

Self-assembly of a M_6L_{12} coordination cube

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1. General

NMR spectra were recorded on a Bruker DRX-500 (500 MHz) spectrometer. The chemical shift values reported here are with respect to an internal TMS standard. CSI-MS (cold-spray ionization mass spectroscopy) spectra were measured on a four-sector (BE/BE) tandem mass spectrometer (JMS-700C, JEOL) equipped with a CSI source. IR measurements were carried out as KBr pellets using a DIGILAB Scimitar FTS-2000 instrument. Melting points were determined on a Yanaco MP-500V melting-point apparatus. Elemental analyses were performed on a Yanaco MT-6. The synchrotron X-ray diffraction study was carried out at 90 K ($\lambda = 0.6883 \text{ \AA}$) at PF-AR of the High Energy Accelerator Research Organization (KEK). The diffraction data were collected by Rigaku CrystalClear, and cell refinement and data reduction were performed using the HKL2000 program. Structural solution was performed using the SHELXS-97 (Sheldrick, 1990) program, and structural refinement was performed using the SHELXL-97 (Sheldrick, 1997) program. Solvents and reagents were purchased from TCI Co., Ltd., WAKO Pure Chemical Industries Ltd., and Sigma-Aldrich Co. All the chemicals were of reagent grade and used without any further purification.

2. Procedure

Synthesis of 2,8-bis(4-pyridylethynyl)dibenzofuran (1)

Tri-*t*-butylphosphine (3.39 mL, 1.36 mmol; 10% solution in hexane) and diisopropylamine (16.5 mL, 116 mmol) was added to a mixture of 2,8-diiododibenzofuran (3.23 g, 11.0 mmol), 4-ethynylpyridine hydrochloride (4.07 g, 29.1 mmol), Pd(PhCN)₂Cl₂ (253 mg, 0.660 mmol) and copper (I) iodide (76.2 mg, 0.400 mmol), and the mixture was stirred in 1,4-dioxane (40 mL) at 40 °C for 12 h under argon atmosphere. The reaction mixture was diluted with ethyl acetate (200 mL) and filtered. After dilution with water (200 mL), the mixture was washed with ethylenediamine (5 mL) and extracted with ethyl acetate. The combined organic layer was dried over anhydrous sodium sulfate and evaporated under reduced pressure, and the residue was purified by column chromatography on silica gel (CHCl₃:MeOH = 100:1) to give the title compound as a white solid (3.01 g, 8.87 mmol) in 81% yield. mp 208.5 °C. ¹H NMR (500 MHz, CDCl₃, 300 K) δ (ppm) 8.64 (d, *J* = 5.5 Hz, 4H), 8.17 (s, 2H), 7.70 (d, *J* = 8.6 Hz, 2H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 5.5 Hz, 4H). ¹³C NMR (125 MHz, CDCl₃, 300 K) δ (ppm) 156.7 (Cq), 149.9 (CH), 131.8 (CH), 131.4 (Cq), 125.5 (CH), 124.7 (CH), 123.9 (Cq), 117.3 (Cq), 112.3 (CH), 93.8 (Cq), 86.3 (Cq). IR (KBr, cm⁻¹) 3040, 2216, 1588, 1535, 1408, 1198, 1024, 813. MS (EI, *m/z*) calcd for C₂₆H₁₄N₂O (M⁺) 370.1, found 370. Anal. Calcd for C₂₆H₁₄N₂O·0.25MeOH: C, 83.32; H, 4.00; N, 7.40. Found: C, 83.48; H, 3.94; N, 7.34.

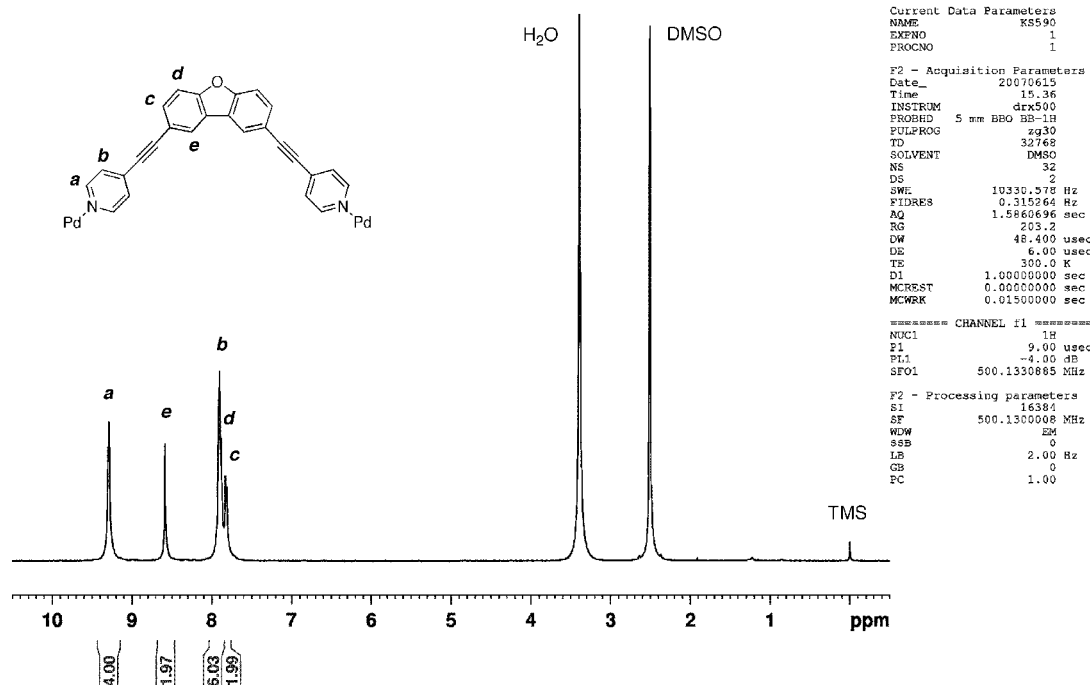
Synthesis of Cube 2

1 (37.0 mg; 0.10 mmol) was treated with Pd(NO₃)₂ (11.5 mg; 0.05 mmol) in dimethyl sulfoxide (10 mL) at 50 °C for 12 h. The addition of ethyl acetate to the resulting solution precipitated a white solid which was separated by centrifugation and dried in vacuo to give **2** (37.8 mg, 78%). mp >280 °C (decomposed). ¹H NMR (500 MHz, DMSO-*d*₆, 300 K) δ (ppm) 9.29 (s, 48H), 8.59 (s, 24H), 7.95–7.85 (m, 72H), 7.81 (d, *J* = 8.6 Hz, 24H). ¹³C NMR (125.77 MHz, DMSO-*d*₆, 300 K) δ (ppm) 156.7 (Cq), 151.0 (CH), 134.6 (CH), 132.6 (Cq), 128.5 (CH), 126.5 (CH), 123.4 (Cq), 115.6 (Cq), 113.1 (CH), 98.7 (Cq), 85.1 (Cq). IR (KBr, cm⁻¹) 3049, 2212, 1611, 1505, 1270, 1196, 1022, 828. Elemental Analysis Calcd for C₃₁₂H₁₆₈N₃₆O₄₈Pd₆·9DMSO·2H₂O: C, 60.36; H, 3.47; N, 7.68. Found: C, 60.23; H, 3.35; N, 7.44. Mass spectrometry was performed after **2** was converted its CF₃SO₃⁻. CSI-MS (CH₃CN/DMSO=10:1, CF₃SO₃⁻ salt): prominent peaks for [M-(CF₃SO₃)_{*n*}+(DMSO)_{*m*}]^{*n*+} (*n* = 4–8, *m* = 0–2) were clearly observed: *m/z* found (calcd.) for 1569.6 (1568.8) [M-(CF₃SO₃)₄]⁴⁺, 1225.5 (1225.3) [M-(CF₃SO₃)₅]⁵⁺, 996.7 (996.3) [M-(CF₃SO₃)₆]⁶⁺, 844.1 (843.8) [M-

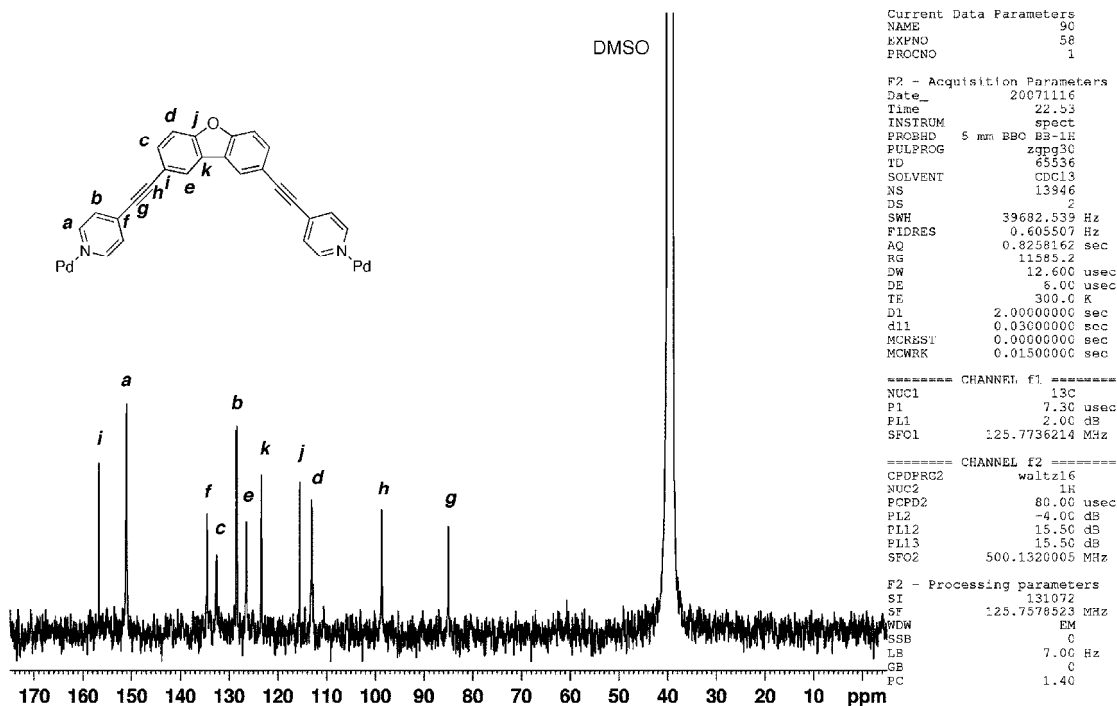


3. NMR and CSI-MS spectra

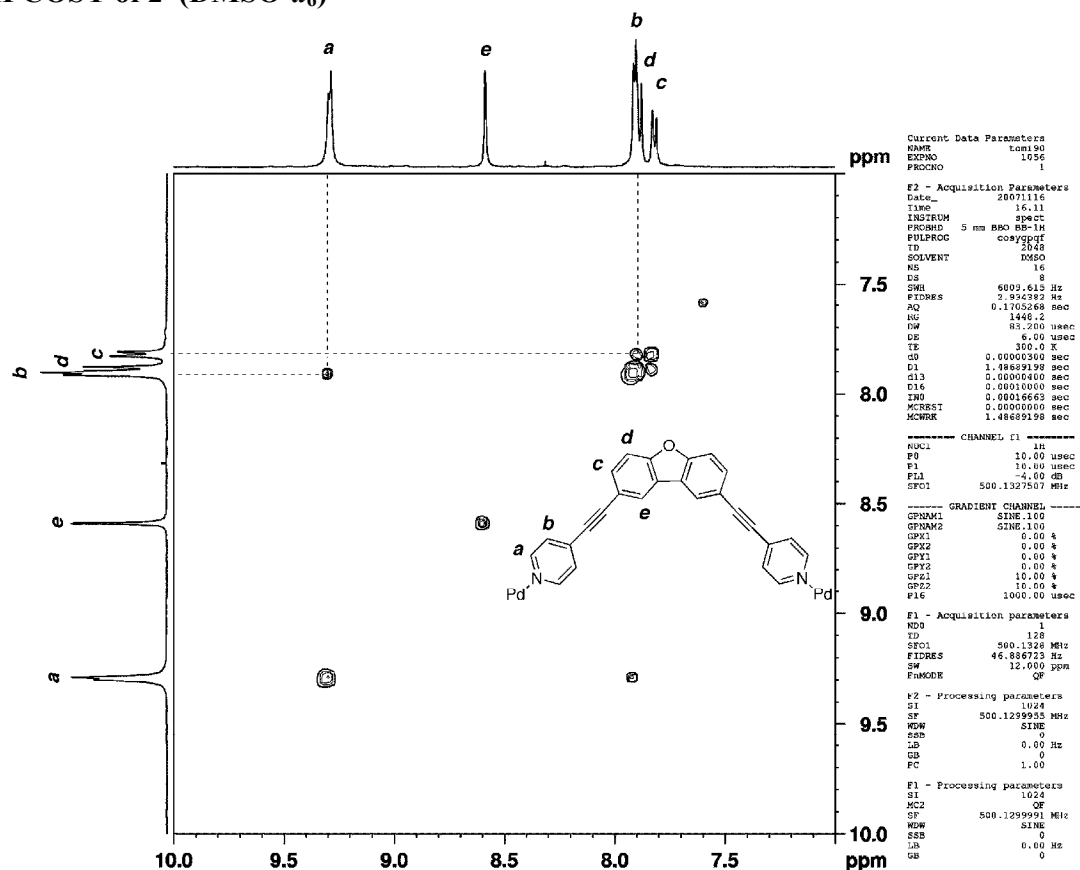
¹H NMR of 2 (DMSO-*d*₆)



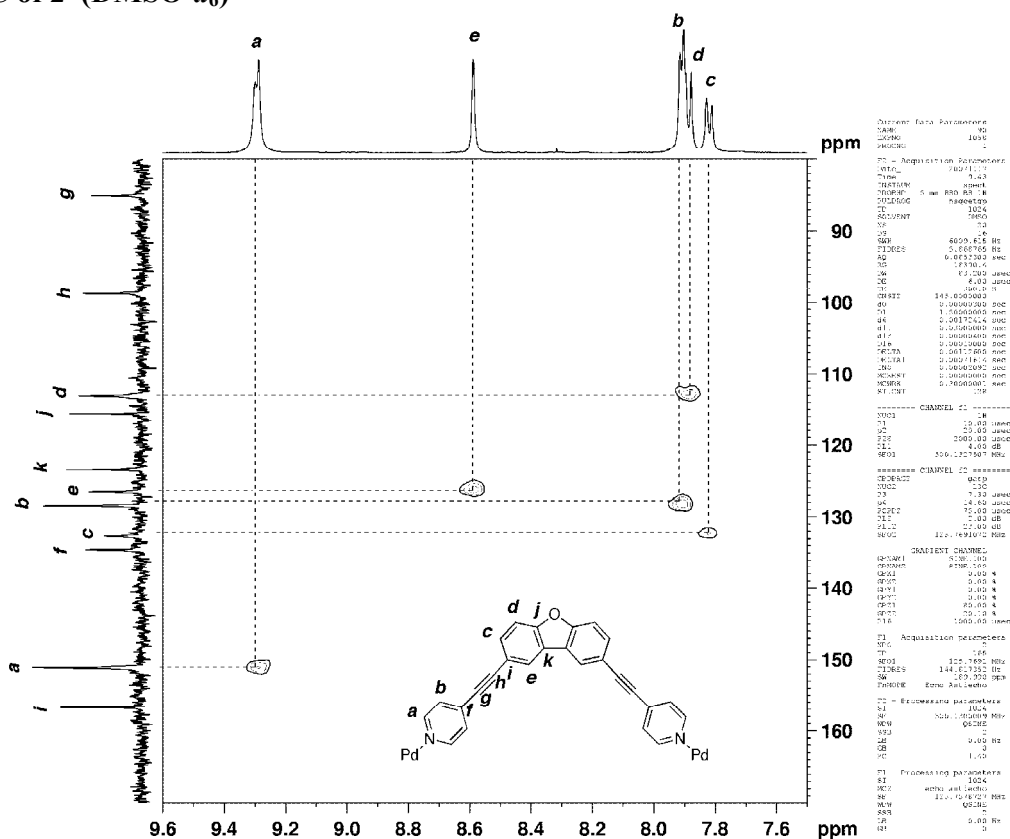
¹³C NMR of 2 (DMSO-*d*₆)



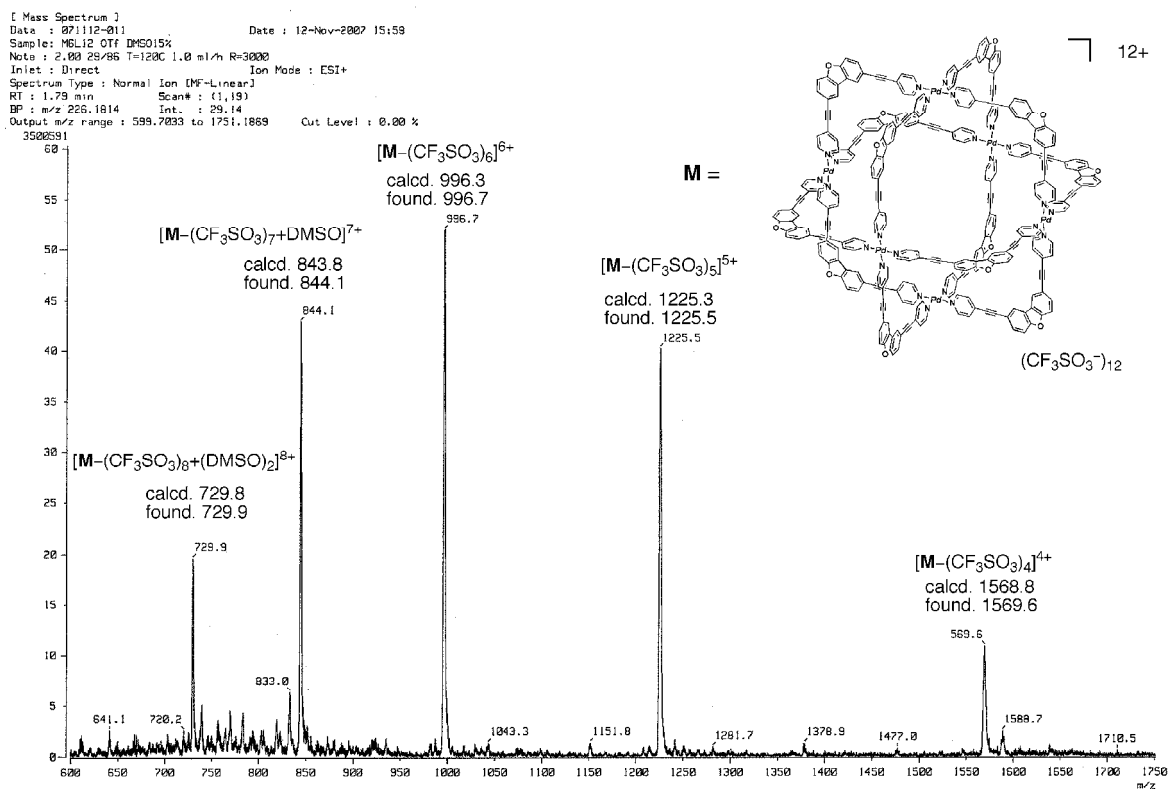
H-H COSY of 2 (DMSO-d₆)



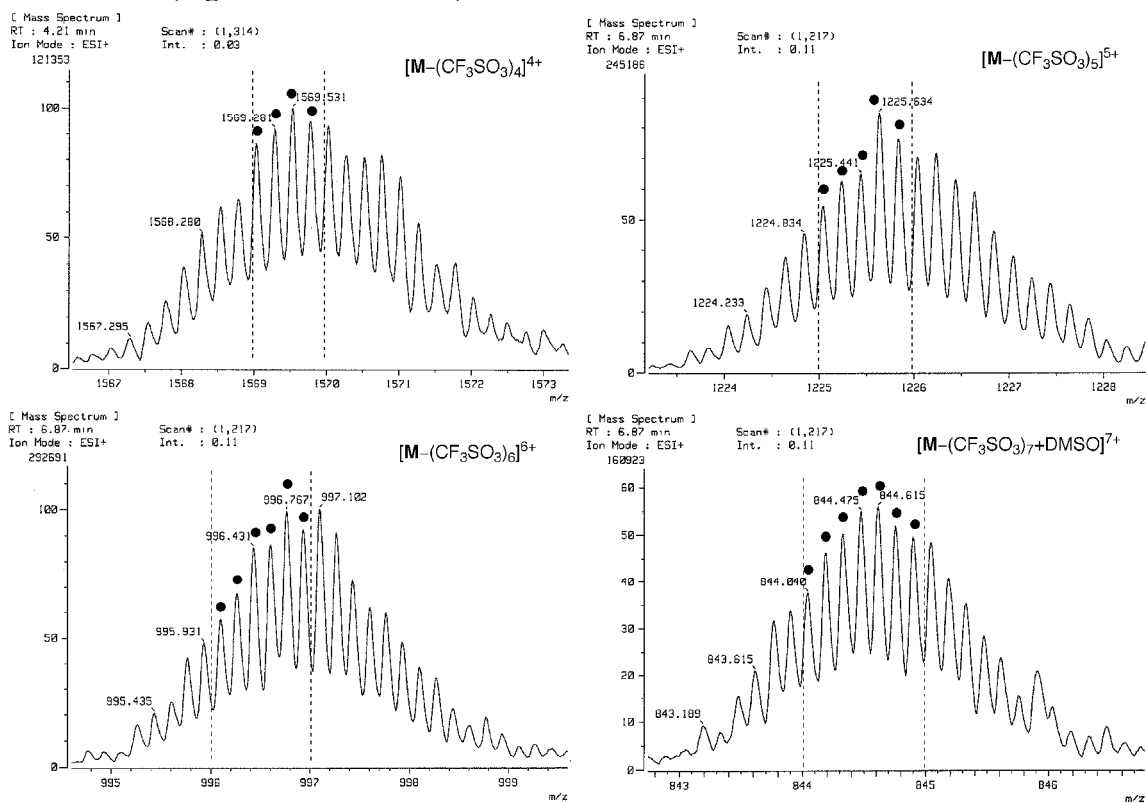
HSQC of 2 (DMSO-d₆)



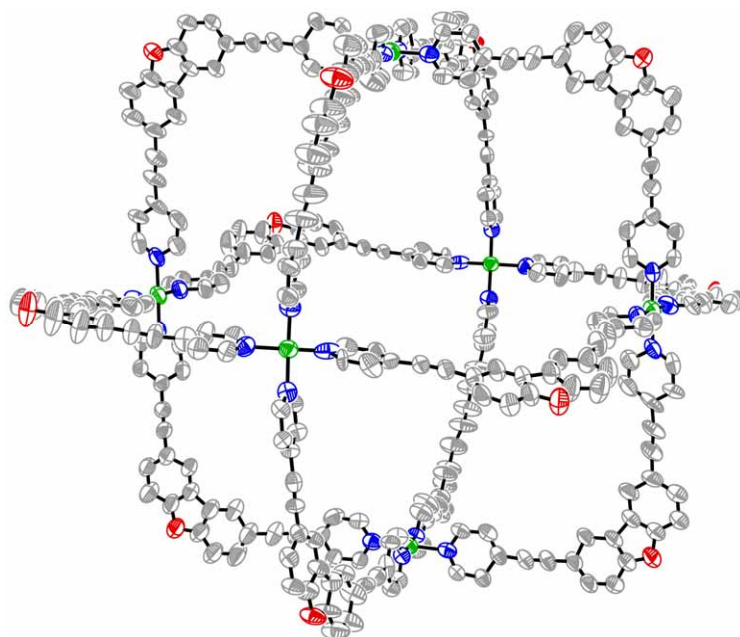
CSI-MS of 2 (CH₃CN:DMSO = 10:1)



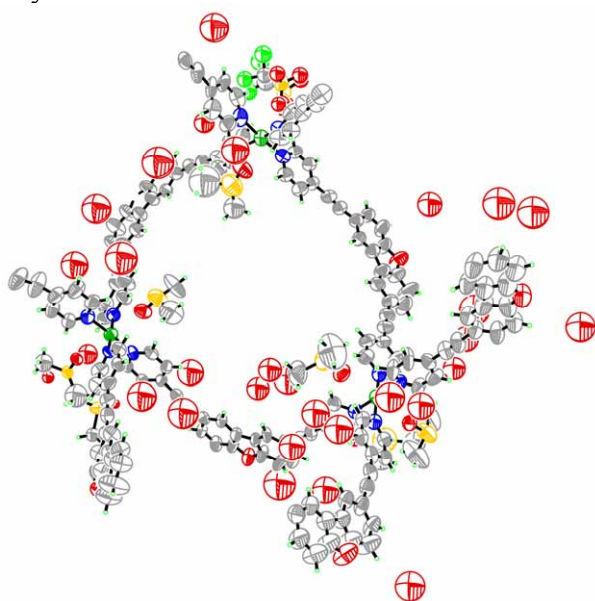
CSI-MS of 2 (high resolution: 7000)



4. X-ray crystallographic analysis of **2**:



Thermal ellipsoid plots (30 % probability level) of the molecular structure of complex **2**. Representation of the cubic structure. Dimethyl sulfoxide, water and triflate ions are omitted for clarity.



Thermal ellipsoid plots (30 % probability level) of the molecular structure of complex **2**. All independent atoms including dimethyl sulfoxide, water and triflate ions.

Comments of crystallographic analysis

Isolated Q peaks were assigned as water, because the presence of water was supported by the elemental analysis.

Disordered solvent molecules and counter anions exist in the large cavity, which could not be assigned in crystallography. The free volume of complex **2** indicates that this compound can contain ca. 50 solvent molecules.