Preparation of cage-shaped hexakis(spiroborate)s

Supporting Information

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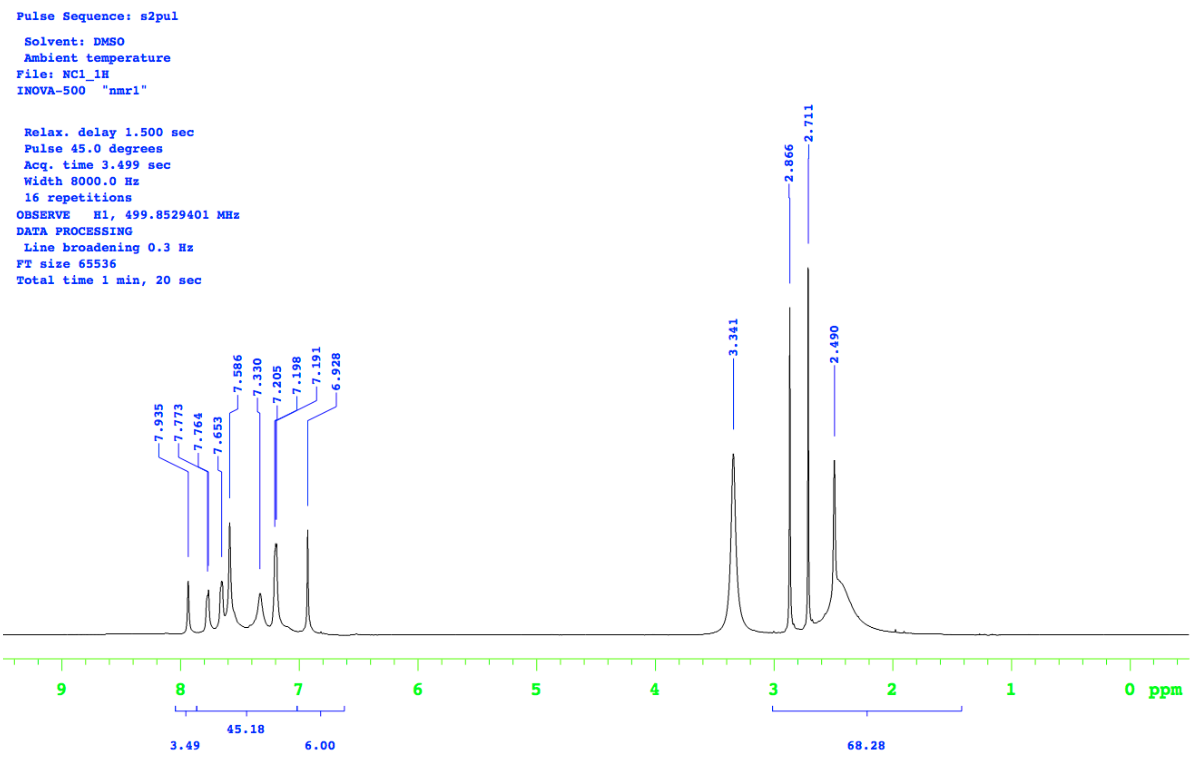
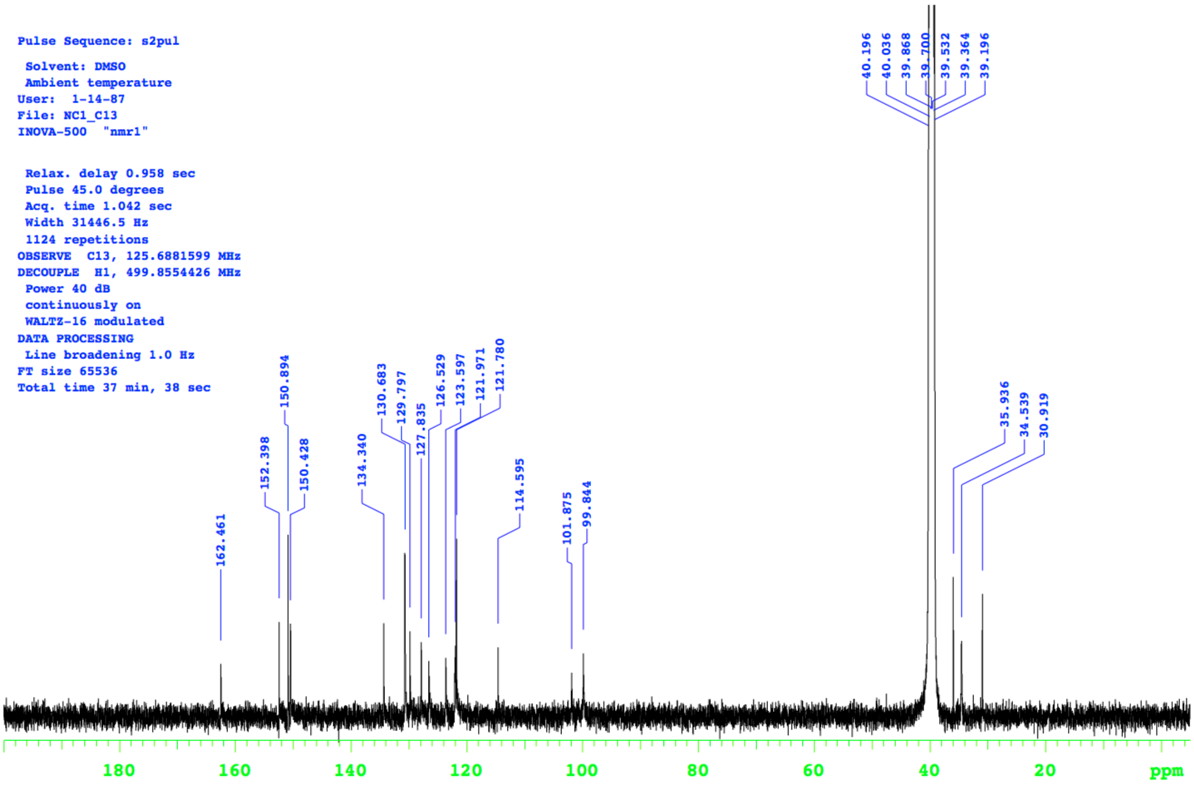
Table of Contents

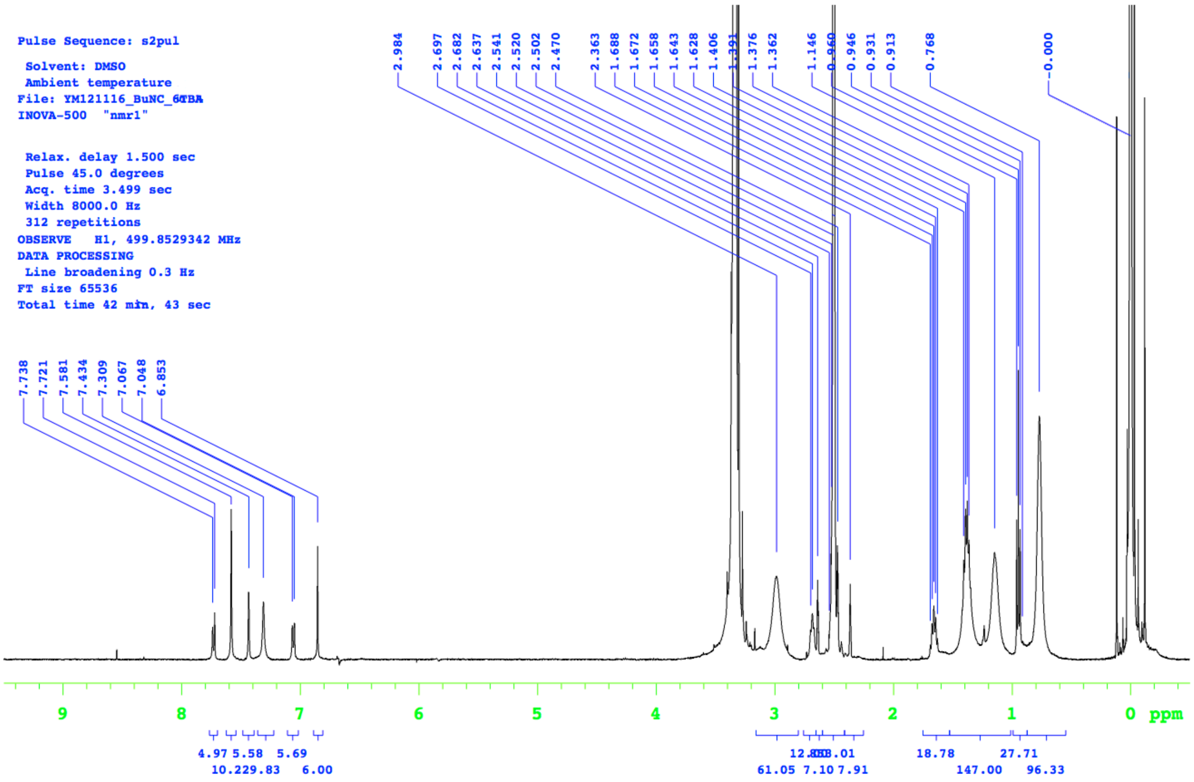
6a·$(Me_2NH_2)_6$, ^{1}H NMR (500 MHz, in DMSO-d_6, 25 °C)



6a·$(Me_2NH_2)_6$, ^{13}C NMR (126 MHz, in DMSO-d_6, 25 °C)



6b·(*n*-Bu$_4$N)$_6$, ^{1}H NMR (500 MHz, in DMSO-*d*$_6$, 25 °C)



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 Solvent: DMSO
 Ambient temperature
File: YM121116_BuNC_6bTBA
INOVA-500  "nmr1"

 Relax. delay 1.500 sec
 Pulse 45.0 degrees
 Acq. time 3.499 sec
 Width 8000.0 Hz
 312 repetitions
OBSERVE   H1, 499.8529342 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 42 min, 43 sec
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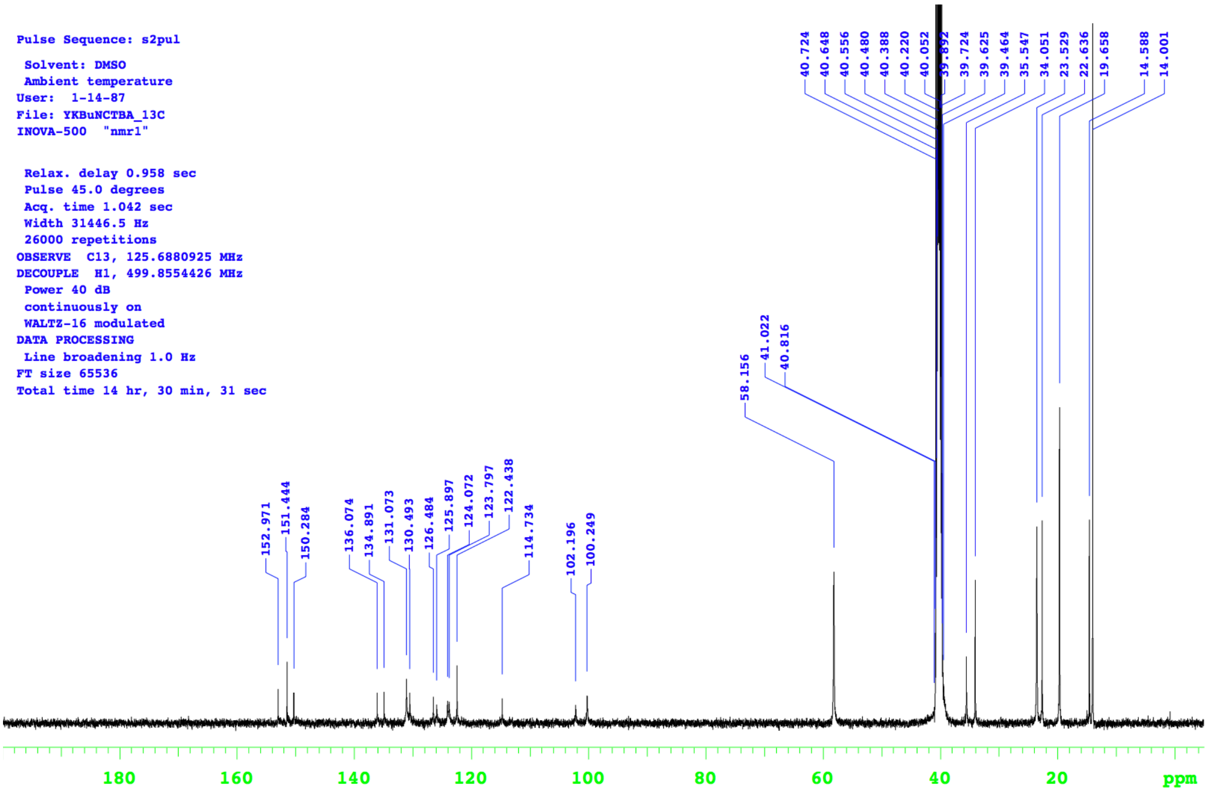
6b·(*n*-Bu$_4$N)$_6$, ^{13}C NMR (126 MHz, in DMSO-*d*$_6$, 25 °C)



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Pulse Sequence: s2pul

 Solvent: DMSO
 Ambient temperature
User:  1-14-87
File: YKBuNCTBA_13C
INOVA-500  "nmr1"

 Relax. delay 0.958 sec
 Pulse 45.0 degrees
 Acq. time 1.042 sec
 Width 31446.5 Hz
 26000 repetitions
OBSERVE   C13, 125.6880925 MHz
DECOUPLE  H1, 499.8554426 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
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Total time 14 hr, 30 min, 31 sec
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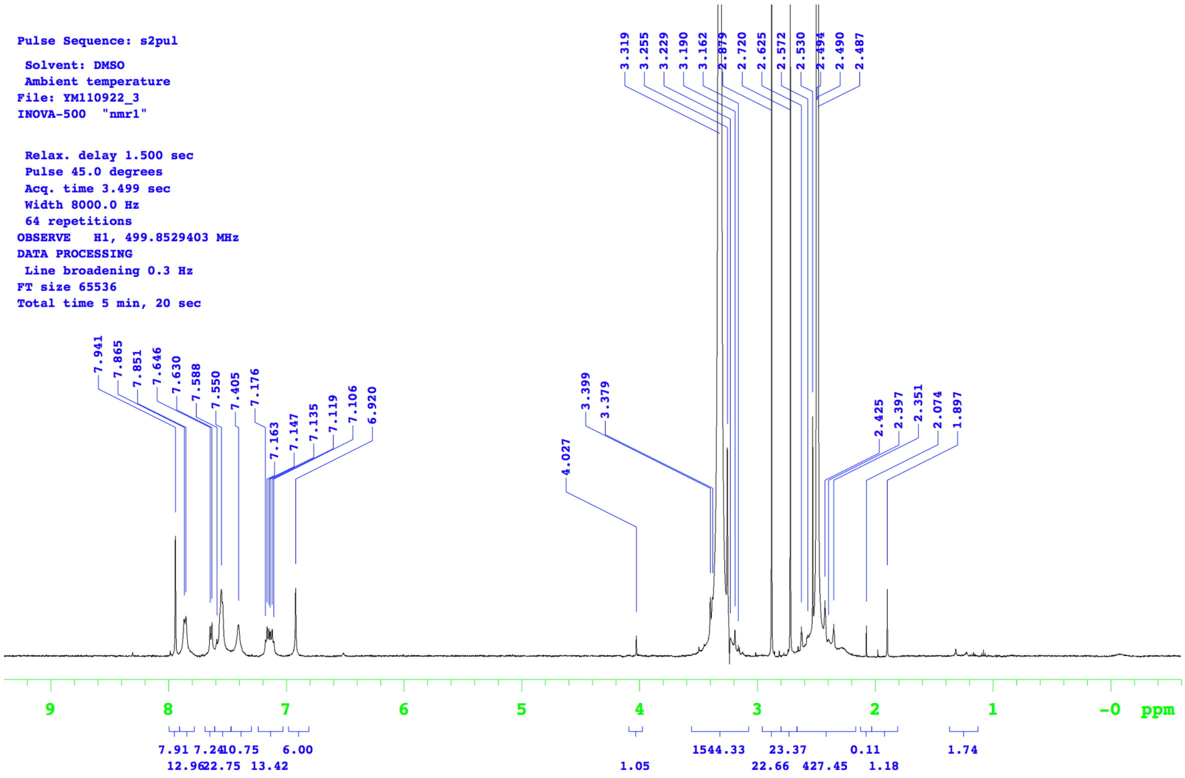
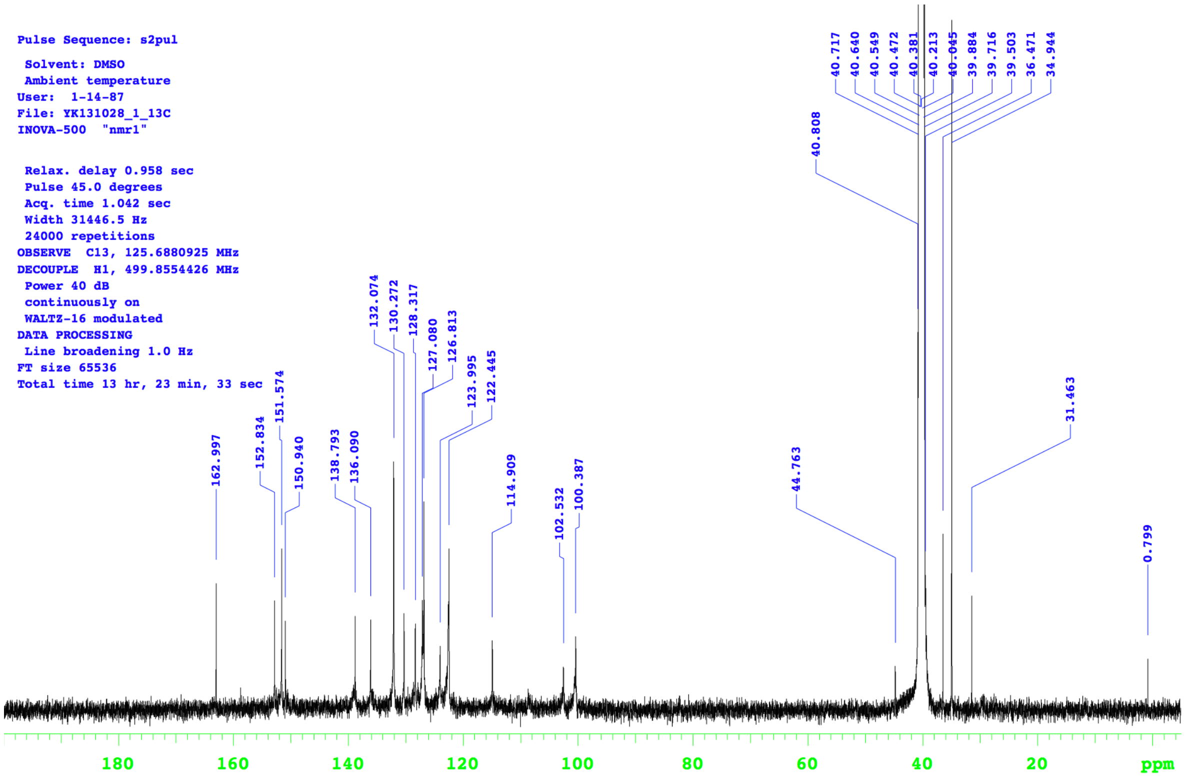
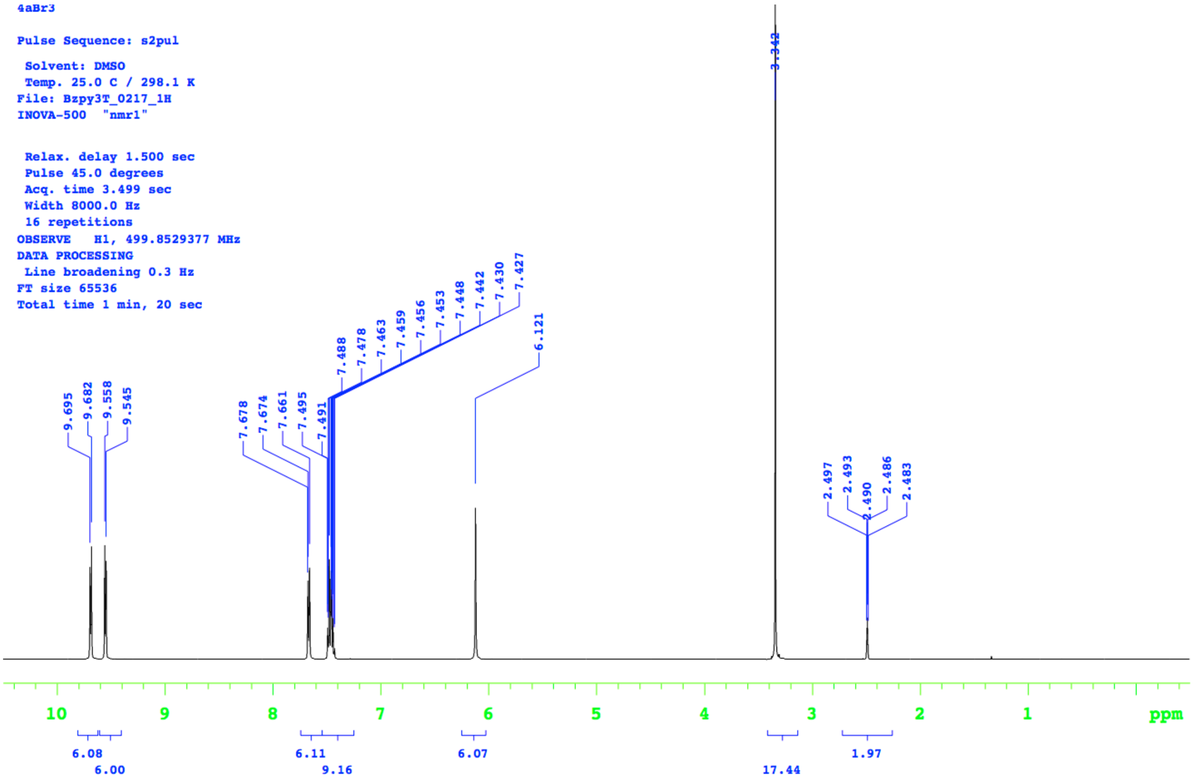


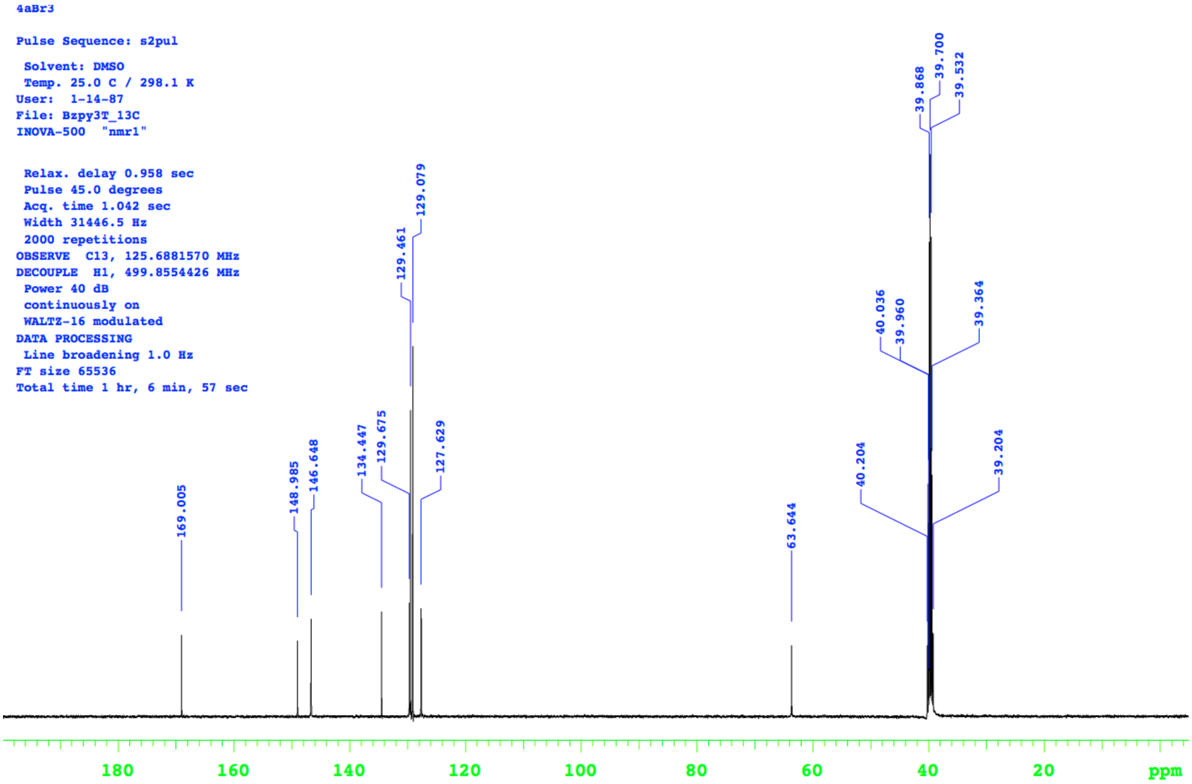
7·(Me2NH2)6, ^{13}C NMR (126 MHz, in DMSO-*d*6, 25 °C)



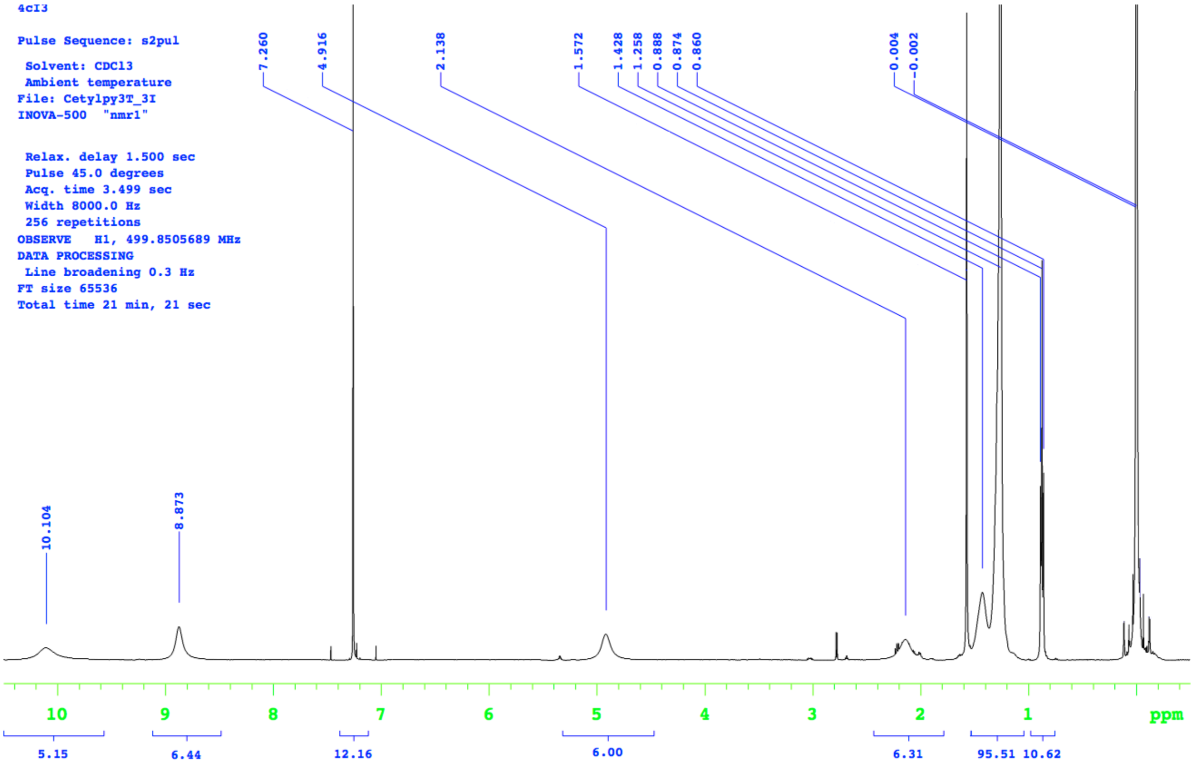
8a·Br$_3$, ^{1}H NMR (500 MHz, in DMSO-d_6, 25 °C)



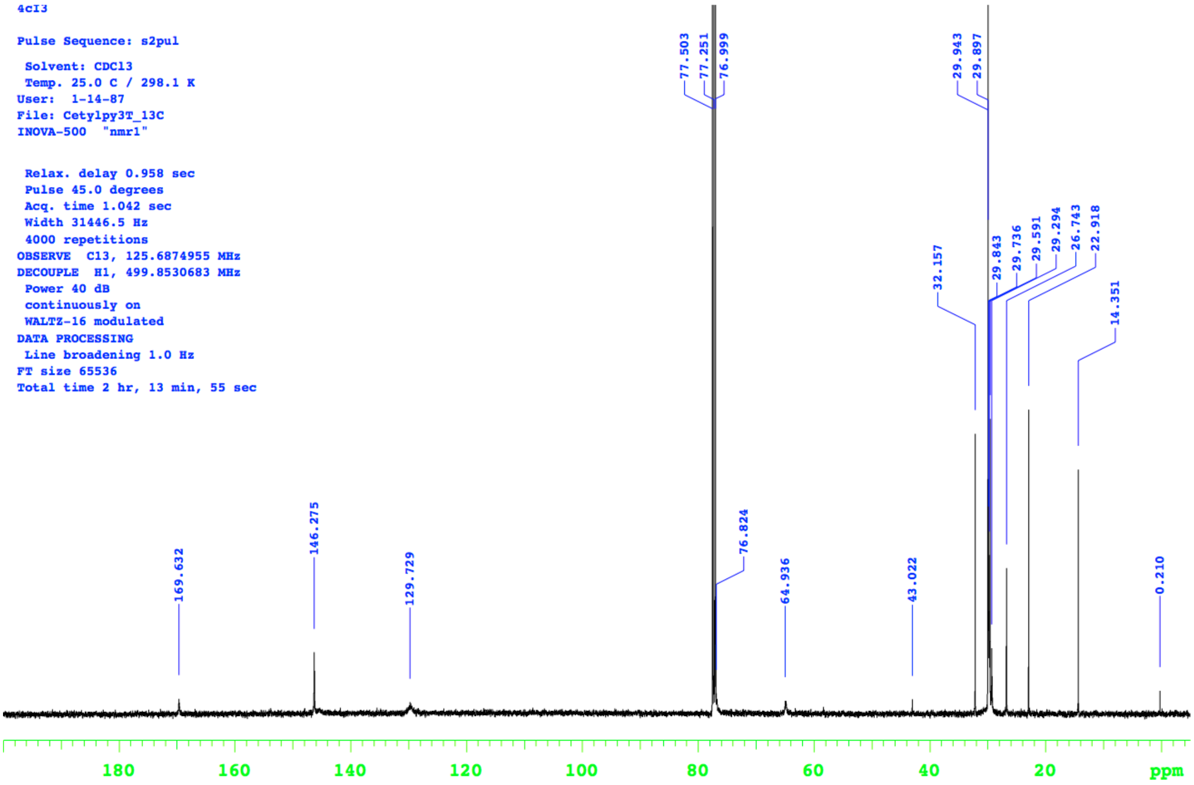
8a·Br$_3$, ^{13}C NMR (126 MHz, in DMSO-d_6, 25 °C)



8b·I3, ^{1}H NMR (500 MHz, in CDCl$_3$, 25 °C)



8b·I3, ^{13}C NMR (126 MHz, in CDCl$_3$, 25 °C)



^{1}H NMR experiment (Fig. 1)

NMR experiments were performed on a Varian UNITY INOVA 500 (500 MHz) at 298 K. In preparation of sample solutions, **3a** (50 μmol) and **5** (33 μmol) were dissolved in DMF-d_7 (0.85 mL) in a 5 mm quartz NMR tube (for (a)); to the solution (a) was added $B(OH)_3$ (100 μmol) (for (b)); the solution (b) was heated at 150 °C for 17 h (for (c)).

Single crystal X-ray diffraction experiment (Fig. 2)

The crystal was obtained from DMF solution of **6a**·$(Me_2NH_2)_6$ and 6 equiv. of *n*-Bu_4NOH by vapor diffusion crystallization with methoxycyclopentane, and was put into a glass capillary with 0.3 mm diameter and placed in a cold nitrogen gas stream at 273 K. X-ray diffraction images of the crystal were collected using a ADSC Q315 CCD area detector with synchrotron radiation at a wavelength of 0.75 Å at the BL38B1 station of SPring-8 (Hyogo, Japan). The distance between the crystal and the detector was 150 mm. Images were processed using software HKL20000 (HKL Research). Structure solution and refinement was performed by using SHELXS-97 and SHELXL-97 (Sheldrick).

6a·(*n*-Bu$_4$N)$_4$(Me$_2$NH$_2$)$_2$; The pale yellow needle (0.20 × 0.10 × 0.04 mm^3), $C_{115}H_{165}B_3N_7O_{14}$, $Mr = 1901.97$; monoclinic, space group $C2/m$, $a = 43.010(9)$, $b = 30.624(6)$, $c = 19.154(4)$ Å, $\alpha = 90.00$, $\beta = 93.98(3)$, $\gamma = 90.00°$, $V = 25168(9)$ Å^3, $Z = 8$, $D_{calc} = 1.004$ g·cm^{-3}, 15077 unique and 12450 observed $[I > 2\sigma(I)]$ reflections, 1433 parameters, final $[I > 2\sigma(I)]$ $R_1 = 0.1011$, $wR_2 = 0.3078$, $S = 2.594$.

7·(*n*-Bu$_4$N)$_6$; The pale brown block (0.50 × 0.30 × 0.20 mm^3), $C_{199.25}H_{217.28}B_6N_{5.13}O_{24.82}$, $Mr = 3168.91$; triclinic, space group P-1, $a = 27.909(6)$, $b = 32.780(7)$, $c = 34.958(7)$ Å, $\alpha = 105.11(3)$, $\beta = 107.86(3)$, $\gamma = 110.03(3)°$, $V = 26097(12)$ Å^3, $Z = 4$, $D_{calc} = 0.807$ g·cm^{-3}, 59104 unique and 43636 observed $[I > 2\sigma(I)]$ reflections, 4884 parameters, final $[I > 2\sigma(I)]$ $R_1 = 0.1348$, $wR_2 = 0.3715$, $S = 1.683$.

^{1}H NMR experiment (Fig. 3)

NMR experiments were performed on a Varian UNITY INOVA 500 (500 MHz) at 298 K. In preparation of sample solutions, **8a**·Br_3 (0.7 μmol) (for (a)), **6b**·(*n*-$Bu_4N)_6$ (0.7 μmol) and **8a**·Br_3 (0.7 μmol) (for (b)), or **6b**·(*n*-$Bu_4N)_6$ (0.7 μmol) (for (c)) were dissolved in 0.7 mL of DMSO-d_6 in a vial, and transferred into a 5 mm NMR tube with adjusting 50 mm of solution height.

Dynamic light scattering (DLS) experiment (Fig. 4)

Dynamic light scattering experiments were performed using the commercially available instrument "Zetasizer-Nano ZS" (Malvern, Instruments Ltd., Worcestershire, UK) equipped with a 4 mW He-Ne laser (633 nm wavelength) at a fixed detector angle of 90°.

Measurements were performed at 20 °C. For data analysis, the viscosity and refractive index of tetrahydrofuran (THF) at 20 °C (0.45 mPa·s and 1.409, respectively) were used. Samples with a concentration of 1.0 mg/mL dissolved in THF were filtered (Millex, 0.45 μm pore size) before measurements. The mixed samples were prepared by mixing the components in THF, concentrated under reduced pressure, and washed with MeOH prior to the measurements. The measurements were performed in square quartz cell. The autocorrelation functions of the backscattered light fluctuations were analyzed (Stokes-Einstein) using the DTS v4.20 software (Malvern) that provided the hydrodynamic diameter, polydispersity and the size distribution.

^{1}H NMR experiment (Fig. S1)

NMR experiments were performed on a Varian UNITY INOVA 500 (500 MHz) at 298 K. In preparation of sample solutions, **6a**·(Me$_2$NH$_2$)$_6$ (0.7 μmol) and/or guest (ca. 0.7 μmol) were dissolved in 0.7 mL of DMSO-d_6 in a vial, and transferred into a 5 mm NMR tube with adjusting 50 mm of solution height.

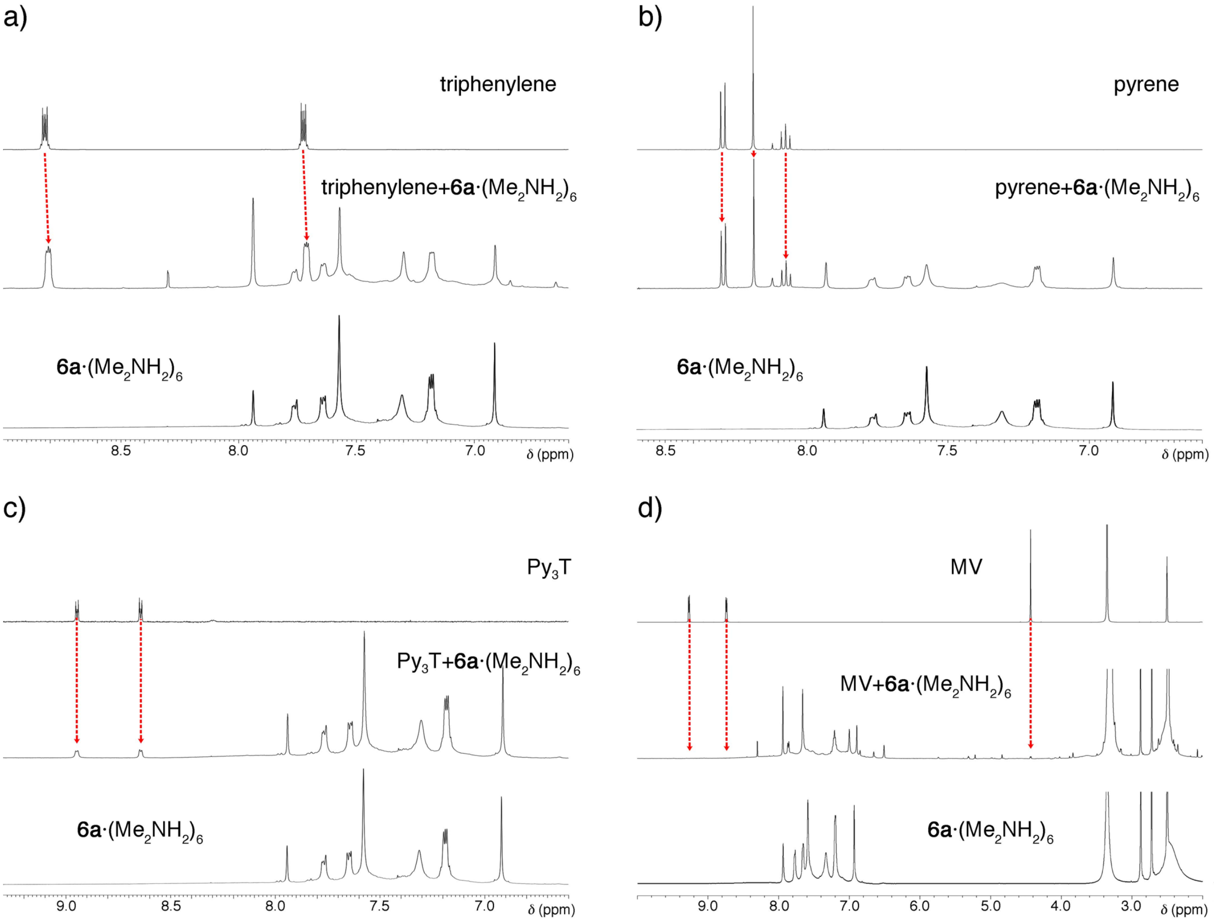


Fig. S1. Partial ^{1}H NMR spectra (500 MHz, 25 °C in DMSO-d_6) of (a) triphenylene (top), tripenylene+**6a**·(Me$_2$NH$_2$)$_6$ (middle), and **6a**·(Me$_2$NH$_2$)$_6$ (bottom); (b) pyrene (top), pyrene+**6a**·(Me$_2$NH$_2$)$_6$ (middle), and **6a**·(Me$_2$NH$_2$)$_6$ (bottom); (c) 2,4,6-tri(4-pyridyl)-1,3,5-triazine (Py$_3$T) (top), Py$_3$T+**6a**·(Me$_2$NH$_2$)$_6$ (middle), and **6a**·(Me$_2$NH$_2$)$_6$ (bottom); and (d) methyl viologen (MV) (top), MV+**6a**·(Me$_2$NH$_2$)$_6$ (middle), and **6a**·(Me$_2$NH$_2$)$_6$ (bottom).

2D-DOSY experiment (Fig. S2)

2D-DOSY experiments were performed on a Varian UNITY INOVA (500 MHz) equipped with a Nalorac DBG500-5F 5 mm Dual Broadband Gradient Probe equipped with gradient capabilities (Performa II, maximum gradient strength of 65 gauss/cm) at 298 K. The DOSY bipolar pulse pair stimulated echo (BPPSTE) sequence$^{11)}$ was used for the determination of the self-diffusion of the different components. In the experiments, 12.3 μsec of the 90° pulse widths were used. In preparation of sample solutions, appropriate amount of **6b**·(n-Bu$_4$N)$_6$ and **8a**·Br$_3$ were dissolved in DMSO-d_6 in a vial to adjust the concentration of each component to 1 mM, and then the solution was transferred into 3 mm NMR tube.

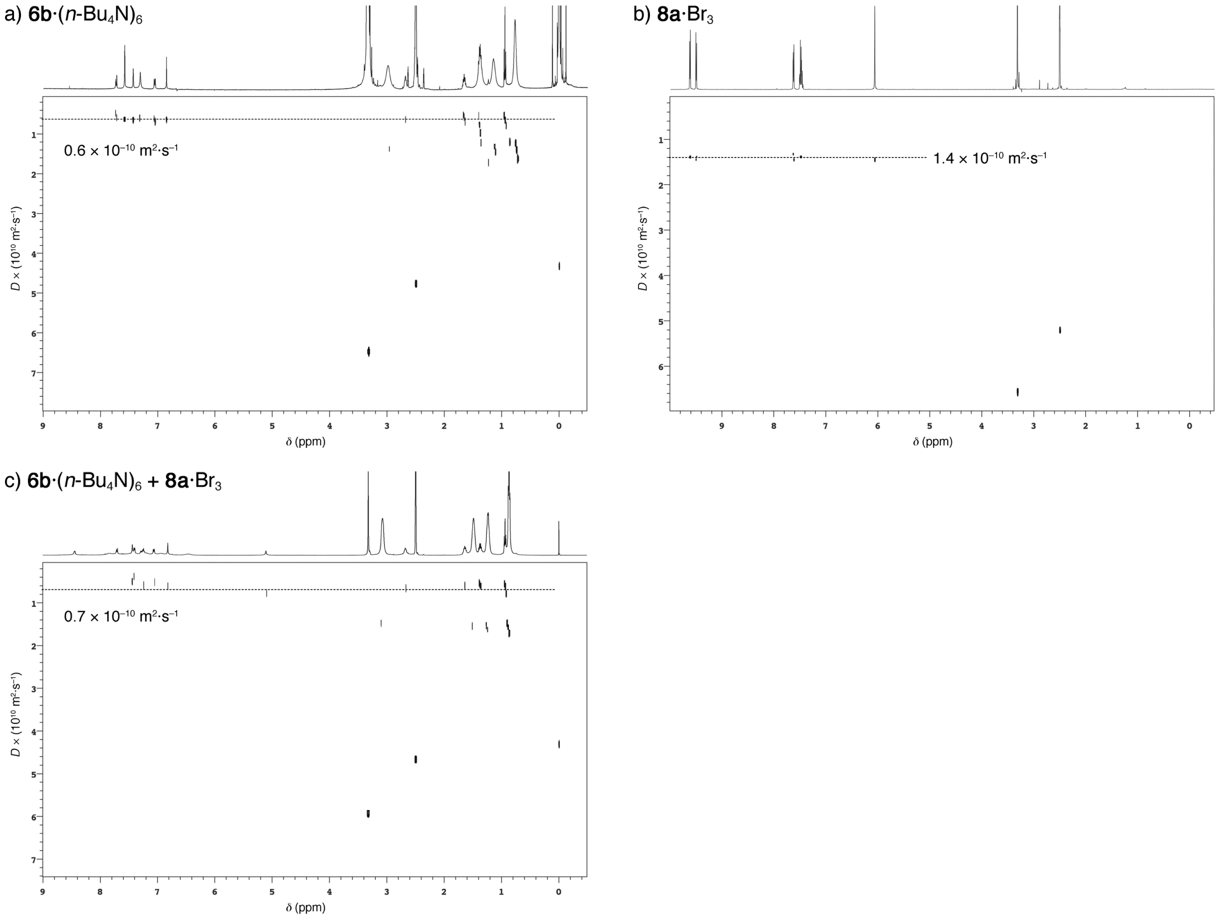


Fig. S2. 2D-DOSY NMR spectra (in DMSO-d_6) of (a) **6b**·(n-Bu$_4$N)$_6$ (1 mM), (b) **8a**·Br$_3$ (1 mM), and (c) **6b**·(n-Bu$_4$N)$_6$ (1 mM) and **8a**·Br$_3$ (1 mM).

CSI-TOF MS experiment (Fig. S3)

Cold spray ionization TOF MS (CSI-TOF MS) experiments were performed on a JMS-T100LC mass spectrometer equipped with a cold spray ion source. The measurement was carried out with the following conditions;

Sample concentration: 0.1 mg/mL in DMF/THF/H_2O (2:7:1)
Ion source: CSI–
Needle voltage: –2200 V
Ring lens voltage: –25 V
Oriffice 1 voltage: –180 V
Oriffice 2 voltage: –5 V

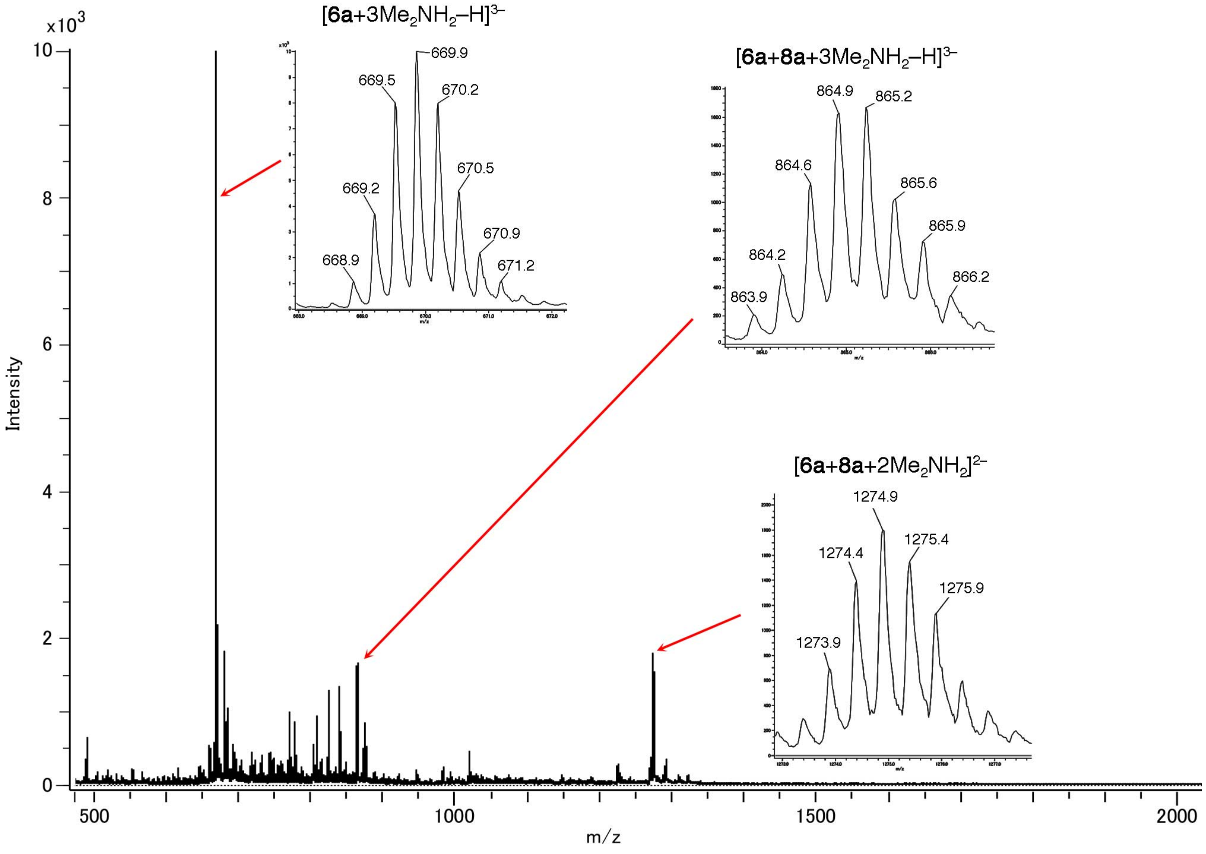


Fig. S3. Negative CSI-Mass spectra of a mixture of **6a**·(Me$_2$NH$_2$)$_6$ and **8a**·Br$_3$.

MALDI-TOF MS experiment (Fig. S4)

MALDI-TOF MS was performed on a Shimadzu Biotech Axima CFRplus instrument using dithiranol as the matrix. Nanocrystal samples were dispersed in dry chloroform, mixed with chloroform solutions of the matrix, and spotted onto a stainless steel target plate. Desorption and ionization of the samples were achieved by irradiation with a pulsed nitrogen laser (337 nm). Nanocrystal mass spectra were measured with the laser at 50 and 100% full power. After desorption, a 20 kV potential accelerated the ions into a 1.5 m flight tube (linear TOF mode), which yielded a resolution of 3000-20000 *m/z* in the final mass spectrum.

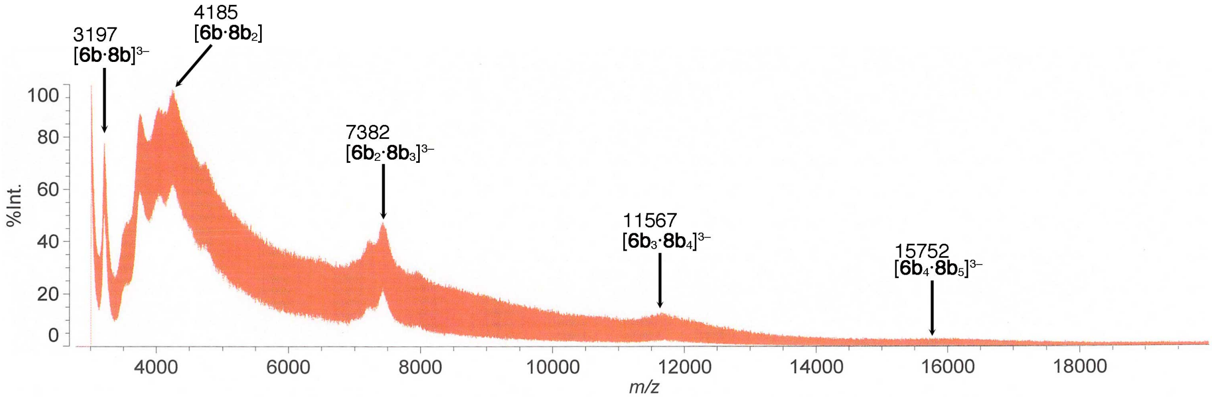


Fig. S4. MALDI-TOF mass spectra of a 1:2 mixture of $\mathbf{6b}\cdot(n\text{-Bu}_4\text{N})_6$ and $\mathbf{8b}\cdot\text{I}_3$.