Electronic Supporting Information (ESI)

Selective encapsulation of volatile and reactive methyl iodide

Yih-Chern Horng, Pin-Shen Huang, Chang-Chih Hsieh, Chih-Hong Kuo, and Ting-Shen Kuo*

Table of Contents

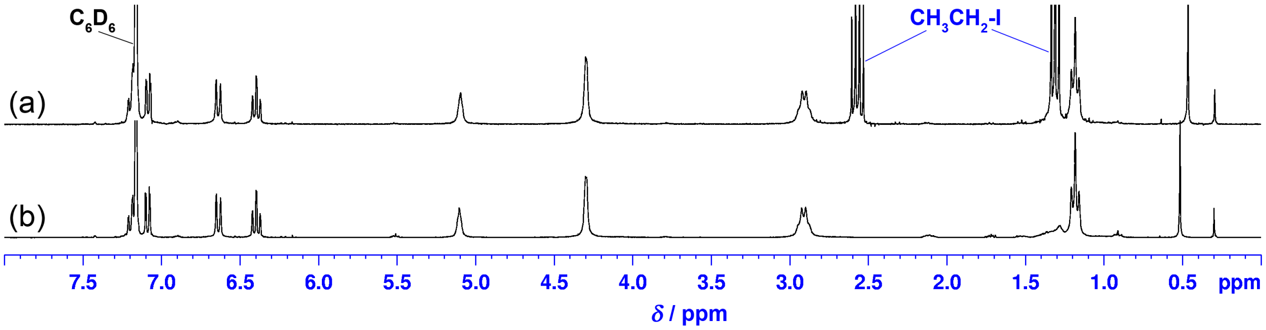


Figure S1. ^{1}H NMR spectra (300 MHz, 298 K, C_6D_6) of (a) **1** mixed with excess EtI (b) purified **1**.

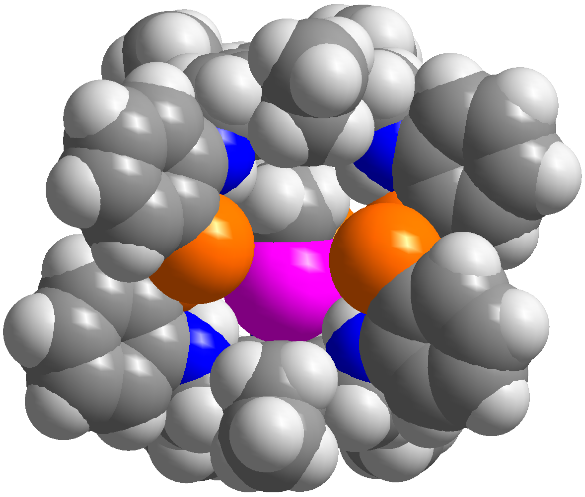


Figure S2. Space filling model of MeI⊂**1**. Colors for the elements: I (pink), S (orange), N (blue), C (grey), H (off white).

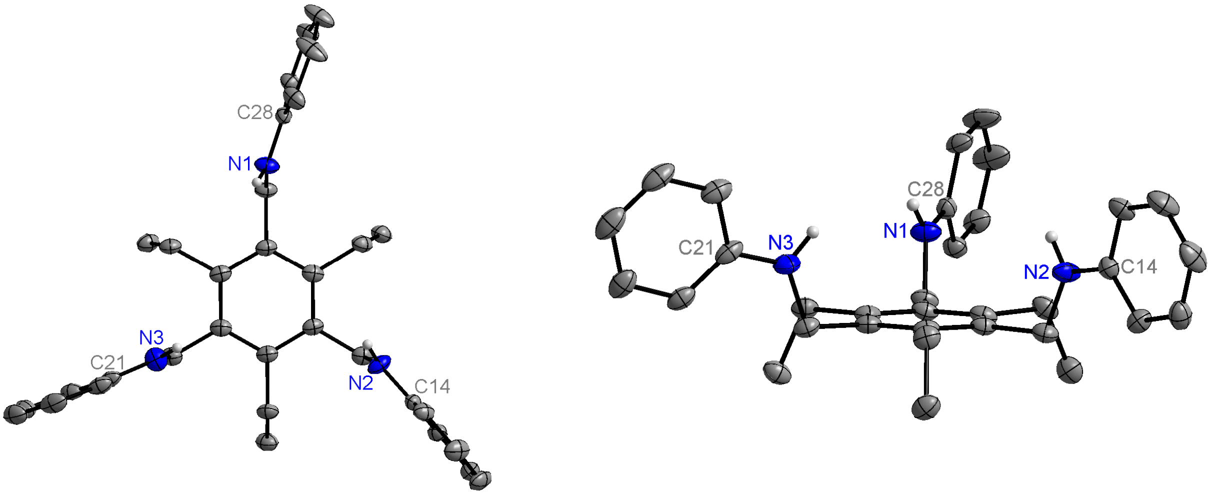


Figure S3. The molecular structure of **2**: top view (left) and side view (right). The thermal ellipsoids are drawn at a 35% probability level. Hydrogen atoms bound to carbon atoms, and the disordered CH_2Cl_2 molecule were omitted for clarity.

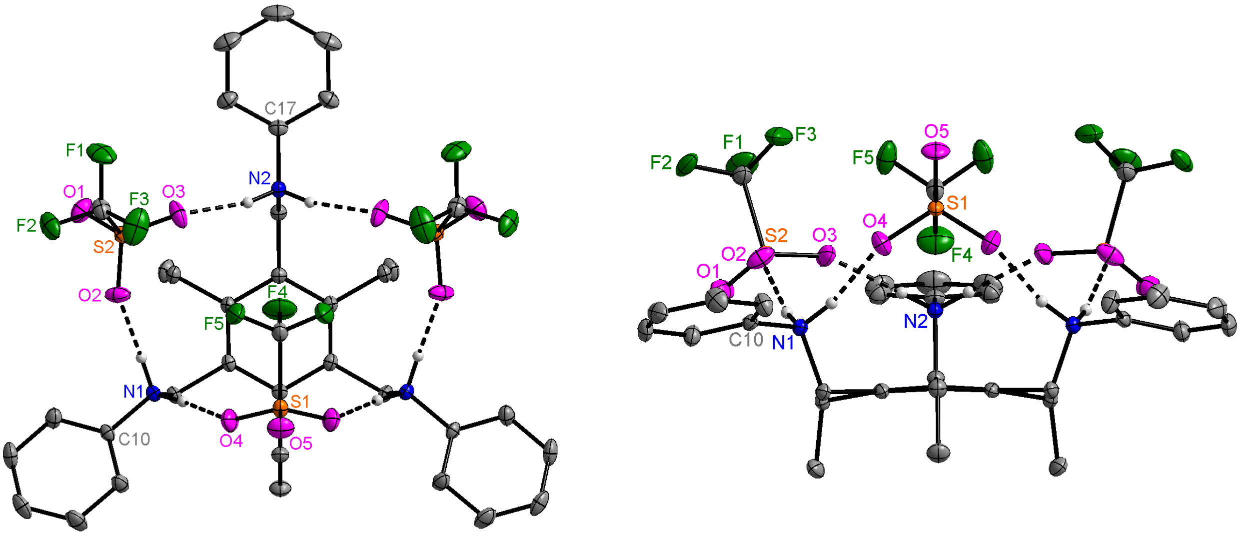


Figure S4. The molecular structure of **2a**: top view (left) and side view (right). The thermal ellipsoids are drawn at a 35% probability level. Hydrogen atoms bound to carbon atoms were omitted for clarity. The dashed lines represent NH···O hydrogen bonding interactions.

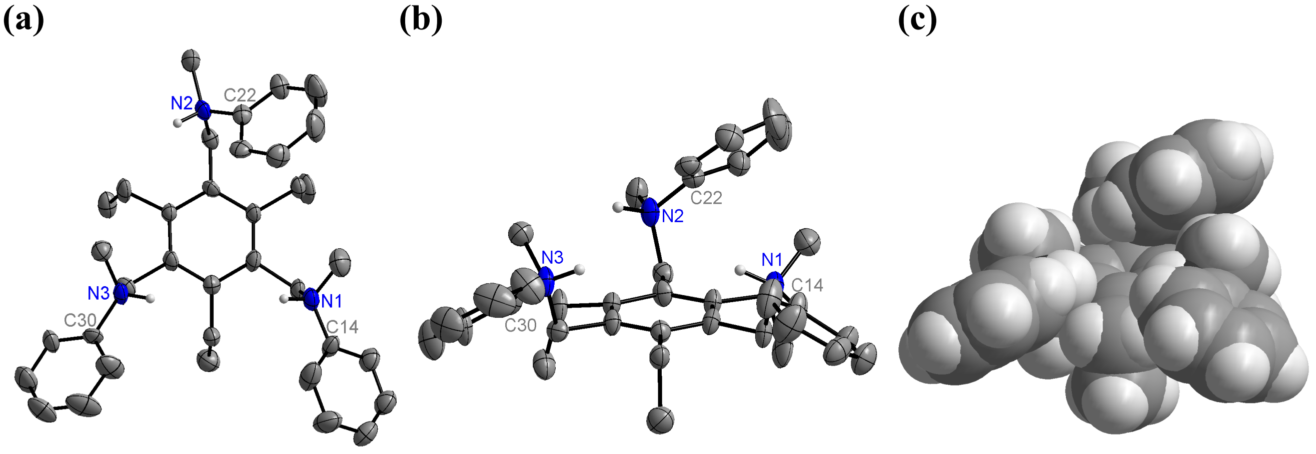


Figure S5. The molecular structure (top view (a); side view (b)) and space-filled model (c) of the cation part of **2b**. The thermal ellipsoids are drawn at a 35% probability level. Hydrogen atoms bound to carbon atoms, and the iodide anions were omitted for clarity. The detailed NH···I hydrogen bonding interactions are shown in Figure S6.

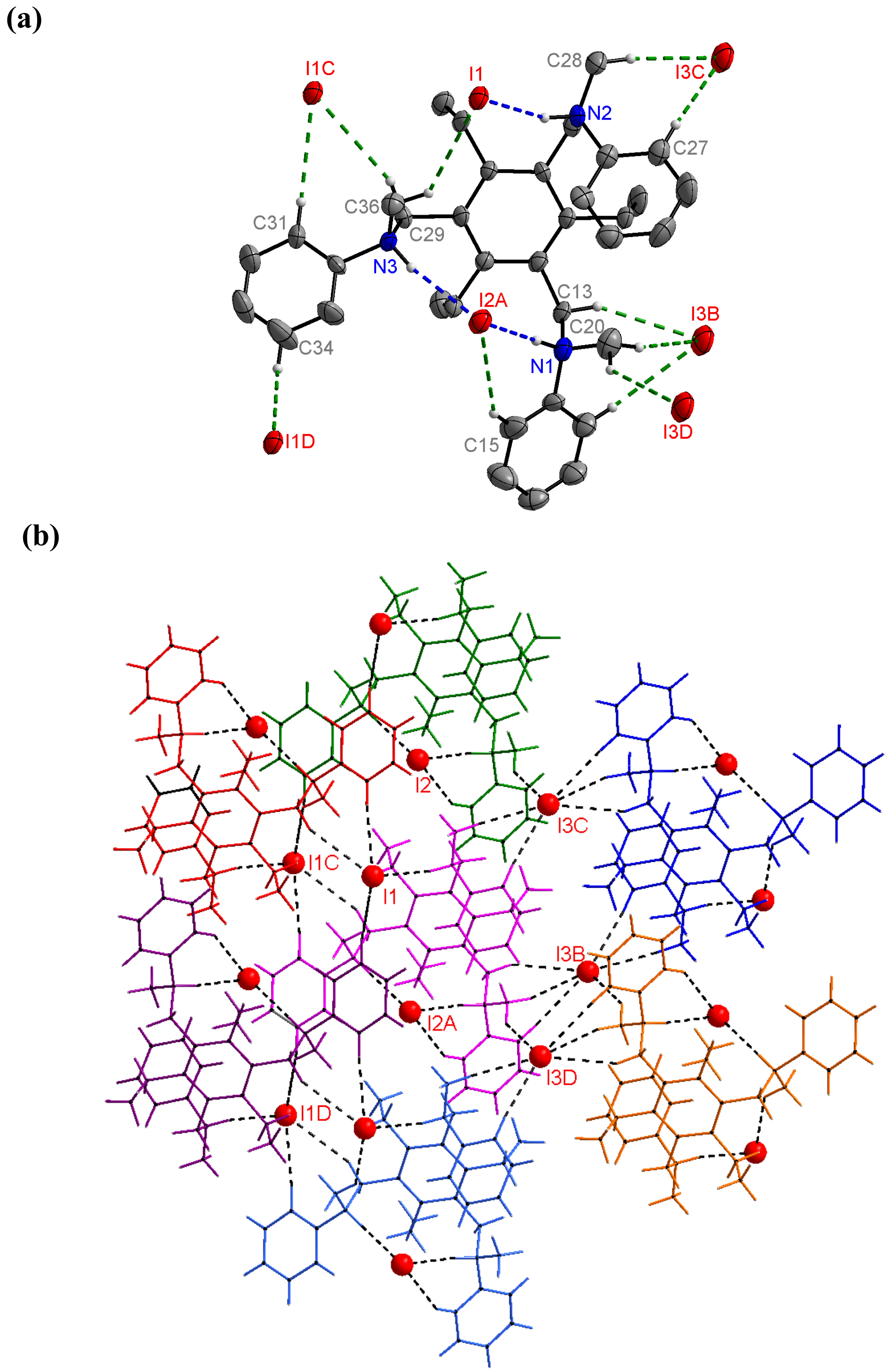
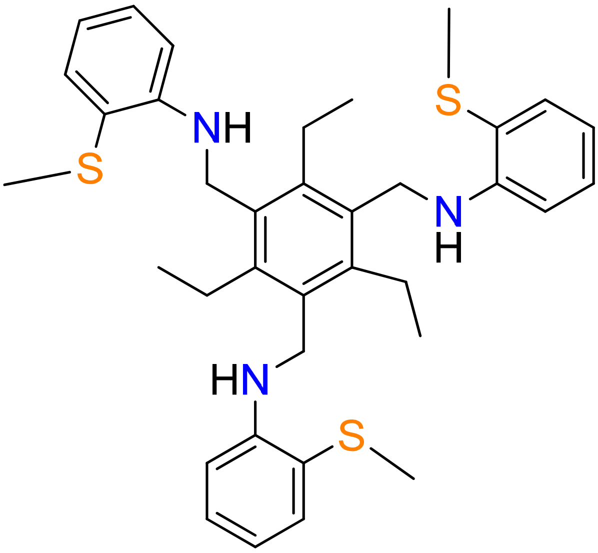


Figure S6. The weak interactions in compound **2b**: (a) Ortep drawing showing the intermolecular interactions. The thermal ellipsoids are drawn at a 35% probability level. Non-interacting hydrogen atoms are omitted for clarity. The dashed blue and green lines represent NH···I hydrogen bonding and CH···I contact interactions, respectively. (b) Two dimentional packing diagram. Each molecule is shown in a different color. The dashed black lines represent weak interactions. Symmetry code: A, 1+x, y, z; B, x, y, 1+z; C, 1-x, 1-y, 1-z; D, 2-x, 1-y, 1-z.

Table S1. Selected structural parameters from the X-ray crystal structures of **1**-related complexes. Data for DCM⊂**1**[a], DMF⊂**1**[a], I_2⊂**1**[b] and **3**[a] are given for comparison.

Complex	S-S [Å]	CSSC [°][c]	Height [Å][d]	(Ph)C-N [Å]
DCM⊂**1**	2.065(2)	96.8(2)	8.976	1.367(4)
DMF⊂**1**	2.049(3)	96.4(2)	9.047	1.361(5)
I_2⊂**1**	2.028(6)	97.0(5)	9.058	1.325(13)
MeI⊂**1**	2.033(3)	95.1(2)	8.985	1.359(7)
2	–	–	–	1.381(5)[e]
2a	–	–	–	1.470(4)[e]
2b	–	–	–	1.488(14)[e]
3	–	–	–	1.386(9)[e]

[a] Values from Ref. (1). [b] Values from Ref. (2). [c] torsion angle. [d] Distance between two centroids of aromatic bases. [e] in average.



3

Table S2. The calculated packing coefficients (PCs)[a] for the encapsulation of selected neutral small molecules in container **1**.

Guest	Volume of Guest [Å^3]	PC (%)
MeI	55	58
EtI	72	76
iPr	91	96
MeOH	36	38
$MeNO_2$	51	54
MeCN	47	49
CH_3Cl	42	44
CH_2Cl_2	56	59
$CHCl_3$	72	76
Toluene	99	104

[a] Packing coefficient = (guest volume)/(cavity volume). The guest volumes were calculated according to Ref. (3). The cavity volume (95 Å^3) of **1** was obtained with DeepView, Swiss PDB Viewer 4.0 using the default molecular probe (1.4 Å).

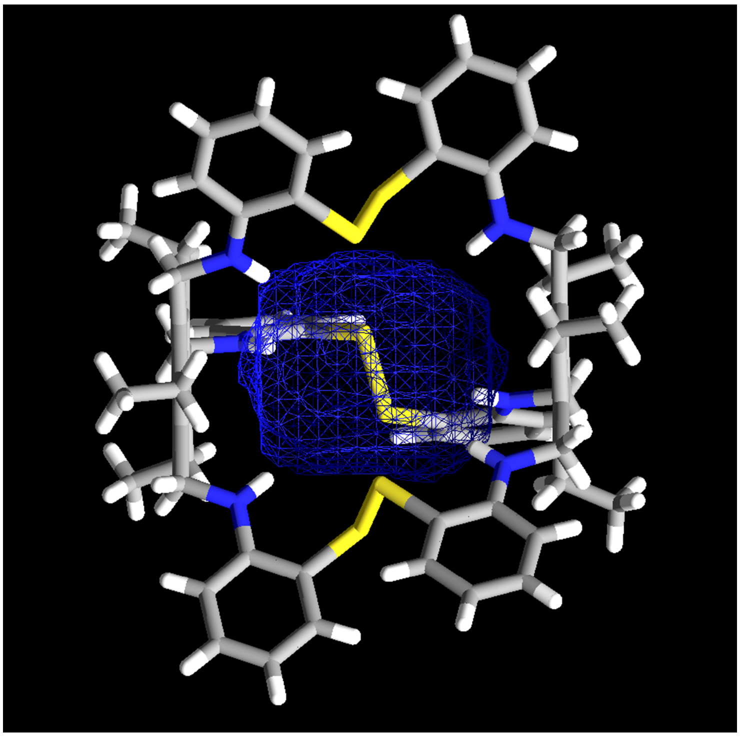


Table S3. The summary of crystallographic data for MeI⊂**1**, **2**, **2a** and **2b**

	MeI⊂**1**	**2**·CH_2Cl_2	**2a**	**2b**
formula	$C_{67}H_{75}IN_6S_6$	$C_{34}H_{41}Cl_2N_3$	$C_{36}H_{42}F_9N_3O_9S_3$	$C_{36}H_{48}I_3N_3$
Fw	1283.65	562.60	927.94	903.47
temp, K	200(2)	150(2)	150(2)	148(2)
cryst syst	Trigonal	Triclinic	Monoclinic	Triclinic
space group	*R -3 c*	*P-1*	*P2(1)/m*	*P-1*
a, Å	17.8042(2)	11.274(5)	9.8069(12)	10.014(7)
b, Å	17.8042(2)	11.548(6)	20.416(2)	10.358(8)
c, Å	47.6257(12)	11.946(6)	10.8597(11)	18.774(12)
α, °	90	95.33(3)	90	86.51(3)
β, °	90	93.62(4)	100.450(5)	88.14(3)
γ, °	120	99.07(4)	90	81.26(3)
Volume, $Å^3$ / Z	13074.2(4)/6	1524.3(13)/2	2138.2(4)/2	1921(2)/2
Density (cald.), Mg/m^3	1.022	1.226	1.441	1.562
Absorption coefficient, mm^{-1}	0.547	0.240	0.267	2.467
crystal size, mm	0.21×0.17×0.10	0.21×0.18×0.15	0.17×0.15×0.12	0.12×0.11×0.07
θ range, deg	2.16 to 25.02	1.80 to 28.87	1.91 to 28.74	2.06 to 29.55
no. of reflns collected	26581	22437	32985	25220
no. of indep reflns	2580	7777	5678	10330
max. and min. trans	0.9473 and 0.8938	0.968 and 0.950	0.974 and 0.958	0.863 and 0.745
no. of data /restraints /params	2580 / 0 / 120	7777 / 0 / 391	5678 / 0 / 291	10330 / 0 / 385
goodness-of-fit on F^2	0.964	0.840	0.901	0.892
final R indices [I>2σ(I)], $R_1{}^a$	0.0744	0.0686	0.0439	0.0639
, $wR_2{}^b$	0.2291	0.1549	0.1285	0.1489
R indices (all data), $R_1{}^a$	0.1222	0.2082	0.0598	0.2652
,$wR_2{}^b$	0.2543	0.2320	0.1438	0.2100
largest diff. peak and hole, e $Å^{-3}$	0.632 and -0.292	0.375 and -0.368	0.504 and -0.387	1.488 and -1.485

[a] $R_1 = \Sigma \mid F_0 \mid - \mid F_c \mid / \Sigma \mid F_0 \mid$

[b] $wR_2 = [\Sigma [\omega(F_0{}^2 - F_c{}^2)^2] / \Sigma [\omega(F_0{}^2)^2]]^{1/2}$

Experimental Sections

Materials and Methods: Commercially available chemicals were purchased from Aldrich or Acros, and used as received. Compound **1** was synthesized according to published procedures.[1] ^{1}H, ^{13}C, ^{1}H–^{1}H NOESY and DOSY NMR spectra were collected on a Bruker Avance 300 spectrometer. Chemical shifts for ^{1}H and ^{13}C{^{1}H} spectra were recorded in ppm relative to the residual proton and ^{13}C of $CDCl_3$ (^{1}H: δ 7.24; ^{13}C: δ 77.0), CD_3CN (^{1}H: δ 1.94; ^{13}C: δ 1.4, 118.7), toluene-d_8 (^{1}H: δ 2.09, 6.98, 7.09; ^{13}C: δ 20.4, 125.5, 128.3, 129.2, 137.9), and C_6D_6 (^{1}H: δ 7.16; ^{13}C: δ 128.4). Infrared spectra were recorded on a Bio-Rad FTS-185 instrument using KBr discs. Elemental analyses were performed on a Heraeus CHN-OS Rapid Elemental Analyzer at the Instruments Center of National Chung Hsing University, Taiwan.

*Synthesis of MeI$\subset$**1***

A solution of cage **1** (0.1 g, 0.088 mmol) in benzene (15 ml) mixed with MeI (6 µl, 0.1 mmol) was stirred under ambient conditions for 30 mins. The light-yellow precipitates were collected by filtration and dried in air to afford MeI$\subset$**1** as a light-yellow solid (0.09 g, 80%). ^{1}H NMR (toluene-d_8, RT): δ 7.190 (t, 6H, J = 9.3Hz), 6.646 (d, 6H, J = 7.8Hz), 6.449 (t, 6H, J = 6.9Hz), 5.294 (s, 6H), 4.295 (s, 12H), 2.853 (s, 12H), 1.504 (s, 3H, MeI), 1.204 (t, 18H, J =7.2Hz); ^{13}C NMR (toluene-d_8, RT): δ 149.29, 144.53, 133.33, 132.30, 119.48, 116.45, 109.91, 42.35, 22.79, 16.80, 1.15 (MeI). IR (KBr, ν_{max}/cm^{-1}): 3370, 3390 (NH). *Anal. Calcd.* for $C_{67}H_{75}N_6S_6I$: C, 62.69; H, 5.89 ; N, 6.55. Found: C, 62.29; H, 5.50; N, 6.64. Crystals of MeI$\subset$**1** suitable for X-ray crystallographic analysis were prepared by slow diffusion of excess pure MeI into a toluene solution of **1** at -20°C for 1 week.

*Synthesis of **2***

A mixture of 2,4,6-tris(bromomethyl)-1,3,5-triethylbenzene (2.00 g, 2.53 mmol), aniline (1.27 g, 13.6 mmol), K_2CO_3 (2.00 g, 14.5 mmol), and acetonitrile (30 ml), placed in a 100 ml flask, was refluxed at 85°C for 12 hrs. After cooled down to RT, the light-orange precipitates were filtered and washed with CH_3CN (about 100 ml) to remove excess aniline. The residues were extracted with dichloromethane and distilled water. The combined dichloromethane portions were dried over anhydrous $MgSO_4$, filtered, and vacuum dried to afford 2.10 g of light-orange solid (yield: 82%). ^{1}H NMR ($CDCl_3$, RT): δ 7.27 (t, 6H, C_6H_5), 6.79 (t, 3H, C_6H_5), 6.72 (d, 6H, C_6H_5), 4.27 (s, 6H, CH_2NH), 3.55 (s, 3H, NH), 2.81 (q, 6H, CH_2CH_3), 1.29 (t, 9H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, RT): δ 148.00, 143.68, 133.23, 129.26, 117.44, 112.36, 42.06, 22.68, 16.86. IR (KBr, ν_{max}/cm^{-1}): 3419 m (NH). *Anal. Calcd.* for $C_{33}H_{39}N_3$: C, 82.97; H, 8.23; N, 8.80. Found: C, 82.94; H, 8.54; N, 8.52. The light-orange crystals of **2**·DCM suitable for X-ray diffraction analysis were obtained by slow evaporation of the concentrated DCM solution of **2** at -20°C.

*Synthesis of **2a***

A mixture of **2** (0.10 g, 0.21 mmol), trifluoromethanesulfonic acid (0.11 g, 0.733 mmol), and dichloromethane (15 ml), placed in a 50 ml flask, was stirred at RT for 3 hrs. The white precipitates were filtered, washed with dichloromethane (about 50 ml) to remove residual reactants, and vacuum dried to afford 0.19 g of white solid (yield: 98%). ^{1}H NMR (CD_3CN, RT): δ 7.62 (s, 15H, C_6H_5), 4.68 (s, 6H, CH_2NH), 2.81 (q, 6H, CH_2CH_3), 1.12 (t, 9H, CH_2CH_3). ^{13}C NMR (CD_3CN, RT): δ 149.90, 135.85, 131.27, 131.14, 127.39, 123.64, 51.56, 25.41, 16.27. IR (KBr, ν_{max}/cm^{-1}): 3509 br (NH). *Anal. Calcd.* for $C_{36}H_{42}F_9N_3O_9S_3$: C, 46.60; H, 4.56 ; N, 4.53. Found: C, 46.34; H, 4.62; N, 4.64. The transparent cubic crystals of **2a** suitable for X-ray diffraction analysis were obtained by slow diffusion of diethyl ether into concentrated CH_3CN solution of **2a** at -20°C.

*Synthesis of **2b***

A sample of **2** (0.20 g, 0.42 mmol) was dissolved in 5 ml of pure MeI, the flask was wrapped in aluminum foil for light protection and the clear solution left undisturbed at ambient temperature for 10 days, after which light-orange crystals suitable for X-ray diffraction analysis were obtained (0.23 g, yield: 61%). IR

(KBr, ν_{max}/cm^{-1}): 3413 br (NH). *Anal. Calcd.* for $C_{36}H_{48}I_3N_3$: C, 47.86; H, 5.35; N, 4.65. Found: C, 47.88; H, 5.21; N, 4.64. Due to low solubility of **2b** in most organic solvents, we could not obtain clean solution NMR spectra of **2b**. However, the neutral trimethylated product, 1,3,5-tris(*N*-methylanilinomethyl)-2,4,6-triethylbenzene, can be obtained in quantitative yield after extraction with $CHCl_3$ and distilled water. ^1H NMR ($CDCl_3$, RT): δ 7.32 (t, 6H, C_6H_5), 6.92 (d, 6H, C_6H_5), 6.80 (t, 3H, C_6H_5), 4.44 (s, 6H, CH_2N), 2.74 (q, 6H, CH_2CH_3), 2.61 (s, 9H, NCH_3), 1.17 (t, 9H, CH_2CH_3). ^{13}C NMR ($CDCl_3$, RT): δ 150.08, 145.29, 131.80, 129.20, 116.98, 112.74, 47.72, 33.57, 22.57, 15.59. *Anal. Calcd.* for $C_{36}H_{45}N_3$: C, 83.19; H, 8.73; N, 8.08. Found: C, 82.89; H, 8.74; N, 8.33.

DOSY NMR experiments

The DOSY measurements of MeI⊂**1** in toluene-d_8 showed two components possessing different diffusion coefficients. The diffusion coefficient of 5.98×10^{-11} m^2/s is almost identical to the diffusion coefficient of **1**. The second component was assigned to MeI with a diffusion coefficient of 1.62×10^{-10} m^2/s, which is much smaller than the one of pure MeI in toluene-d_8 (2.66×10^{-9} m^2/s). Thus, a significant interaction between **1** and MeI was evidenced by DOSY NMR experiments.

Crystallographic Studies

The crystals suitable for structure analysis were mounted on a glass fiber with silicone grease and placed in the cold stream of a Bruker APEX II or a NONIUS Kappa CCD diffractometer with graphite monochromated Mo K_α radiation (λ = 0.71073Å). All structures were solved by direct methods using SHELXS-97 and refined by full-matrix least squares methods against F^2 with SHELXL-97.[4] Tables of neutral atom scattering factors, f' and f'', and absorption coefficients are from a standard source.[5] All atoms except hydrogen atoms were refined with anisotropic displacement parameters. In general, hydrogen atoms were fixed at calculated positions, and their positions were refined by a riding model. Crystallographic data collection and refinement parameters were listed in Table S3. The crystal structure of MeI⊂**1** contains heavily disordered solvent molecules in the void spaces. These disordered solvent molecules were not further identified or refined. Instead, a new set of F^2 (hkl) values with the contribution from solvent molecules withdrawn was obtained by the SQUEEZE procedure implemented in PLATON program.[6] Crystallographic data (excluding structure factors) for the structures of MeI⊂**1**, **2**, **2a** and **2b** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 883531, 883532, 883533 and 883534. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0) 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk].

References

1 Y.-C. Horng, T.-L. Lin, C.-Y. Tu, T.-J. Sung, C.-C. Hsieh, C.-H. Hu, H. M. Lee and T.-S. Kuo, *Eur. J. Org. Chem.*, 2009, 1511-1514.

2 P.-S. Huang, C.-H. Kuo, C.-C. Hsieh and Y.-C. Horng, *Chem. Commun.*, 2012, **48**, 3227-3229.

3 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441-451.

4 G. M. Sheldrick, *SHELXTL, Version 5.1*. Bruker AXS Inc., Madison, WI, 1998.

5 L. E. Sutton, *Tables of Interatomic Distances and Configurations in Molecules and Ions*, Chemical Society Publications, UK, 1965.

6 P. van der Sluis, A. L. Spek, *Acta Cryst.* 1990, **A46**, 194-201.