Spherand Complexes with Li^+ and Na^+ Ions in the Gas Phase: Encapsulation Structure and Characteristic Unimolecular Dissociation

Motoki Kida, Kanako Wada, Satoru Muramatsu, Rong Shang, Yohsuke Yamamoto*, and Yoshiya Inokuchi*

Department of Chemistry, Graduate School of Advanced Science and Engineering,
Hiroshima University, Higashi-Hiroshima, Hiroshima 739-8526, Japan

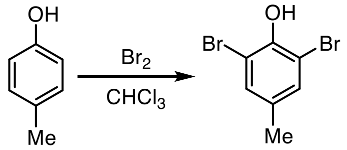
Supplementary Information

Detailed procedure for the synthesis of spherands

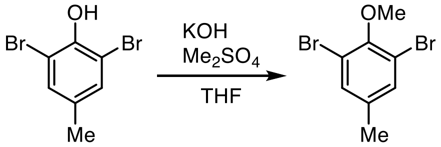
General considerations

All manipulations were performed under Ar or N_2 atmosphere by using standard Schlenk or glove box techniques. All the solvents were dried prior to use. Column chromatography was carried out using Merck silica gel 60 and KANTO CHEMICAL silica gel 60N. The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using a JEOL EX-400 spectrometers. The chemical shift (δ) are reported from the internal $CHCl_3$ for ^{1}H (δ 7.26) and from the internal $CDCl_3$ for ^{13}C (δ 77.0).

Preparation of 2

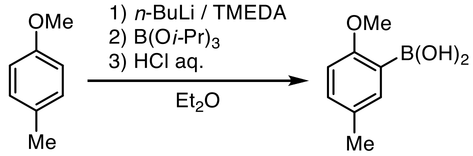


Br_2 (5.0 ml, 98 mmol) was added dropwise to a solution *p*-cresol (3.20 ml, 30.6 mmol) in $CHCl_3$ (30 ml) at 0 °C. The resulting solution was stirred at 0 °C for 30 min. The reaction was quenched with aqueous $Na_2S_2O_3$, filtered, and extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated to give the crude product. The crude product was purified by column chromatography (SiO_2, *n*-hexane) to give 7.79 g (29.3 mmol, 98 %) of a light-yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.26(s, 3H), 5.71 (s, 1H), 7.26 (s, 2H).



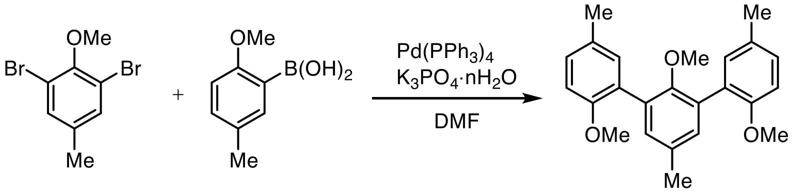
To a stirred mixture of KOH (5.76 g, 103 mmol) in H_2O (0.9 ml) and 2,6-dibromo-4-methylphenol (7.79 g, 29.3 mmol) in THF (47 ml) was added Me_2SO_4 (4.7 ml, 50 mmol) dropwise at room temperature. The mixture was stirred at reflux temperature for 2 h, to which H_2O was added until the white solid dissolved. The mixture was extracted with CH_2Cl_2 and the combined organic layer were washed with aq. KOH (1 M) followed by brine, dried over anhydrous magnesium sulfate, filtered, and concentrated to give the crude product. The crude product was purified by column chromatography (SiO_2, *n*-hexane: CH_2Cl_2 = 1 : 1) to give 8.32 g (29.7 mmol, 100 %) of a light yellow oil; ^{1}H NMR ($CDCl_3$) δ 2.28 (s, 3H), 3.85 (s, 3H), 7.31 (s, 2H).

Preparation of 3



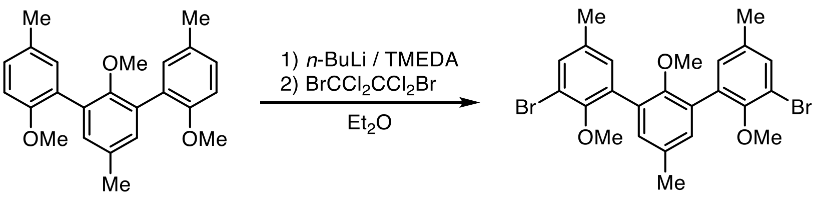
A solution of *n*-BuLi (50.0 ml, 80.0 mmol; 1.6 M in *n*-hexane) was added dropwise to a mixture of 4-methylanisole (5.0 ml, 40 mmol) and TMEDA (1.3 ml, 8.0 mmol) in ether (60 ml) at 0 °C over 10 min. The solution was stirred for 1 h at room temperature before cooled to –78 °C, to which triisopropyl borate (23.0 ml, 120 mmol) was added dropwise. The solution was stirred at –78 °C for 1 h and warmed to room temperature (12 h). The reaction was quenched with 10 % HCl aq. and stirred for 30 min. The resulting mixture was extracted with ether, and the combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated to give the crude product as a light-yellow oil. The crude product was left at room temperature for several days and white precipitate formed. The solid was filtered and washed with *n*-hexane to give 6.26 g (94 % of a white solid; ^{1}H NMR ($CDCl_3$) δ 2.31 (s, 3H), 3.89 (s, 3H), 5.80 (s, 2H), 6.82 (d, 1H, ^3J = 8 Hz), 7.24 (dd, 1H, ^3J = 8 Hz, ^4J = 2 Hz), 7.63 (d, 1H, ^4J = 2 Hz).

Preparation of 4



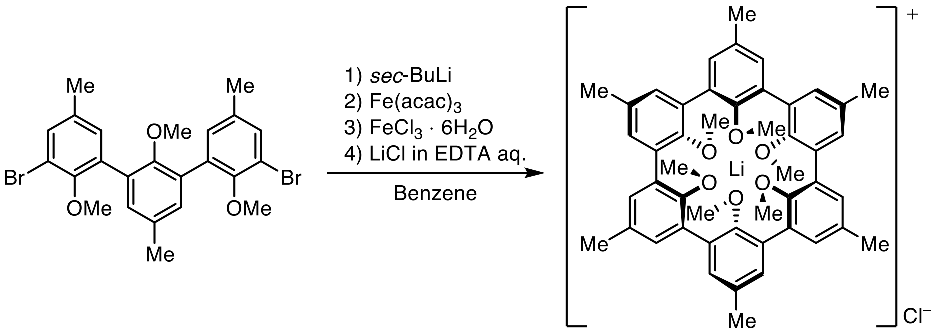
The flask equipped with a reflux condenser was charged with $Pd(PPh_3)_4$ (0.118 g, 0.102 mmol), 2,6-dibromo-4-methylanisole (0.290 g, 1.04 mmol), 2-methoxy-5-methyl-phenylboronic acid (0.494 g, 2.98 mmol) and $K_3PO_4 \cdot nH_2O$ (0.976 g, 4.60 mmol). The flask was flushed with argon and charged with DMF (3.10 mL). The mixture was heated in an oil bath at 100 °C for 1 d. The flask was cooled to room temperature, and the mixture was filtered, and extracted with ether. The combined organic solution was washed with H_2O followed by brine, dried over anhydrous magnesium sulfate, filtered and concentrated to give the crude product. The crude product was purified by column chromatography (SiO_2, *n*-hexane : CH_2Cl_2 = 1 : 1) to give 0.337 g (0.929 mmol, 89%) of white solid; ^{1}H NMR ($CDCl_3$), δ 2.31 (s, 6H), 2.34 (s, 3H), 3.19 (s, 3H), 3.77 (s, 6H), 6.86 (d, 2H, ^3J = 8 Hz), 7.05 (s, 2H), 7.11 (d, 2H, ^3J = 8 Hz), 7.12 (s, 1H).

Preparation of 5



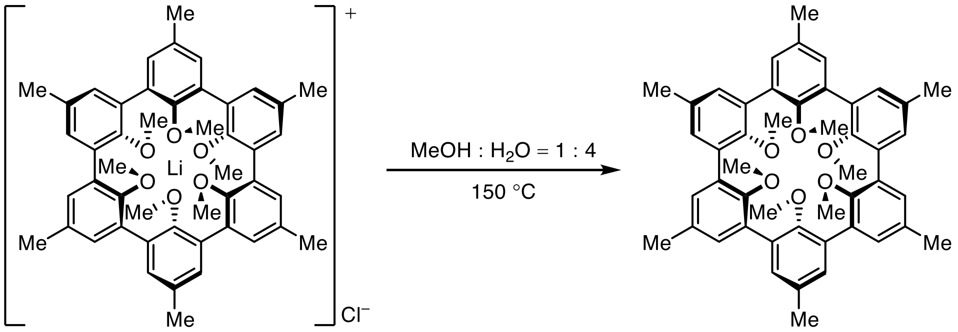
The flask was charged with 2,2',2''-trimethoxy-5,5',5''-trimethyl[1,1':3',1''-terphenyl] (376 mg, 1.03 mmol). The flask was flushed with argon, charged with ether (24.0 ml) and TMEDA (1.0 ml, 6.6 mmol) and cooled to 0 °C, to which a solution of *n*-BuLi (39.0 ml, 64.0 mmol; 1.64 M in *n*-hexane) was added slowly. The resulting solution was stirred at 0 °C for 10 min followed by 3 h at room temperature. Then it was cooled to –78 °C before $BrCCl_2CCl_2Br$ (28.8 g, 88.3 mmol) in ether (72.0 ml) was added dropwise. The resulting solution was stirred at –78 °C for 30 min and then at room temperature overnight before being quenched with 10 % HCl aq. and extracted with ether. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, filtered, and concentrated to give crude products. The crude products were purified by column chromatography (SiO_2, *n*-hexane: CH_2Cl_2 = 1 : 1) to give 7.89 mg (15.2 mmol, 95 %) of white solid; ^1H NMR ($CDCl_3$), δ 2.32 (s, 6H), 2.35 (s, 3H), 3.23 (s, 3H), 3.57 (s, 6H), 7.14 (d, 2H, ^4J = 2 Hz), 7.13 (s, 2H), 7.37 (d, 2H, ^4J = 2 Hz).

Preparation of 1•LiCl



To a solution of 3,3″-dibromo-2,2′,2″-trimethoxy-5,5′,5″-trimethyl [1,1′:3′,1″-terphenyl] (2.61 g, 5.03 mmol) in dry THF (54 mL) stirred at –78 °C under argon was added a 1.04 M solution of *sec*-BuLi in cyclohexane and *n*-hexane (16.0 mL, 16.6 mmol). The mixture was stirred for 30 min and then transferred into a vigorously refluxing solution of dry $Fe(acac)_3$ (8.00 g, 22.6 mmol) dissolved in dry benzene (1.0 L) via cannula under argon. The reaction mixture was refluxed for 45 min. The resulting suspension of heavy red precipitate was cooled and mixed with 360 mL of 2 M HCl aq. containing $FeCl_3 \cdot 6H_2O$ (3.99 g, 14.7 mmol) and stirred for 11 h at room temperature. The reaction mixture was then extracted with CH_2Cl_2. The combined organic layers were concentrated to afford the crude product, which was washed with ether, dissolved in CH_2Cl_2 and washed with distilled H_2O. The organic layers were stirred vigorously with two 300 mL portions of a 0.2 M LiCl solution and sat. EDTA aq. successively, before finally washed with distilled H_2O. The organic layers were concentrated to give the crude product, which was washed with ether to give 0.366 g (0.502 mmol, 20%) of white solid; ^{1}H NMR ($CDCl_3$) δ 2.50 (s, 18H), 3.09 (s, 18H), 7.33 (s, 12H). ^{13}C NMR ($CDCl_3$), δ 21.3 (CH_3), 63.0 (CH_3), 129.8 (CH), 130.5 (C), 135.9 (C), 153.8 (C).

Preparation of 1 (Decomplexation of 1•LiCl).



A pressure reactor containing spherandLi$^+$Cl$^-$ (220 mg, 0.285 mmol) suspended in MeOH: H_2O = 1 : 4 (33 ml) was heated in an oil bath at 150 °C for 5 days. After cooling to room temperature, EtOH was added. The solvent of the solution was then removed under reduced pressure. The resulting residue was washed with distilled H_2O to give 163 mg (0.226 mmol, 79 %) of white solid; ^{1}H NMR ($CDCl_3$), δ 2.41 (s, 18H), 2.85 (s, 18H), 7.17 (s, 12H).

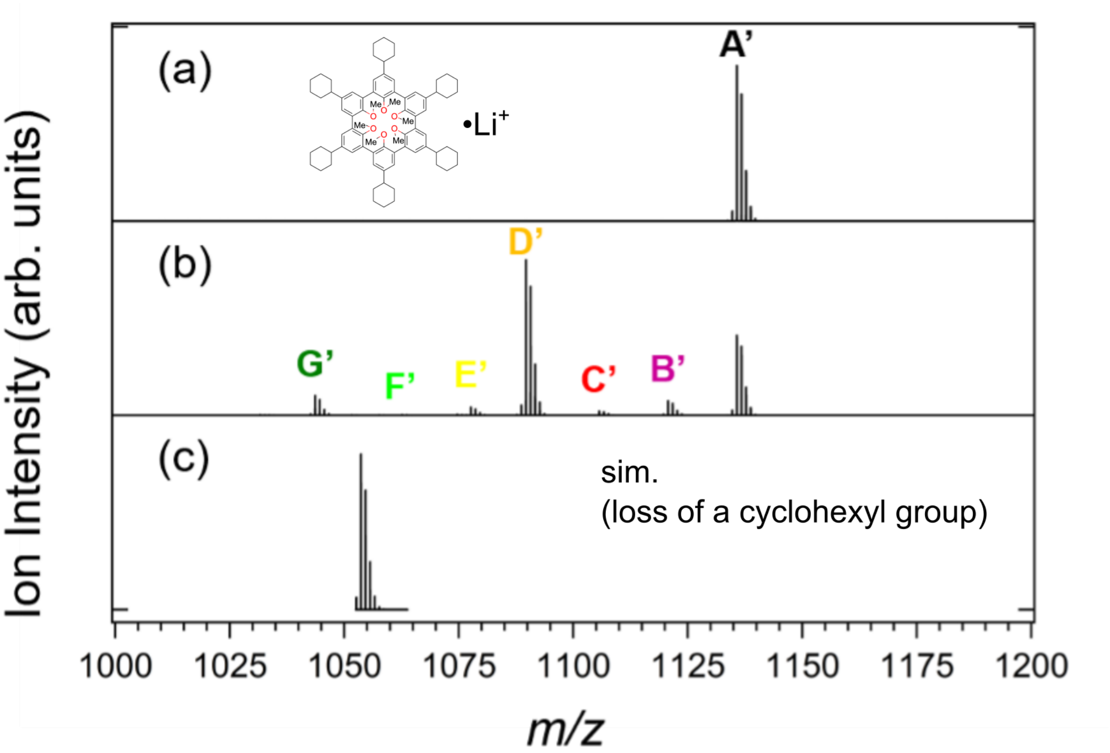


Figure S1. CID mass spectra of the (cyclohexyl-SPR)•Li^+ complex. The kinetic energy in the center of mass frame was adjusted to (a) 0 and (b) 2.5 eV. Cyclohexyl-loss ion of a simulation mass spectrum with isotope pattern analysis is also shown in (c).

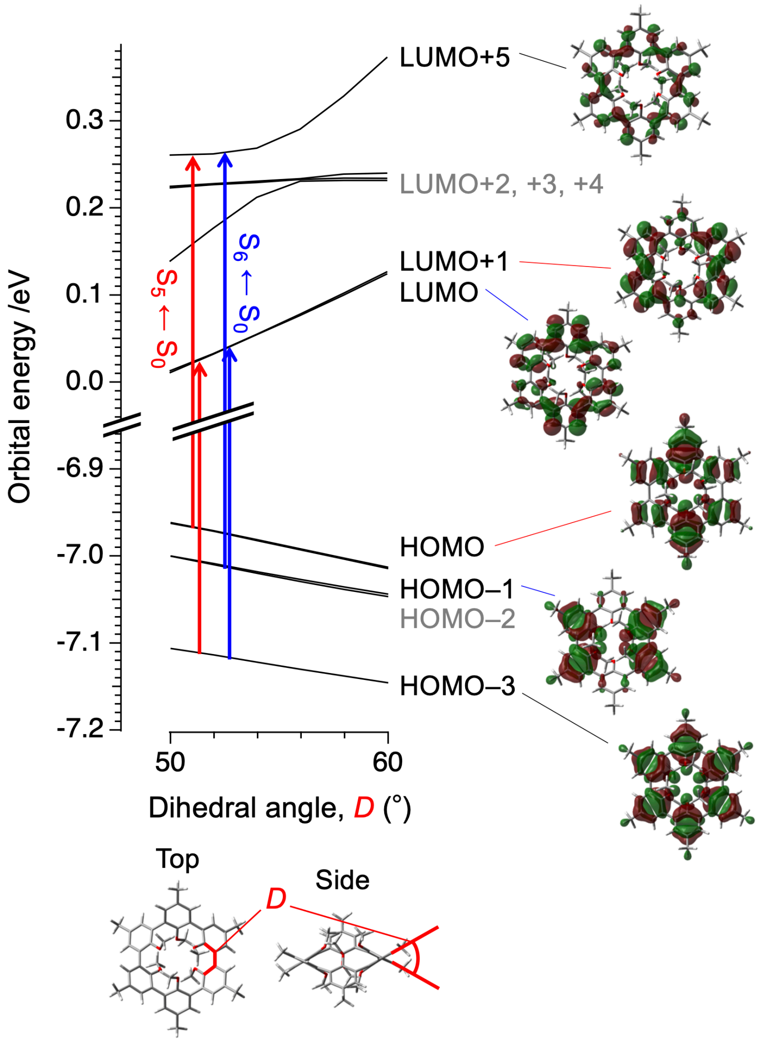


Figure S2. Walsh diagram of Kohn-Sham orbitals of **1** (from HOMO–3 to LUMO+5) as a function of the dihedral angle of aryl-aryl plane, *D* (see top and side view of the molecule). Calculations (M06-2X/6-31+G(d,p) level) were performed by scanning the dihedral angle at 2.0º intervals while optimizing the other structural parameters. Isodensity surface of each orbital (at *D* = 54.0º) is also shown. Red and blue arrows indicate transitions between orbitals that mainly contributes the $S_5 \leftarrow S_0$ and $S_6 \leftarrow S_0$, respectively (|CI coefficients| > 0.3 for bare **1**). The energies of occupied orbitals (HOMO and HOMO–*n* (*n* = 1–3)) are raised while those of unoccupied ones (LUMO and LUMO+*n* (*n* = 1, 2)) are lowered at smaller *D* value, qualitatively explaining the redshift of $S_5 \leftarrow S_0$ and $S_6 \leftarrow S_0$ transitions at small *D*.

Table S1. Distances and Angles in the **1**•Li$^+$ and **1**•Na$^+$ complexes.

Structural parameter	**1**	**1**•Li$^+$-I	**1**•Na$^+$-I
	Distances (Å)		
O to O, pseudoortho[a]	2.92	2.70	2.92
O to O, pseudometa[a]	3.34	3.18	3.38
O to O, pseudopara[a]	4.43	4.18	4.46
M$^+$ to O	–	2.09	2.23
	Angles (deg)		
Aryl-Aryl planes (dihedral)[a]	56	51	58
C-O-CH_3 planes and Aryl planes[a]	90	81	90
Aryl-O-CH_3[a]	112	112	112

[a] Average values of each part in the complexes.

Table S2. Peak Assignment of CID Mass Spectra of the (Cyclohexyl-SPR)•Li$^+$ complex.

Peak label	$Me_x(MeOMe)_y$-loss ions (x, y)
A'	(0, 0)
B'	(1, 0)
C'	(2, 0)
D'	(0, 1)
E'	(1, 1)
F'	(2, 1)
G'	(0, 2)

Label **A'-G'** in these results corresponds to label **A-G** in the results of the **1**•Li$^+$ complex.