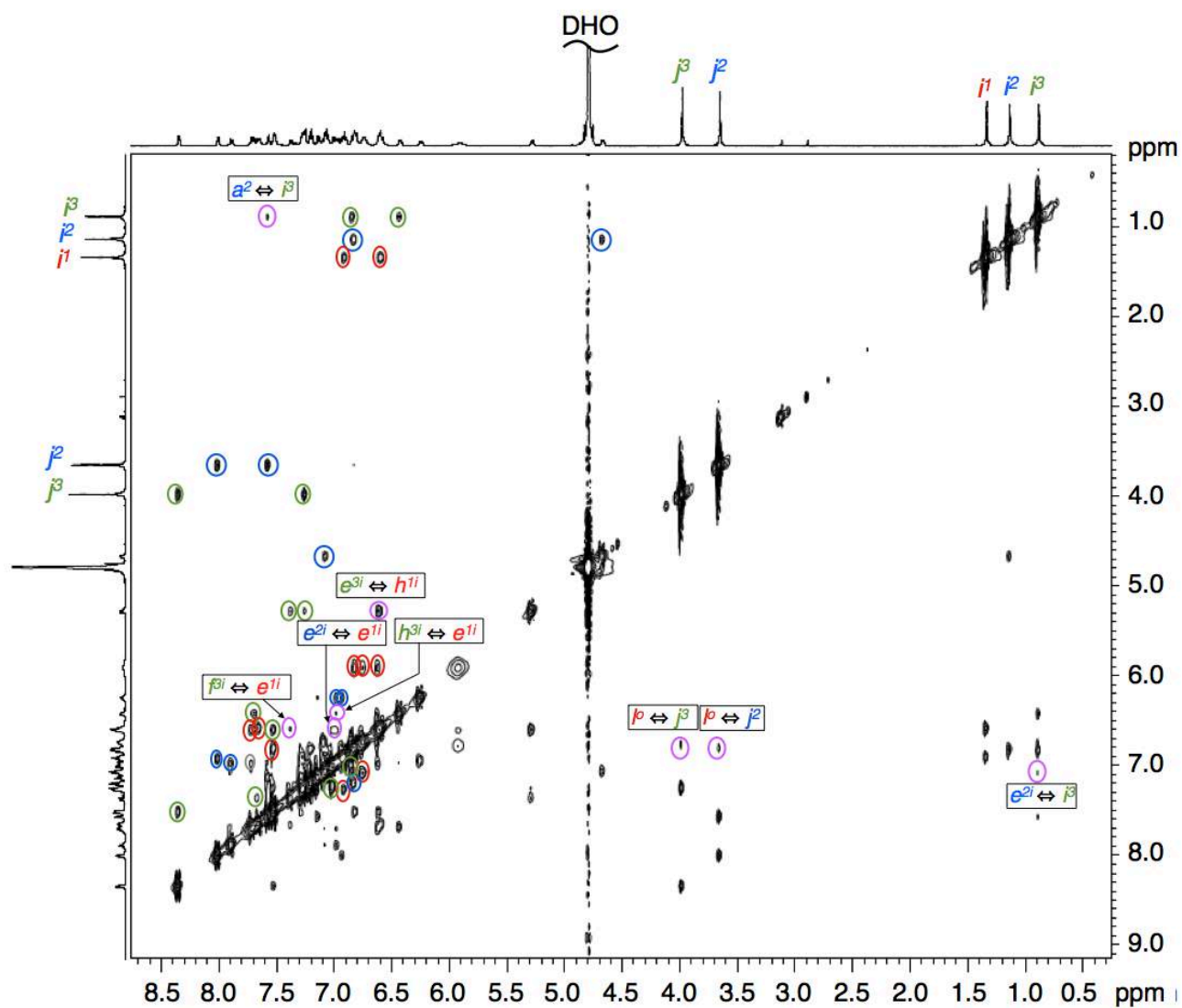




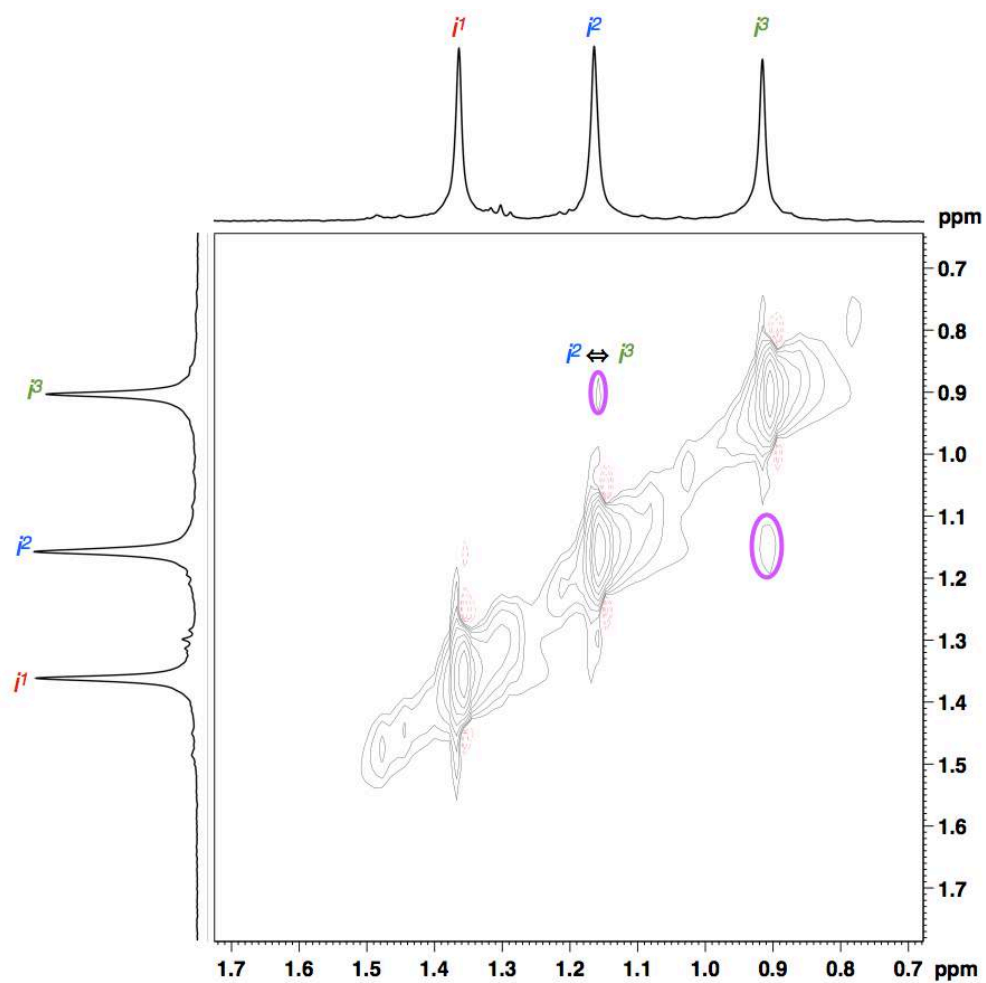
Supplementary Figure 12. ^1H DOSY spectra of a mixture of $\mathbf{1}_6$ and $\text{PCCP}_2@1_6$ nanocubes (500 MHz, 298 K, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0 \text{ mM}$). (a) A full spectrum. (b) Aliphatic region from -1 to 3 ppm. PCCP indicates pentacyanocyclopentadienide. Red and black solid circles indicate the *p*-tolyl methyl signals of $\text{PCCP}_2@1_6$ and $\mathbf{1}_6$, respectively. The diffusion coefficient of $\text{PCCP}_2@1_6$ and $\mathbf{1}_6$ was determined by the average D value of the two upfield signals of the *p*-tolyl methyl groups of $\text{PCCP}_2@1_6$ (1.117 ppm, 0.864 ppm) and $\mathbf{1}_6$ (1.137 ppm, 0.887 ppm), respectively. The ^1H NMR signal at 1.339 ppm is composed of 65% $\text{PCCP}_2@1_6$ and 35% $\mathbf{1}_6$ based on the integral value the *p*-tolyl methyl groups and its diffusion coefficient is $1.35 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, which is between the diffusion coefficient of $\text{PCCP}_2@1_6$ and $\mathbf{1}_6$. r_{H} indicates hydrodynamic radius, which was determined by using the Stokes-Einstein equation. (c) The fitting curves of the *p*-tolyl methyl groups of $\text{TBM}_2@1_6$ and $\mathbf{1}_6$.



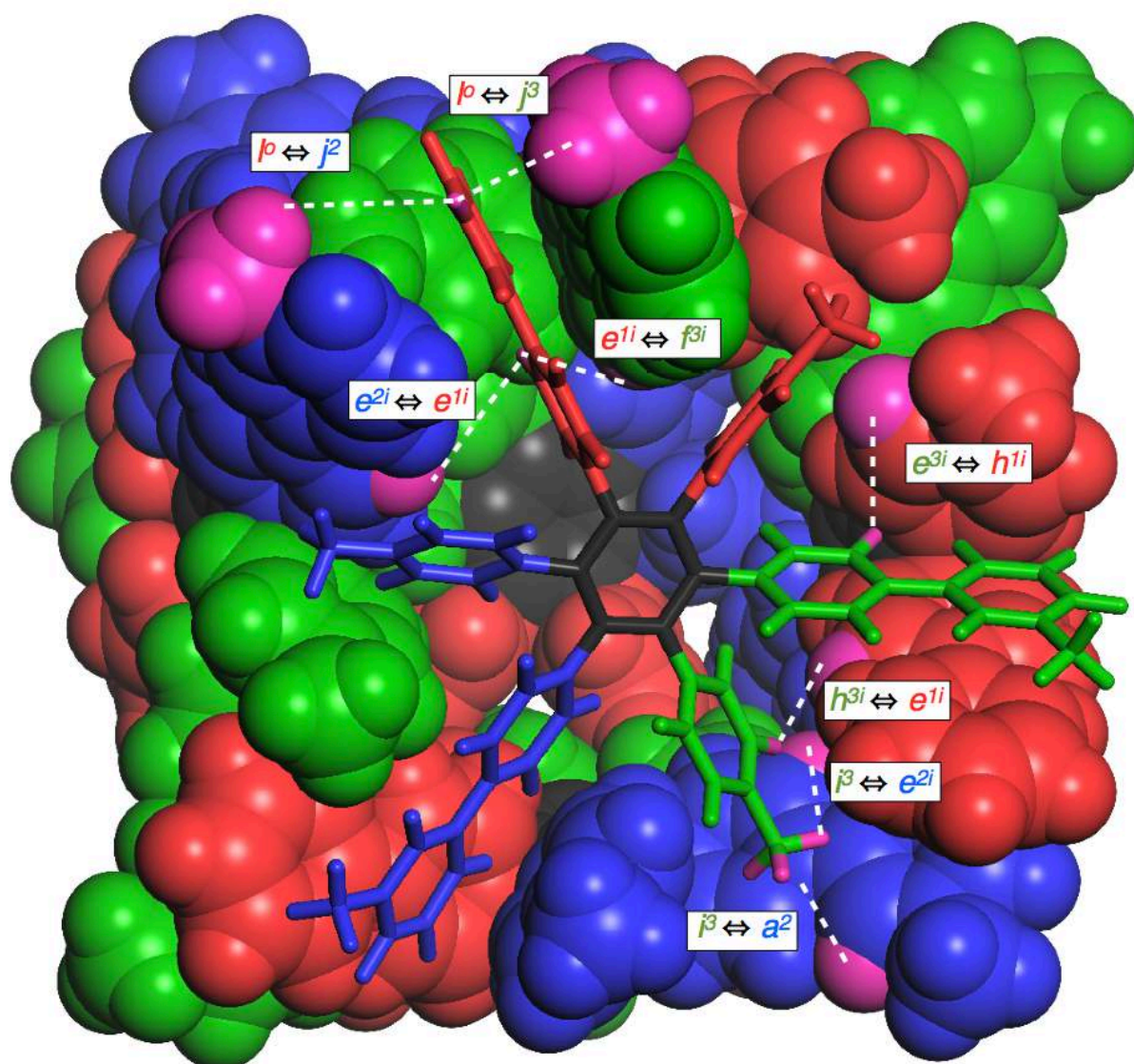
Supplementary Figure 13. ^1H - ^1H COSY spectra of **1₆** nanocube (500 MHz, D_2O , 298 K). Red, blue, and green circles indicate *ortho* coupling between protons, which belong to groups 1, 2, and 3, respectively.



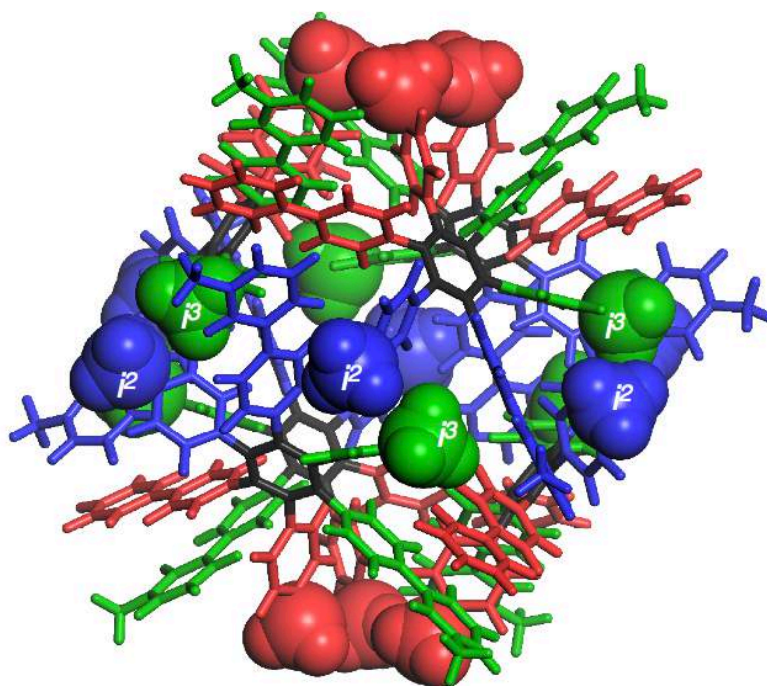
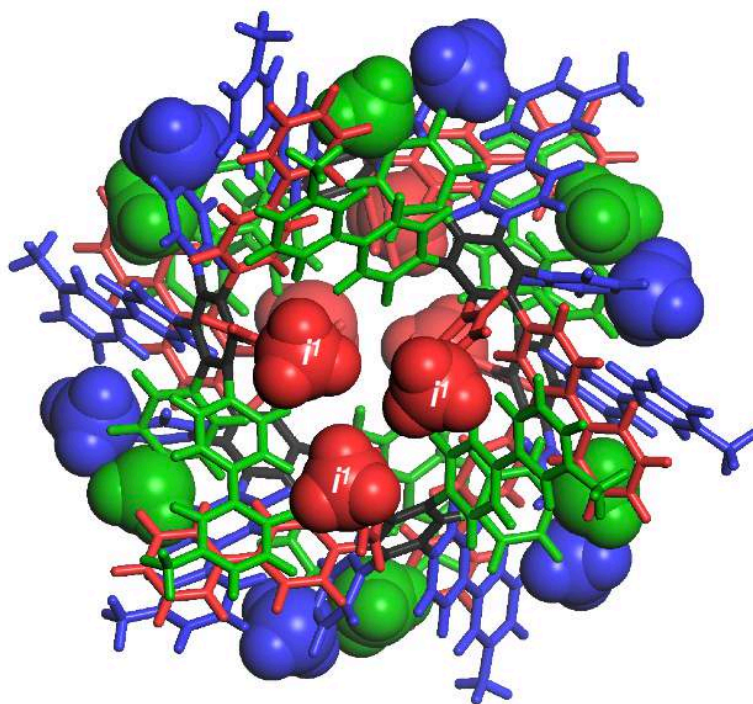
Supplementary Figure 14. ^1H - ^1H NOESY spectrum of the I_6 nanocube (500 MHz, D_2O , 298 K, mixing time = 0.5 s). Magenta circles indicate intermolecular NOE. Red, blue, and green circles indicate intramolecular NOEs between protons belonging to groups 1, 2, and 3, respectively.



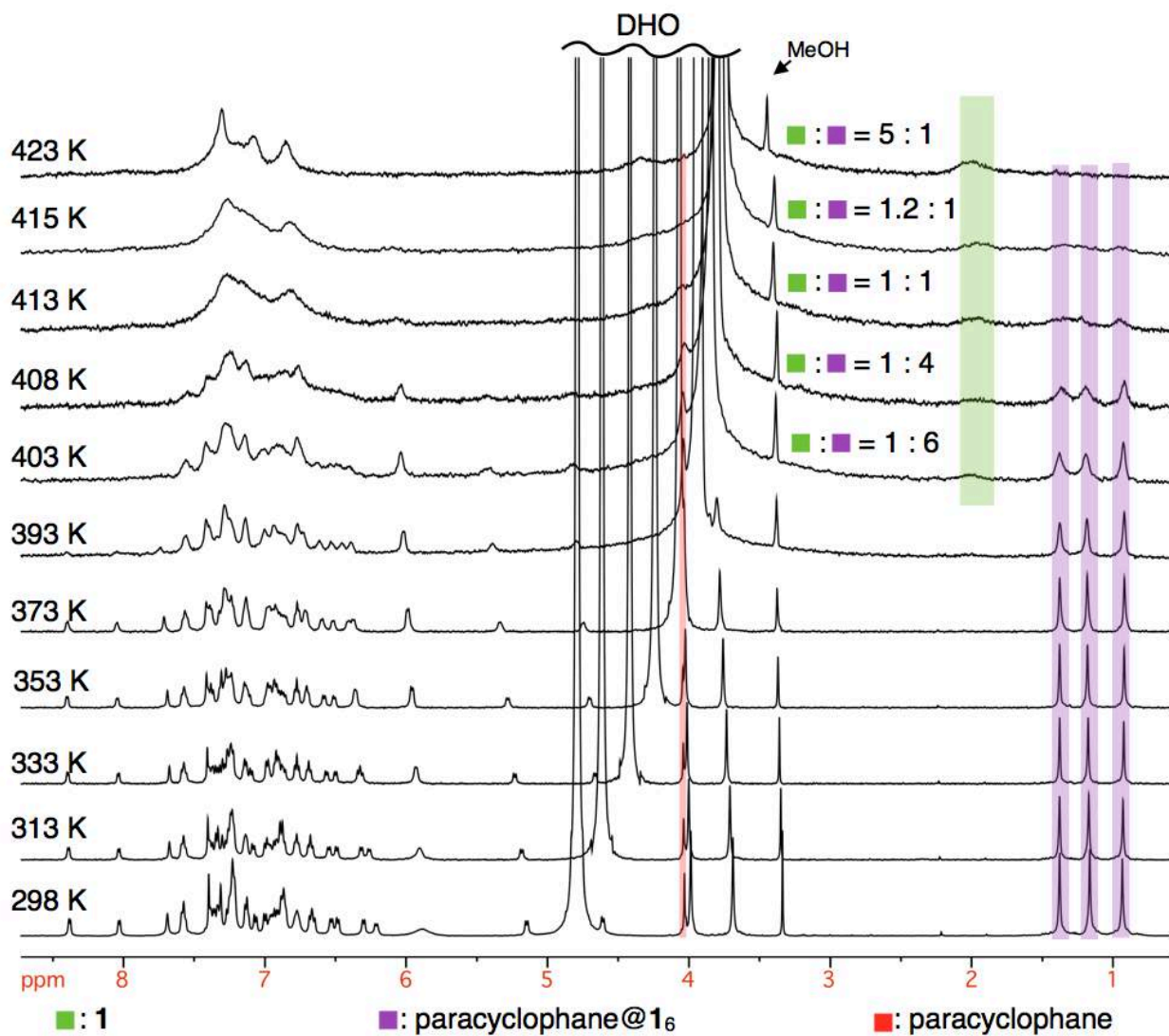
Supplementary Figure 15. ^1H - ^1H NOESY spectrum of the 1_6 nanocube (500 MHz, D_2O , 298 K, mixing time = 0.2 s). Magenta circles indicate intermolecular NOE between i^2 and i^3 .



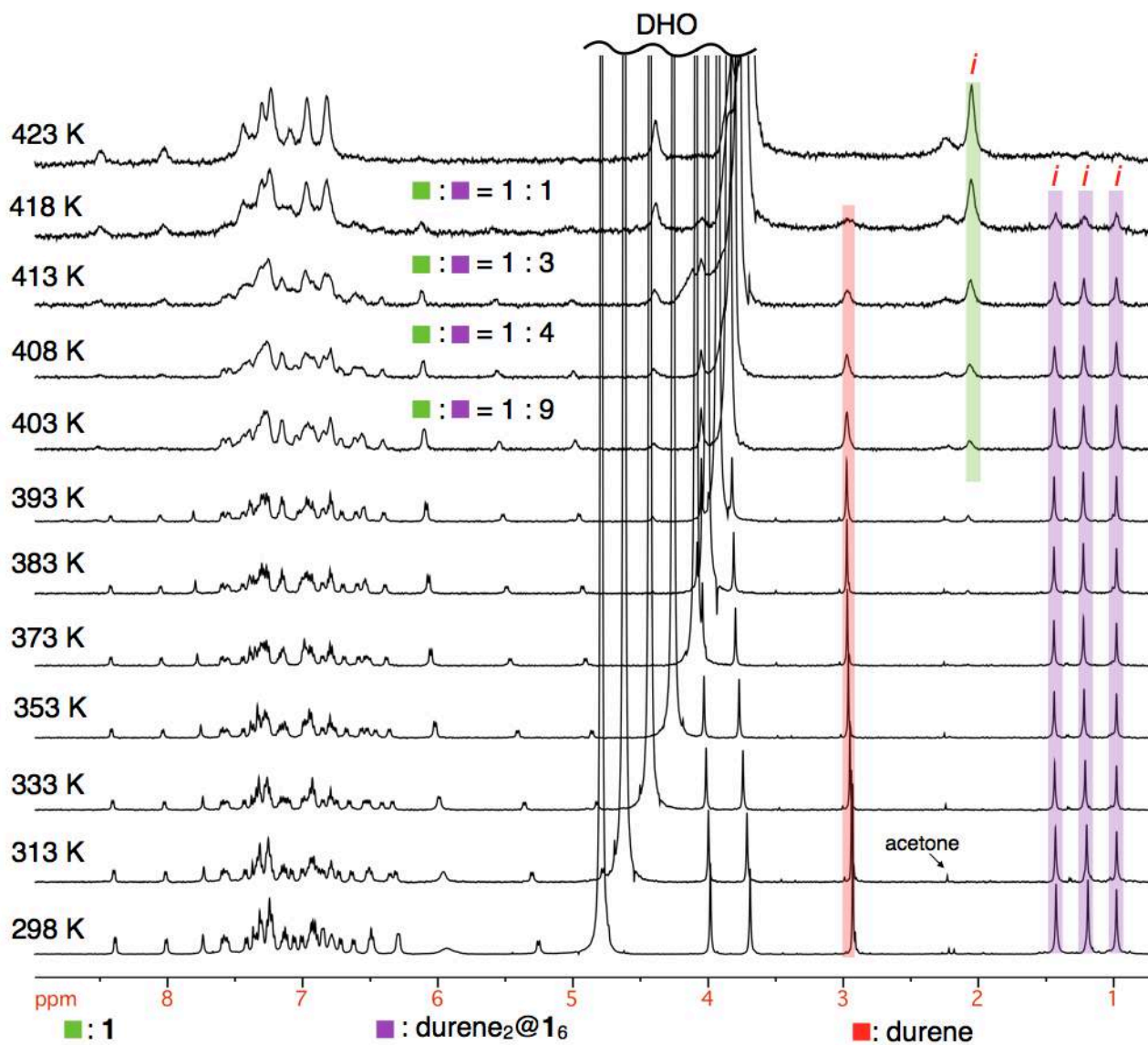
Supplementary Figure 16. The structure of 1_6 indicative of the intermolecular proton pairs where NOE cross peaks were observed (See Supplementary Figure 14). White dotted lines denote the pairs of protons (colored in magenta) where intermolecular NOE cross-peaks were observed.



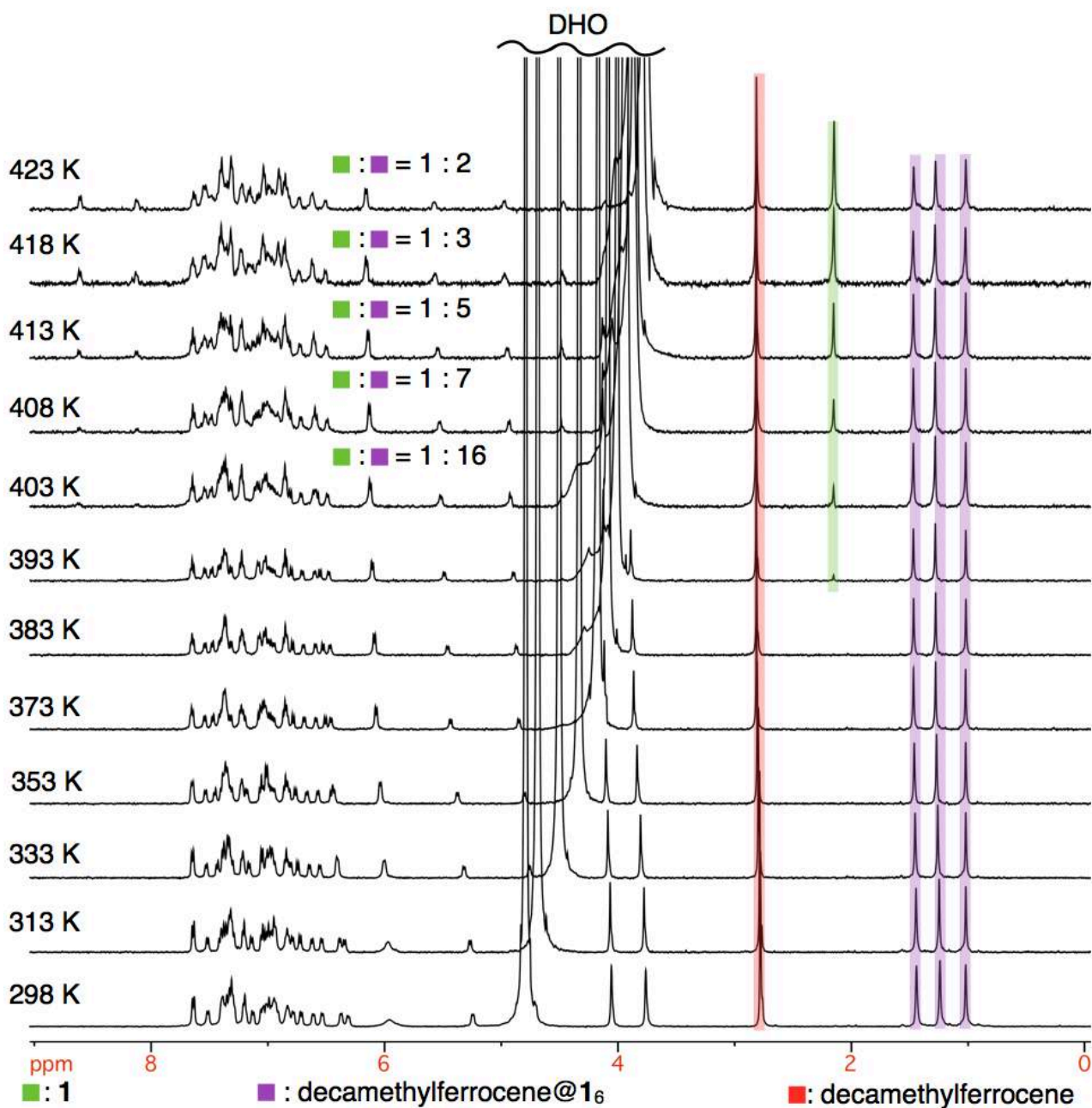
Supplementary Figure 17. Schematic description of the positions of three *p*-tolyl methyl groups, which are shown as space-filling model. Red methyl groups (i^1) are close to each other, while Blue methyl groups (i^2) and green ones (i^3) are close to each other.



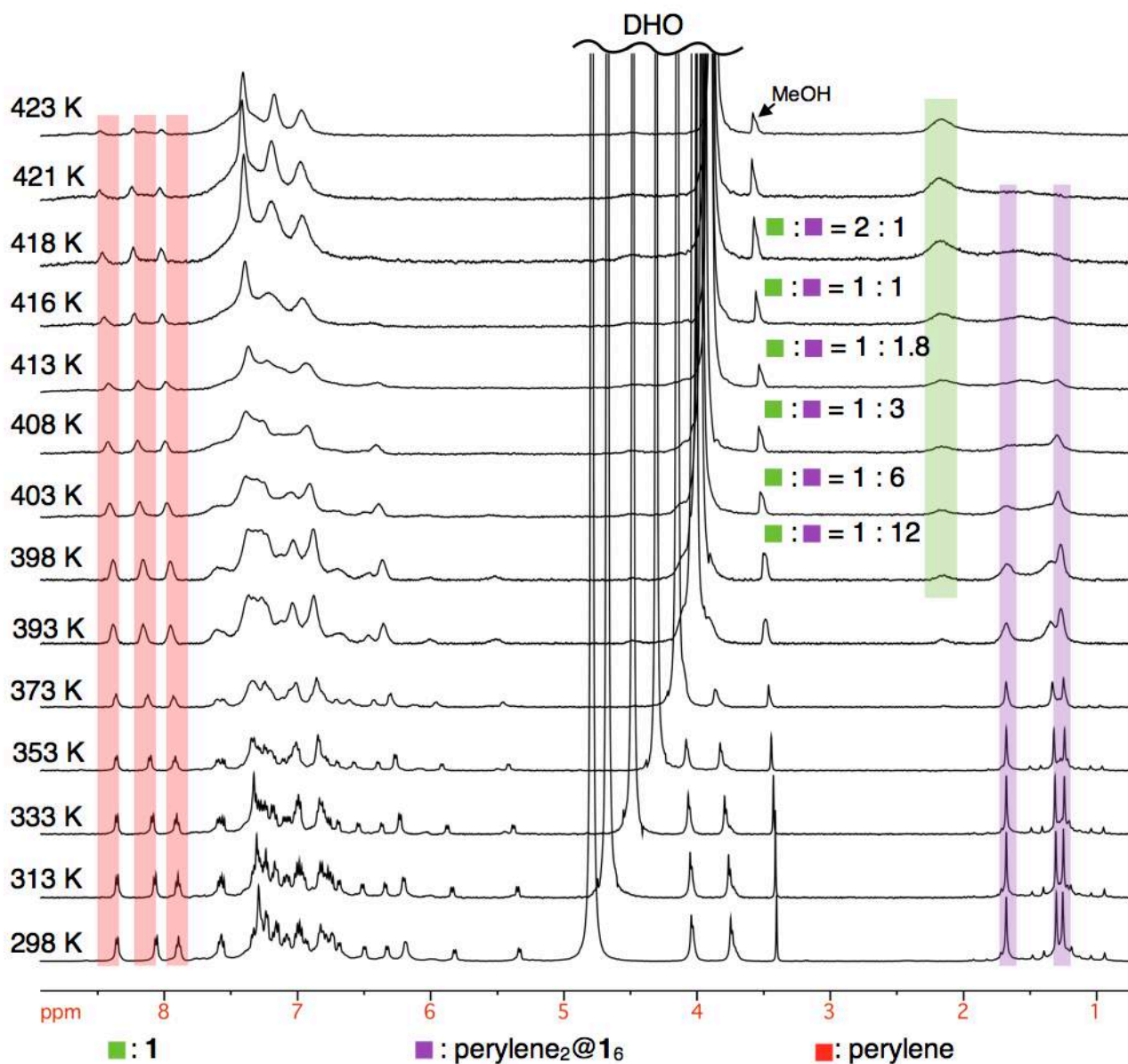
Supplementary Figure 18. Variable temperature ^1H NMR spectra of PC@ $\mathbf{1}_6$ (500 MHz, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0$ mM). PC indicates [2.2]paracyclophane.



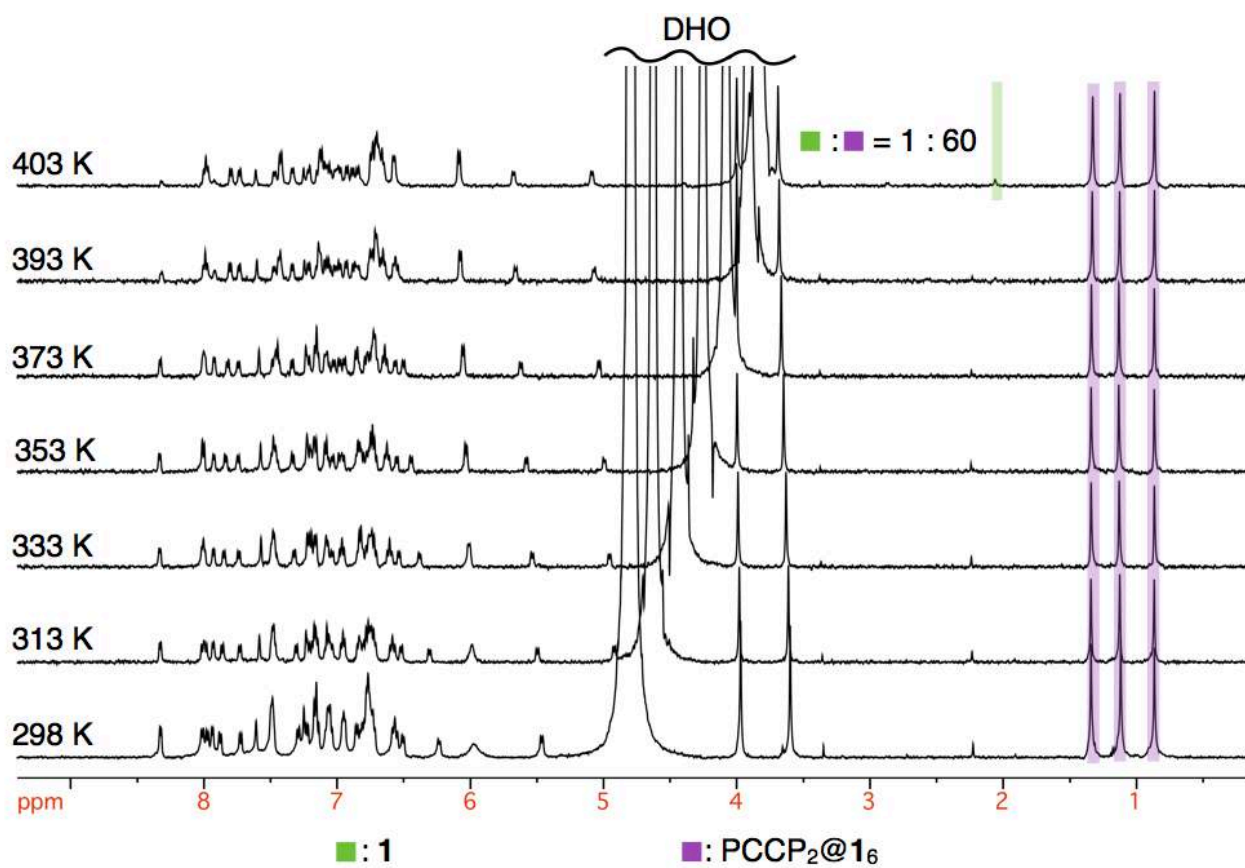
Supplementary Figure 19. Variable temperature ^1H NMR spectra of $\text{DU}_2@1_6$ (500 MHz, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0$ mM). DU indicates durene.



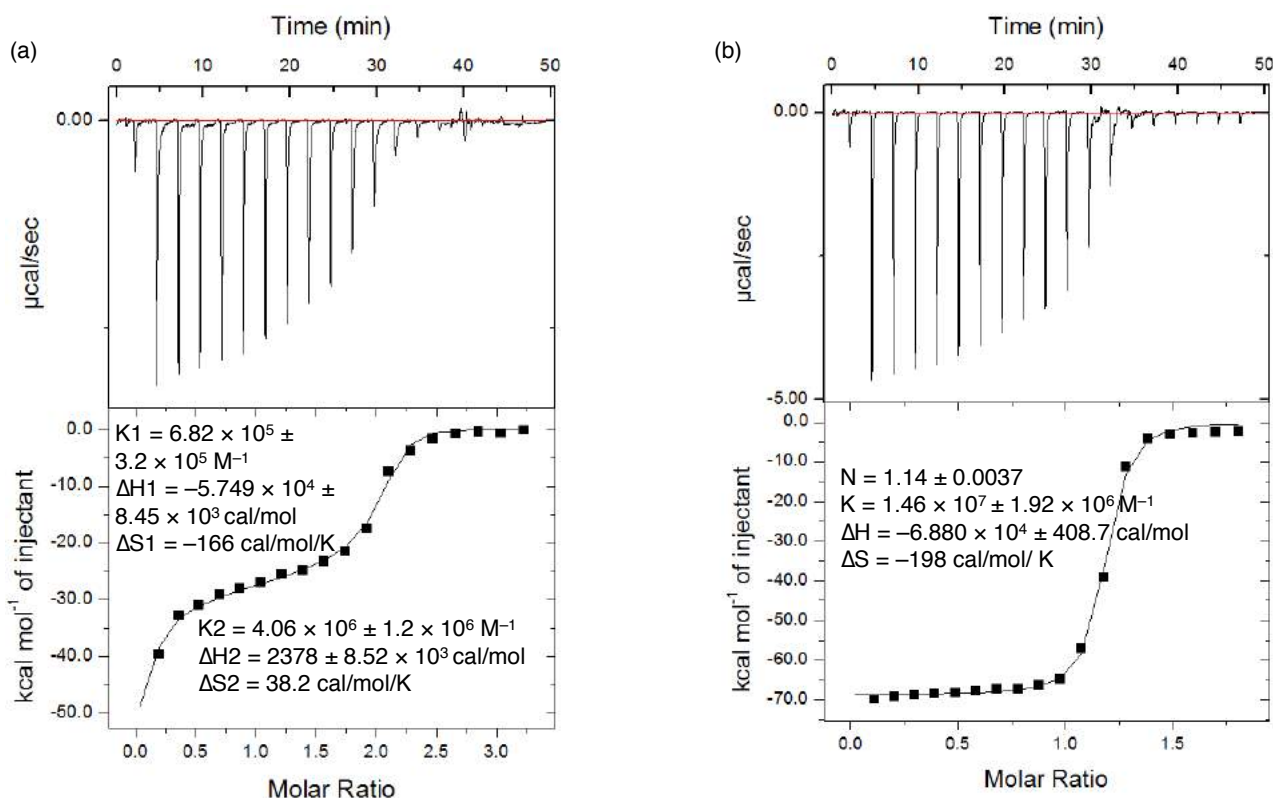
Supplementary Figure 20. Variable temperature ^1H NMR spectra of DF@ 1_6 (500 MHz, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0$ mM). DF indicates decamethylferrocene.



Supplementary Figure 21. Variable temperature ^1H NMR spectra of $\text{PE}_2@1_6$ (500 MHz, D_2O , $[\mathbf{1}]_{\text{total}} = 1.0$ mM). PE indicates perylene.



Supplementary Figure 22. Variable temperature ^1H NMR spectra of PCCP₂@1₆ (500 MHz, D₂O, [1]_{total} = 1.0 mM). PCCP indicates pentacyanocyclopentadienide



Supplementary Figure 23. ITC titration curves for the encapsulation of anionic guests (PCCP or CB) in the nanocube obtained at 298 K. (a) A titration of PCCP (0.5 mM) to $\mathbf{1}_6$ ($[\mathbf{1}]_{\text{total}} = 0.2 \text{ mM}$). Integrations of the heat released were fitted to a sequential binding model with two binding sites. As a result of fitting analysis, the thermodynamic parameters were determined as follows: $\Delta G_1 = -8.0 \text{ kcal mol}^{-1}$, $\Delta H_1 = -57.5 \text{ kcal mol}^{-1}$, $T\Delta S_1 = -49.5 \text{ kcal mol}^{-1}$, $\Delta G_2 = -9.0 \text{ kcal mol}^{-1}$, $\Delta H_2 = 2.4 \text{ kcal mol}^{-1}$, $T\Delta S_2 = 11.4 \text{ kcal mol}^{-1}$. (b) A titration of CB (0.3 mM) to $\mathbf{1}_6$ ($[\mathbf{1}]_{\text{total}} = 0.2 \text{ mM}$). Integrations of the heat released were fitted to a 1:1 binding model. As a result of fitting analysis, the thermodynamic parameters were determined as follows: $\Delta G = -9.8 \text{ kcal mol}^{-1}$, $\Delta H = -68.8 \text{ kcal mol}^{-1}$, $T\Delta S = -59.0 \text{ kcal mol}^{-1}$.

Supplementary Tables

Supplementary Table 1. Encapsulation behavior of **1**₆

guest	volume (Å ³)	length of longest distance (Å)	Number of guests	Δi^{1a} (ppm)	Δi^{2a} (ppm)	Δi^{3a} (ppm)	total Shift $\Delta\delta^b$ (ppm)	volume × encapsulate number (Å ³)
toluene	112	8.3	3	0.117	0.079	0.149	0.345	336
<i>o</i> -xylene	134	8.3	2	0.059	0.055	0.085	0.199	268
<i>p</i> -xylene	133	9.3	2	0.074	0.064	0.085	0.223	266
<i>m</i> -xylene	135	8.8	3	0.143	0.079	0.187	0.409	405
naphthalene	139	9.6	2	0.073	0.056	0.070	0.199	278
mesitylene	158	8.8	2	0.081	0.064	0.049	0.194	316
durene (DU)	174	9.3	2	0.102	0.071	0.107	0.280	348
anthracene	187	12.0	2	0.224	0.062	0.165	0.450	374
1,3,5-tribromo mesitylene (TBM)	220	9.8	2	0.113	0.081	0.199	0.393	440
hexamethyl benzene	216	9.3	2	0.131	0.079	0.182	0.392	432
1,3,5-triiodo mesitylene	246	10.2	2	0.177	0.181	0.224	0.582	492
[2.2]paracyclophane (PC)	248	9.8	1	0.056	0.049	0.065	0.170	248
perylene (PE)	254	12.0	2	0.301	0.129	0.331	0.760	508
decamethyl ferrocene (DF)	407	10.8	1	0.097	0.099	0.129	0.325	407
<i>n</i> -propane	74	6.8	3	0.097	0.069	0.124	0.290	222
<i>n</i> -butane	95	8.0	3	0.090	0.071	0.114	0.275	285
<i>n</i> -pentane	114	8.6	3	0.109	0.069	0.133	0.311	343
<i>n</i> -hexane	137	9.4	3	0.152	0.094	0.180	0.426	411
cyclohexane	122	7.4	3	0.141	0.059	0.177	0.377	367
<i>n</i> -heptane	157	11.1	2	0.084	0.058	0.114	0.256	314
<i>n</i> -octane	179	13.2	2	0.098	0.064	0.129	0.291	358
<i>n</i> -decane	223	15.7	2	0.159	0.092	0.200	0.451	445
<i>n</i> -dodecane	265	18.3	1	0.060	0.045	0.084	0.189	265
<i>n</i> -tetradecane	307	20.8	1	0.087	0.059	0.109	0.255	307
<i>n</i> -hexadecane	351	23.4	1	0.103	0.063	0.129	0.295	351
<i>n</i> -octadecane	394	25.9	1	0.127	0.077	0.161	0.365	394
<i>n</i> -eicosane	438	28.5	1	0.156	0.087	0.205	0.448	438
<i>n</i> -docosane	482	31.1	1	0.193	0.106	0.256	0.555	482
<i>n</i> -tetracosane	535	33.6	1	0.236	0.125	0.300	0.661	535
PCCP	193	10.3	2	-0.002	-0.019	-0.023	-0.044	386
CB	403	9.1	1	-0.038	0.007	0.009	-0.022	403
methane	30	4.2	0					
ethene	42	5.5	0					
naphthacene	235	14.3	0					
<i>p</i> -di- <i>tert</i> -butylbenzene	287	12.0	0					
coronene	325	12.6	0					
fullerene	533	10.4	0					
tetra-<i>n</i>-butyl ammonium bromide	446	13.5	0					

^a $\Delta i^1 = \delta(i^1)$ of $G_n@1_6$ (G : guest molecule) $- \delta(i^1)$ of **1**₆. $\Delta i^2 = \delta(i^2)$ of $G_n@1_6$ (G : guest molecule) $- \delta(i^2)$ of **1**₆. $\Delta i^3 = \delta(i^3)$ of $G_n@1_6$ (G : guest molecule) $- \delta(i^3)$ of **1**₆.

^b Total chemical shift change of the *p*-tolyl methyl signals. $\Delta\delta = \Delta i^1 + \Delta i^2 + \Delta i^3$

Supplementary Table 2. Free energy changes for the formation of host-guest complexes of **1**₆, ΔG_a , around $T_{1/2}$ in D₂O.

Nanocube complexes	GSA / mM	T / K	Formation ratio ([monomer] / 6[hexamer])	K_a / M^{-5}	$\Delta G_a /$ kJ mol ⁻¹	$-\Delta G /$ kJ mol ⁻¹
PC@ 1 ₆	1.0	403	1/6	1.7×10^{19}	-148	148
		408	1/5	2.1×10^{18}	-143	143
		413	1	5.3×10^{15}	-124	124
		415	1.2	2.9×10^{15}	-123	123
		423	5	8.3×10^{13}	-113	113
DU ₂ @ 1 ₆	1.0	403	1/9	1.5×10^{20}	-156	156
		408	1/4	2.1×10^{18}	-143	143
		413	1/2	8.1×10^{16}	-134	134
		418	1	5.3×10^{15}	-126	126
DF@ 1 ₆	1.0	403	1/16	3.8×10^{21}	-166	166
		408	1/7	3.8×10^{19}	-153	153
		413	1/5	6.5×10^{18}	-149	149
		418	1/3	5.1×10^{17}	-142	142
		423	1/2	8.1×10^{16}	-137	137
PE ₂ @ 1 ₆	1.0	398	1/12	7.4×10^{20}	-159	159
		403	1/6	1.7×10^{19}	-148	148
		408	1/3	5.1×10^{17}	-138	138
		413	1/1.8	5.2×10^{16}	-132	132
		416	1	5.3×10^{15}	-125	125
		418	2	6.3×10^{14}	-118	118
PCCP ₂ @ 1 ₆	1.0	403	1/60	8.5×10^{24}	-192	192

*The temperature colored in red indicates the $T_{1/2}$ for the nanocube.

* $T_{1/2}$ value of DF@**1**₆ is higher than 423 K, which is the highest limit of our NMR instrument.

Supplementary Table 3. longitudinal relaxation time (T_1) of the **1** and **1**₆ nanocubes

Compounds	T_1^a / s
1 ^b	0.908
1 ₆	2.148
PCCP ₂ @ 1 ₆	2.560

^a T_1 is the average of T_1 values of the *p*-tolyl methyl groups, i^1 , i^2 , and i^3 .

^b T_1 value of the **1** is measured in CD₃OD.