**Electronic Supplementary Information**

# Strapped calix[4]pyrrole as a lithium salts selective receptor through separated ion-pair binding

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## 1. Materials and Measurements

All commercially available reagents were reagent grade and used without further purification. Tetrahydrofuran (THF) and $CH_2Cl_2$ were freshly distilled before each use. $^1H$ and $^{13}C$ NMR spectra were recorded using a Bruker DPX 400 (400 MHz) spectrometer at 25 °C in MeOD, $CDCl_3$, $CD_2Cl_2$. MALDI-TOF-MS was performed on a Bruker Daltonics LRF20 with dithranol as the matrix. UV-Vis absorption spectra were recorded on a JASCO V-660 spectrometer. The SEM analysis of $Li_2CO_3$ was conducted by using a JEOL 7610F-PLUS instrument with energy-dispersive x-ray photoelectron spectroscopy (XPS) on a K-Alpha (Thermo Scientific, U.K.).

## 2. Synthesis

**3**: Chloroacetone (3.4 mL, 42 mmol) and sodium azide (5.4 g, 83 mmol) were added in acetone (100 mL) and the reaction mixture was stirred for 23 h at 25 °C. After the solvent was removed, the residue was extracted with $CH_2Cl_2/H_2O$, and the organic layer was concentrated. The residue was purified by column chromatography eluting with 16% ethylacetate/hexane to give **3** (4.2 g, 61%). $^1H$ NMR (400MHz, $CDCl_3$, 25 °C) $\delta$ (ppm): 3.95 (s, 2 H), 2.20 (s, 3 H).

**4**: Trifluoroacetic acid (1.5 mL) was added dropwise to **3** (2.0 g, 20 mmol) in pyrrole (50 mL, excess), and the reaction mixture was refluxed for 100 min. Triethylamine (1.5 mL) was added to a solution and the solution was concentrated under high vacuum to remove pyrrole. After extraction with $CH_2Cl_2/H_2O$ and organic layer was washed with brine, the residue was

purified by column chromatography eluting with 40% $CH_2Cl_2$/Hexane to give **4** (3.4 g, 78%). $^1$H NMR (400 MHz, $CD_2Cl_2$, 25 °C) $\delta$ (ppm): 8.15 (broad s, 2 H), 6.69 – 6.67 (m, 2 H), 6.15 – 6.13 (m, 2 H), 6.09 – 6.07 (m, 2 H), 3.73 (s, 2 H), 1.65 (s, 3 H).

**5**: NaH (540 mg, 22 mmol) was added to Schlenk flask, which was degassed under high vacuum. Anhydrous THF (20 mL) and triethyleneglycol (1.0 mL, 7.5 mmol) were added to the flask at 0 °C under $N_2$ and the reaction mixture was stirred. After 1 h, propargyl bromide (4.1 mL, 38 mmol) and KI (3 spoons with spatula) were added to the mixture solution, and stirred for 18 h at 25 °C. The reaction mixture was concentrated under high vacuum to remove propargyl bromide. After extraction with $CH_2Cl_2$/$H_2O$ and organic layer was washed with brine, the residue was purified by column chromatography eluting with 40% ethylacetate/hexane to give **5** (1.6 g, 96%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C) $\delta$ (ppm): 4.21 - 4.20 (d, J = 4 Hz, 4 H), 3.72 - 3.67 (m, 12 H), 2.43 - 2.42 (t, J = 4 Hz, 2 H).

**6**: **4** (410 mg, 1.9 mmol) and **5** (196 mg, 0.86 mmol) were added in anhydrous THF (30 mL). $CuSO_4 \cdot 5H_2O$ (552 mg, 3.50 mmol) and sodium ascorbate (685 mg, 3.50 mmol) dissolved in $H_2O$ were added, and the reaction mixture was refluxed for 12 h. After filtration, the solution was extracted with NaCl(aq)/$CH_2Cl_2$, and the organic layer was concentrated. The residue was purified by column chromatography eluting with 5% MeOH/Ethylacetate to give **6** (173 mg, 30%). $^1$H NMR (400 MHz, $CDCl_3$, 25 °C) $\delta$ (ppm): 8.77 (broad s, 4 H), 6.63 (s, 4 H), 6.45 (s, 2 H), 6.09 (s, 4 H), 5.99 (s, 4 H), 4.82 (s, 4 H), 4.42 (s, 4 H), 3.52 – 3.48 (broad d, 12 H), 1.47 (s, 6 H); MALDI-TOF-MS m/z : cald. for $C_{34}H_{44}N_{10}O_4$: 656.78 $[M+H]^+$; found : 657.524.

**1**: $BF_3 \cdot OEt_2$ (0.5 mL) was added dropwise to **6** (483 mg, 0.74 mmol) in acetone (200 mL, excess), and the reaction mixture was stirred for 2 days at room temperature. Triethylamine (0.5 mL) was added to a solution and the reaction mixture was extracted with $CH_2Cl_2/H_2O$, and the organic layer was concentrated. The residue was purified by column chromatography eluting with 5% MeOH/Ethylacetate to give **1** (91 mg, 17%). $^1H$ NMR (400 MHz, $CD_2Cl_2$, 25 °C) $\delta$ (ppm): 7.68 (broad s, 4 H), 7.01 (s, 2 H), 6.08 – 5.95 (m, 8 H), 4.87 (s, 4 H), 4.55 (s, 4 H), 3.61 – 3.59 (broad d, 12 H), 1.66 (s, 6 H), 1.54 (s, 6 H), 1.50 (s, 6 H); $^{13}C$ NMR (100 MHz, $CD_2Cl_2$, 25 °C) $\delta$ (ppm): 144.73, 138.65, 132.85, 123.93, 105.41, 104.24, 70.50, 70.35, 70.09, 64.58, 40.93, 35.47, 31.12, 28.98, 26.84; MALDI-TOF-MS m/z : cald. for $C_{40}H_{52}N_{10}O_4$: 736.91 $[M+H]^+$; found : 737.660.

## 3. The procedure for precipitation experiments

**Using $K_2CO_3$ diluted in MeOH**: Through liquid-liquid extraction, LiCl in aqueous phase were extracted to organic phase using **1** in a vial. To remove aqueous phase, the solution was filtered on hydrophobic membrane. The organic solution ($CH_2Cl_2$) became turbid upon addition of $K_2CO_3$ diluted in MeOH.

**Using $CO_2$(g) bubbling**: the excess of LiCl(s) was poured to the solution containing 5 mg/mL of **1** in $CH_2Cl_2$ and then the mixture was stirred for 1 h to extract LiCl. After the solution was filtered to remove salt, deionized water (1.0 mL) was added to the residue. Gaseous $CO_2$ bubbling was conducted at 0 $^oC$.

## 4. X-ray crystallographic data of 1•LiCl complex

### Data collection

The diffraction data from yellow crystals of **1**•LiCl (0.095 × 0.054 × 0.034 mm3) mounted on a MiTeGen MicroMount© were collected at 100 on a ADSC Quantum 210 CCD diffractometer with synchrotron radiation (0.7000 Å) at Supramolecular Crystallography 2D, Pohang Accelerator Laboratory (PAL), Pohang, Korea. The ADSC Q210 ADX program[1] was used for data collection (detector distance is 63 mm, omega scan; $\Delta\omega = 1^{o}$, exposure time is 1 sec/frame for 1•LiCl and HKL3000sm (Ver. 703r)[2] was used for cell refinement, reduction and absorption correction. The crystal structures of 1•LiCl was solved by the direct method with SHELX-XT (Ver. 2014/5)[3] and refined by full-matrix least-squares calculations with the SHELX-XL (Ver. 2016/4) [4] program package.

### Structure solution and refinement

The systematic absences in the diffraction data were uniquely consistent for the triclinic space group P-1 that yielded chemically reasonable and computationally stable results of refinement.[4-5]

A successful solution by the direct methods provided most non-hydrogen atoms from the E-map. The remaining non-hydrogen atoms were located in an alternating series of least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined with anisotropic displacement coefficients. All hydrogen atoms were included in the structure factor calculation at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients.

The final least-squares refinement of 597 parameters against 10770 data resulted in residuals R (based on F2 for I≥2σ) and wR (based on F2 for all data) of 0.0526 and 0.1559, respectively. The final difference Fourier map was featureless.

**Summary**

Crystal Data for C43H62.5ClLiN11.5O7 (M =894.93 g/mol): triclinic, space group P-1 (no. 2), a = 9.7210(19) Å, b = 14.384(3) Å, c = 17.153(3) Å, α = 88.50(3)°, β = 86.85(3)°, γ = 77.08(3)°, V = 2334.0(9) Å3, Z = 2, T = 100 K, μ(synchrotron) = 0.138 mm-1, Dcalc = 1.273 g/cm3, 20744 reflections measured (3.672° ≤ 2Θ ≤ 55.996°), 10770 unique (Rint = 0.0198, Rsigma = 0.0310) which were used in all calculations. The final R1 was 0.0526 (I > 2σ(I)) and wR2 was 0.1559 (all data).

**Table S1**. Crystal data and structure refinement for **1**•LiCl

| | |
|---|---|
| Identification code | HCCP3 |
| Empirical formula | C43H62.5ClLiN11.5O7 |
| Formula weight | 894.93 |
| Temperature/K | 100 |
| Crystal system | triclinic |
| Space group | P-1 |
| a/Å | 9.7210(19) |
| b/Å | 14.384(3) |
| c/Å | 17.153(3) |
| α/° | 88.50(3) |
| β/° | 86.85(3) |
| γ/° | 77.08(3) |
| Volume/Å3 | 2334.0(9) |
| Z | 2 |
| ρcalcg/cm3 | 1.273 |
| μ/mm-1 | 0.138 |
| F(000) | 954.0 |
| Crystal size/mm3 | 0.095 × 0.054 × 0.034 |
| Radiation | synchrotron (λ = 0.700) |
| 2Θ range for data collection/° | 3.672 to 55.996 |
| Index ranges | -13 ≤ h ≤ 13, -19 ≤ k ≤ 19, -20 ≤ l ≤ 21 |
| Reflections collected | 20744 |
| Independent reflections | 10770 [Rint = 0.0198, Rsigma = 0.0310] |
| Data/restraints/parameters | 10770/0/597 |
| Goodness-of-fit on F2 | 1.059 |
| Final R indexes [I>=2σ (I)] | R1 = 0.0526, wR2 = 0.1503 |
| Final R indexes [all data] | R1 = 0.0605, wR2 = 0.1559 |
| Largest diff. peak/hole / e Å-3 | 0.62/-0.56 |

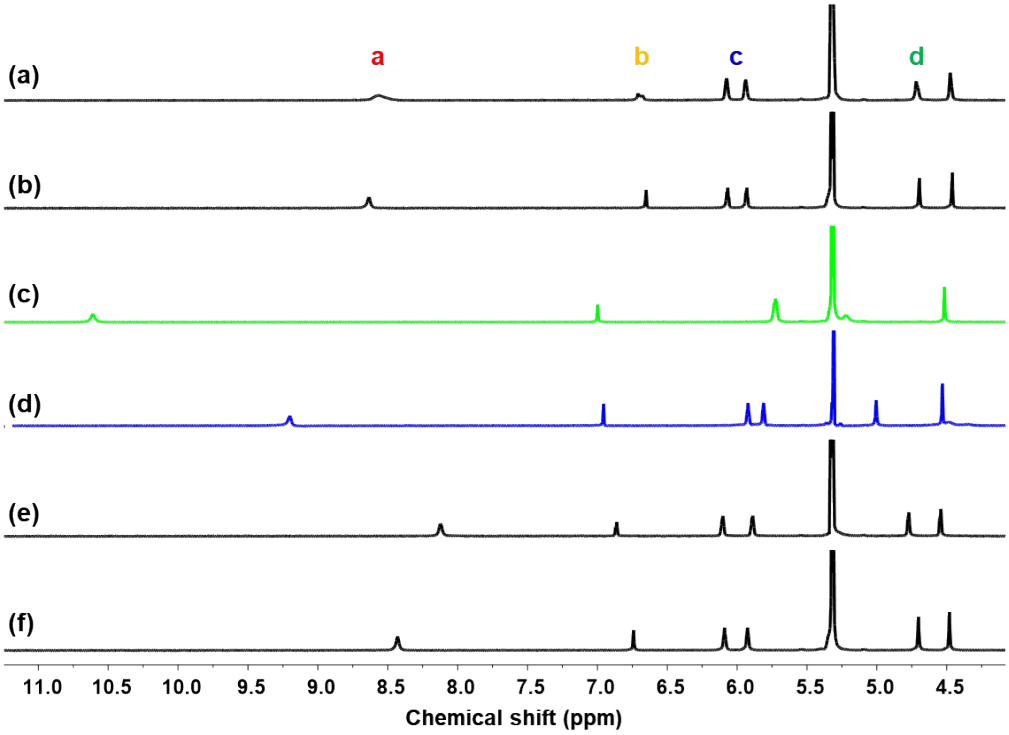



**Figure S1.** Partial $^1$H NMR spectra of (a) **1** and **1** with excess of (b) LiF(s), (c) LiCl(s), (d) LiBr(s), (e) LiI(s), and (f) $LiClO_4$(s) (400 MHz, $CD_2Cl_2$:$CD_3OD$=9:1, 297 K).

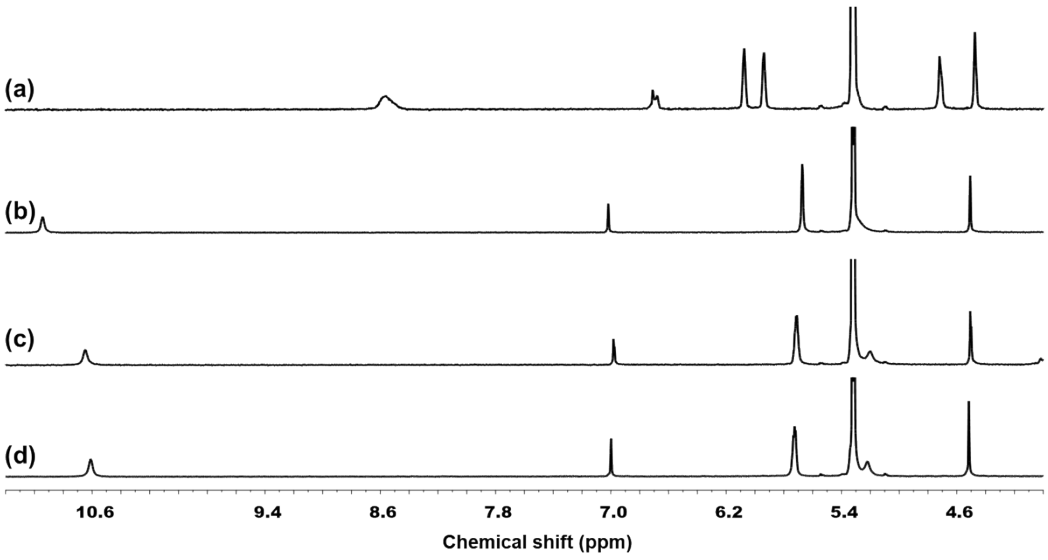



**Figure S2.** Partial $^1$H NMR spectra to confirm complexation of **1**•LiCl in solution state. (a) only **1** (10 mM) and **1** with (b) excess of TBACl, (c) TBACl followed by excess of $LiClO_4$, (d) excess of LiCl. (all spectra were recorded in 10% $CD_3OD/CD_2Cl_2$, 297 K)

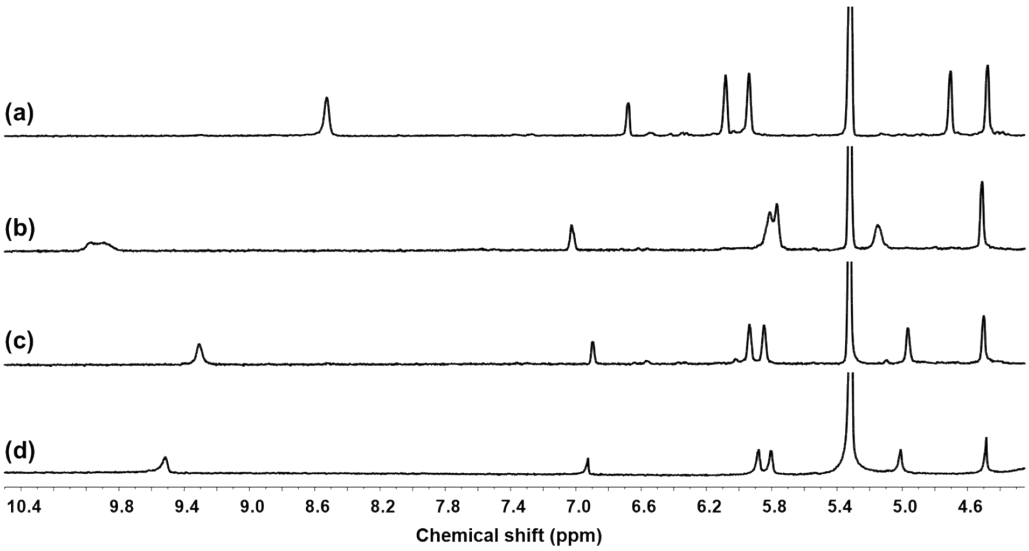



**Figure S3.** Partial $^{1}$H NMR spectra to confirm complexation of **1**•LiBr in solution state. (a) only **1** and **1** with (b) excess of TBABr, (c) TBABr followed by excess of $LiClO_4$, (d) excess of LiBr.(all spectra were recorded in 10% $CD_3OD/CD_2Cl_2$, 297 K)

**Table S2**. The binding constants of **1** with various guests in 10% MeOD-$CD_2Cl_2$.

| $K_a$ ($M^{-1}$) | TBACl | TBABr | $LiClO_4$ | LiCl | LiBr |
|---|---|---|---|---|---|
| **1** | 377±1.07 | 61±1.04 | 4.4±1.13 | 60.5±1.02 | 19.5±1.01 |

**Table S3**. The binding constant of other system in literatures.

| Reference | Guest | Solvent | Binding constant |
|---|---|---|---|
| Ref. 7 | LiCl | 10% MeOD-$CD_2Cl_2$ | 45±1 |
| Ref. 8 | LiCl | 10% $D_2O$-THF-$d_8$ | (8.3±0.3)x$10^2$ |

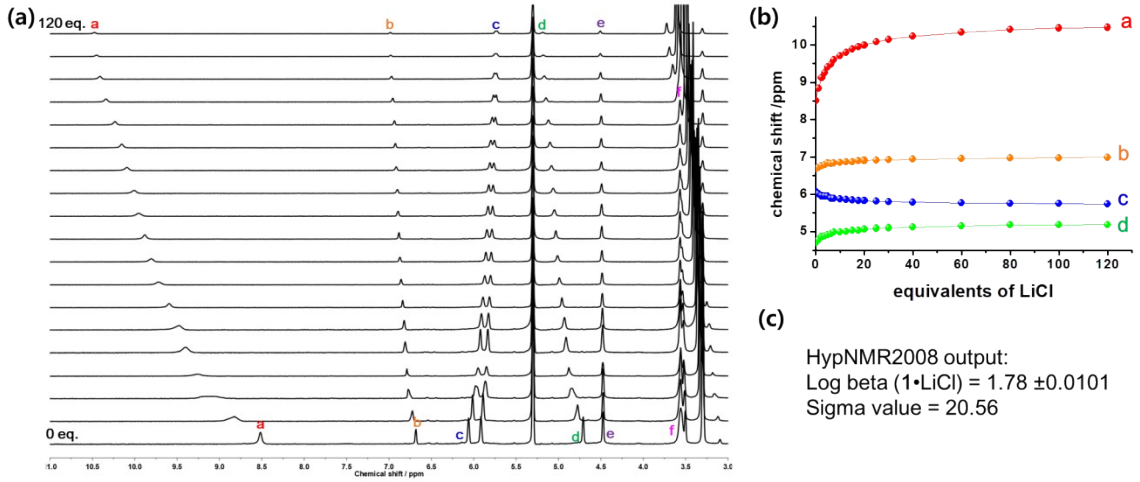



**Figure S4**. (a) stacked partial $^1$H NMR spectra of **1**(10 mM) with LiCl in 10% $CD_3OD/CD_2Cl_2$, (b) chemical shift changes of **1**'s protons upon addition of LiCl, (c) binding constant of **1**• LiCl calculated by HypNMR2008.

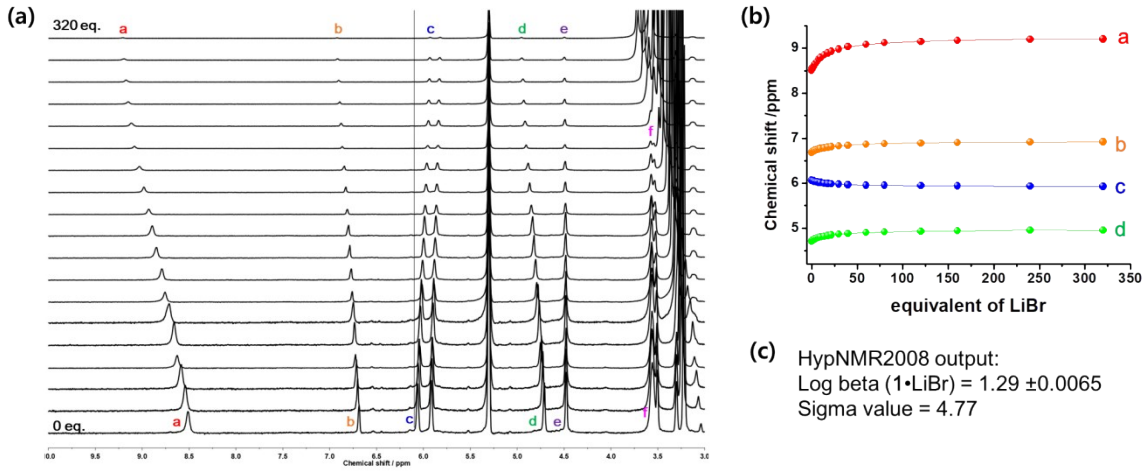



**Figure S5**. (a) stacked partial $^1$H NMR spectra of **1** (10 mM) with LiBr in 10% $CD_3OD/CD_2Cl_2$, (b) chemical shift changes of **1**'s protons upon addition of LiBr, (c) binding constant of **1**• LiBr calculated by HypNMR2008.

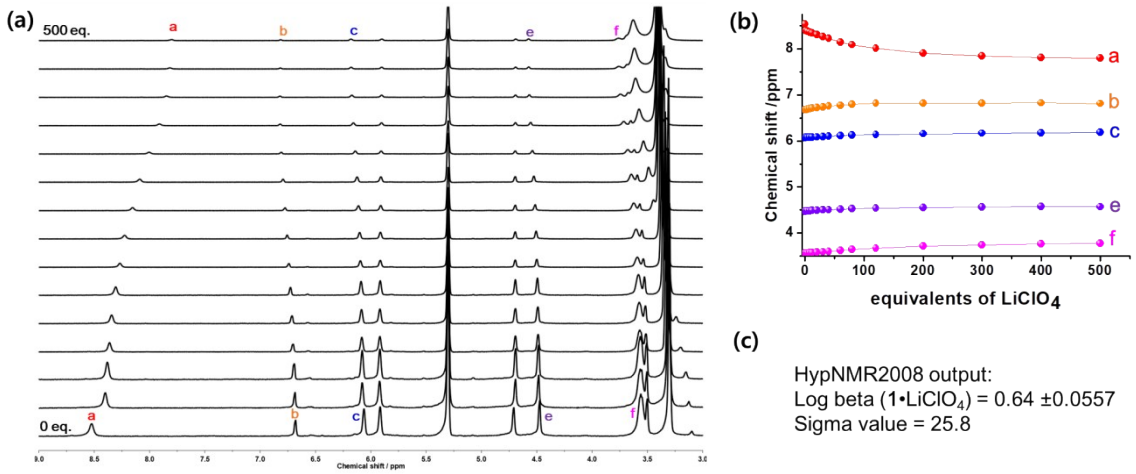



**Figure S6**. (a) stacked partial $^1$H NMR spectra of **1** (10 mM) with $LiClO_4$ in 10% $CD_3OD/CD_2Cl_2$, (b) chemical shift changes of **1**'s protons upon addition of $LiClO_4$, (c) binding constant of **1**•$LiClO_4$ calculated by HypNMR2008.

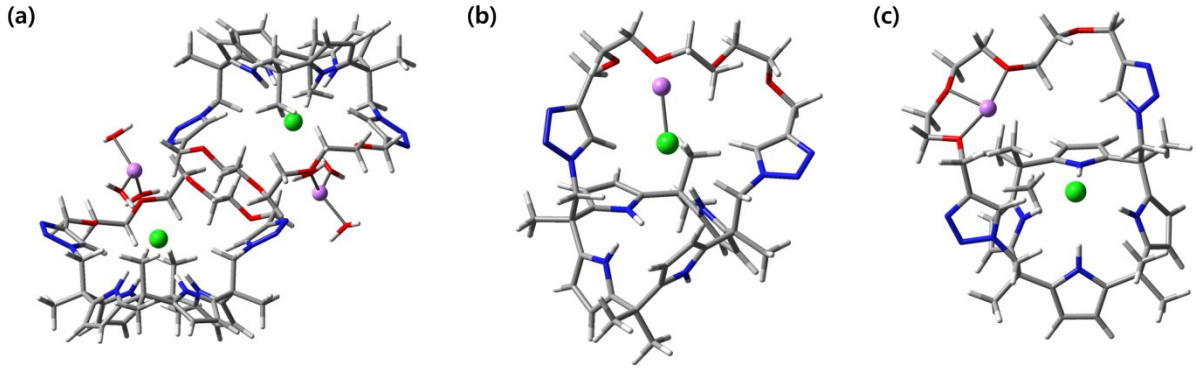



**Figure S7.** DFT optimized structure of **1**•LiCl complex, (a) water-separated ion pair (solvent bridged), (b) contact ion pair, and (c) separated ion pair.[6]

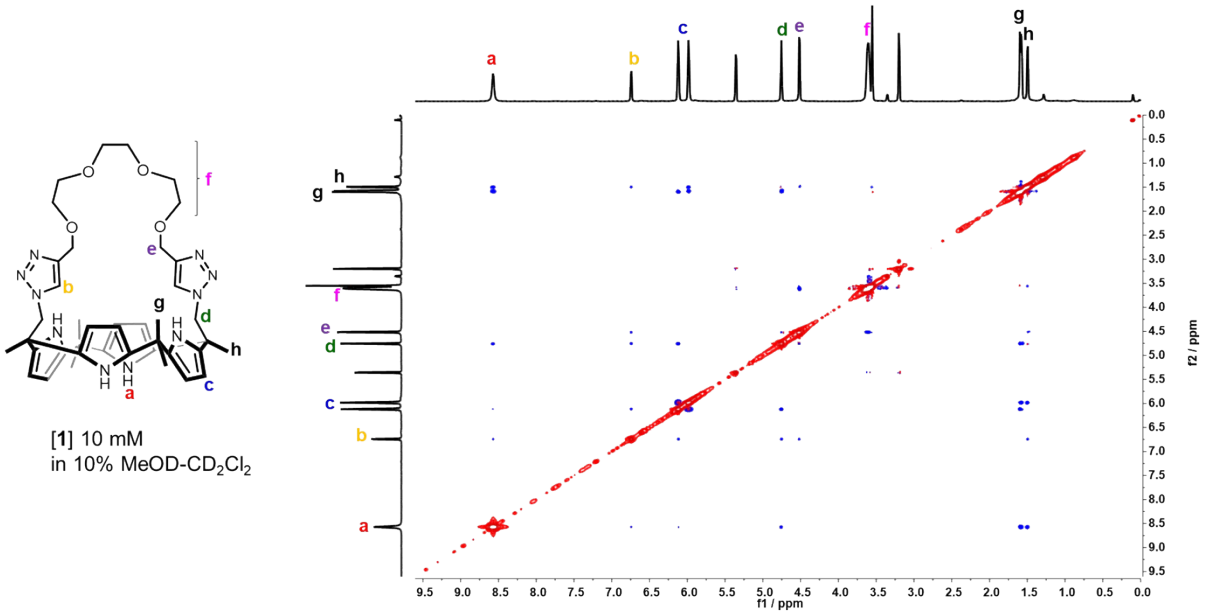



**Figure S8**. $^{1}$H-NOESY spectrum of **1** (10 mM) in 10% MeOD-$CD_2Cl_2$.

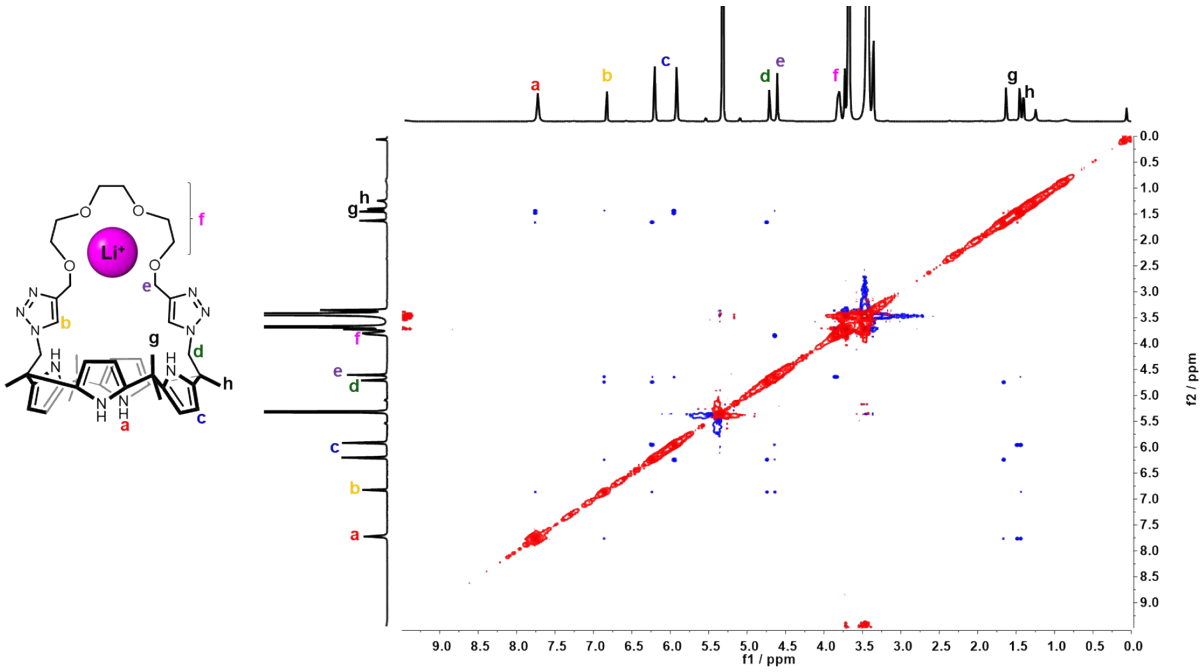



**Figure S9**. $^{1}$H-NOESY spectrum of **1**·$LiClO_4$ (10 mM) in 10% MeOD-$CD_2Cl_2$.

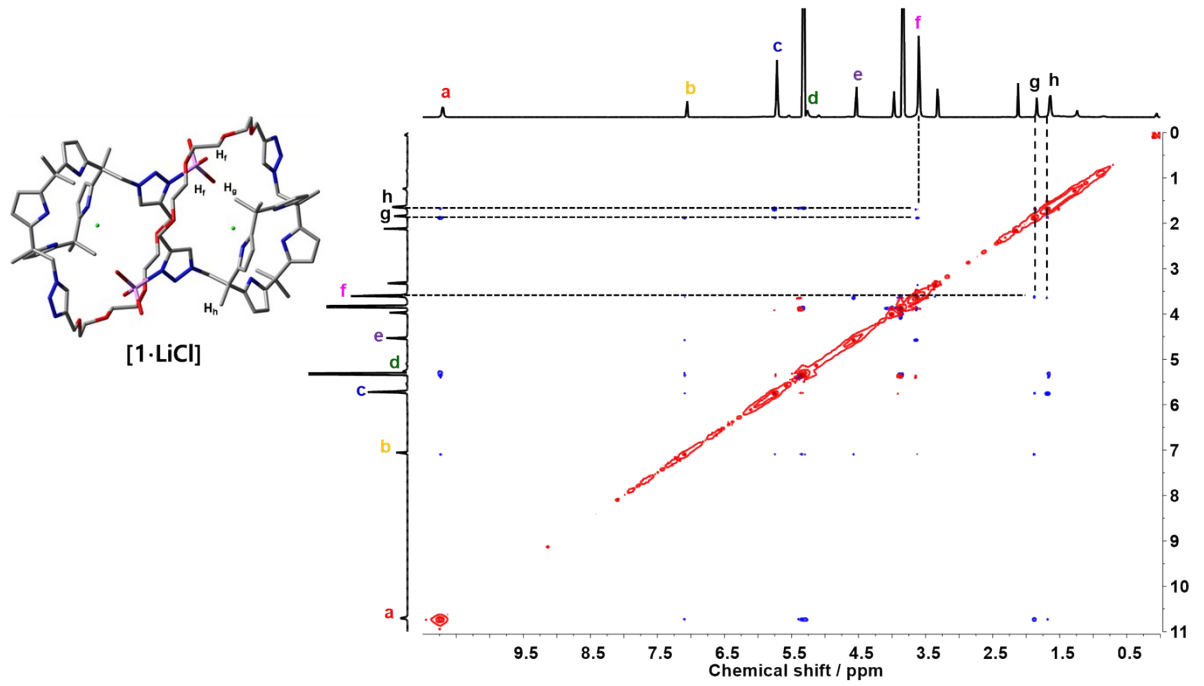



**Figure S10**. $^{1}$H-NOESY spectrum of **1**·LiCl (2.5 mM) in 10% MeOD-$CD_2Cl_2$.

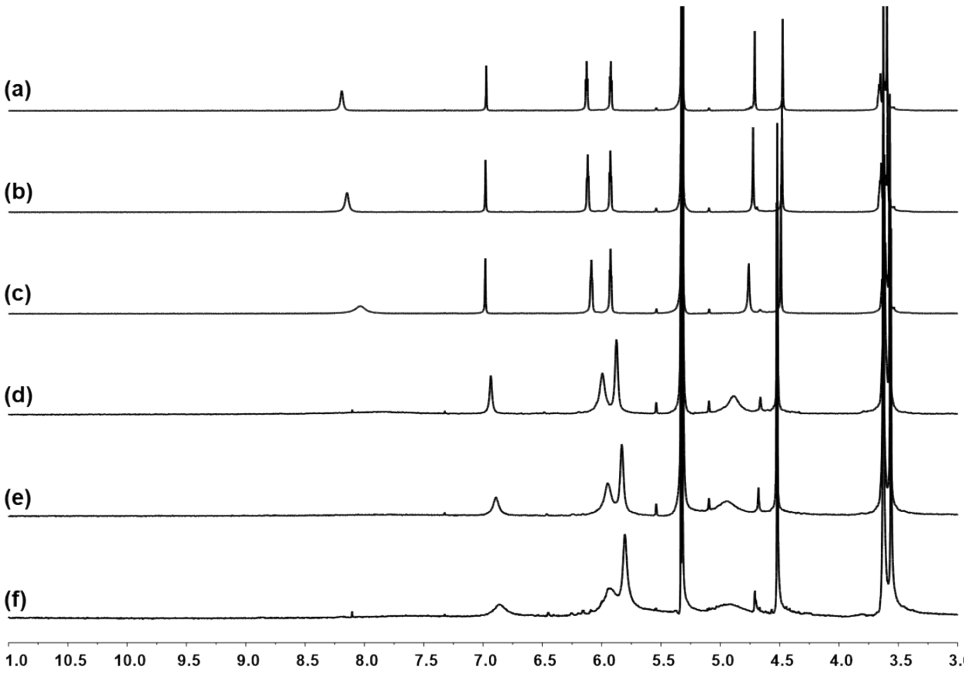



**Figure S11.** $^1$H NMR spectra of (a) **1** (5 mM) and **1** after extraction with (b) 25% saturated LiCl (aq), (c) 50% saturated LiCl (aq). (d) 80% saturated LiCl (aq), (e) 95% saturated LiCl (aq), and (f) 100% saturated LiCl (aq). (all spectra were recorded $CD_2Cl_2$, 297 K).

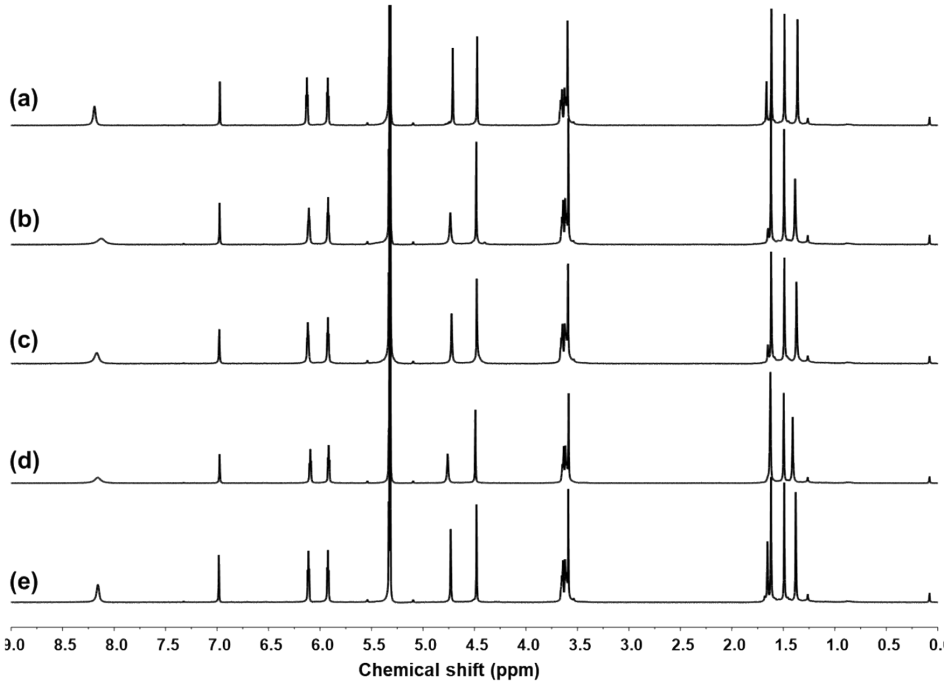



**Figure S12.** $^1$H NMR spectra of (a) **1** (5 mM) and **1** after extraction with excess of (b) NaCl(aq), (c) KCl(aq), (d) NaBr(aq), and (e) KBr(aq) (all spectra were recorded $CD_2Cl_2$, 297 K).

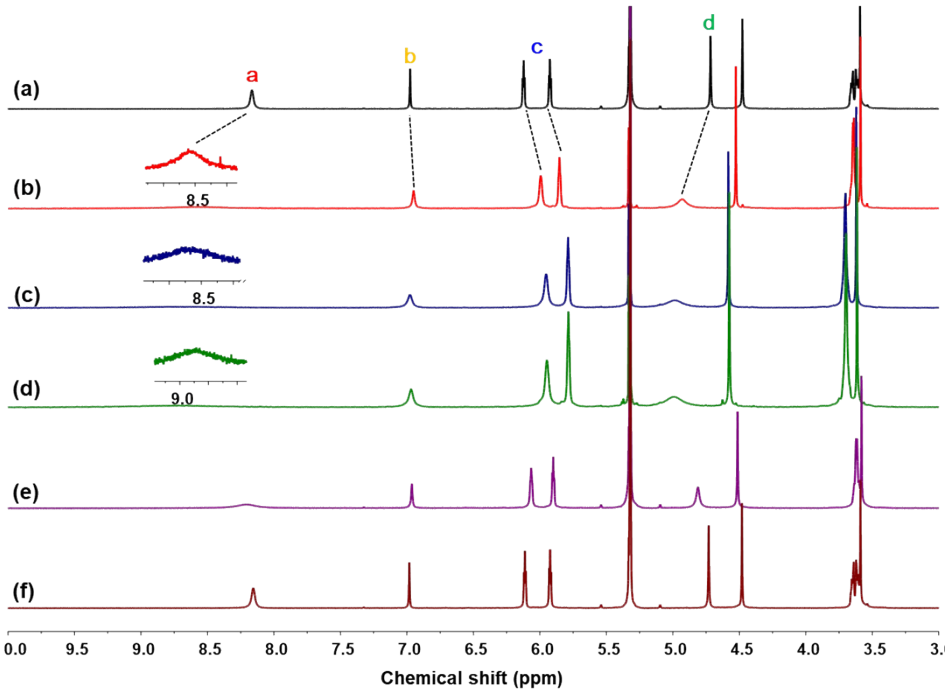



**Figure S13.** $^{1}$H NMR spectra of (a) **1** (5 mM) and **1** after extraction with (b) saturated LiBr(aq), (c) excess LiBr(s), (d) excess LiBr(s), NaBr(s) and KBr(s), (e) excess of NaBr (s), and (f) excess of KBr (s) (400 MHz, $CD_2Cl_2$, 297 K).

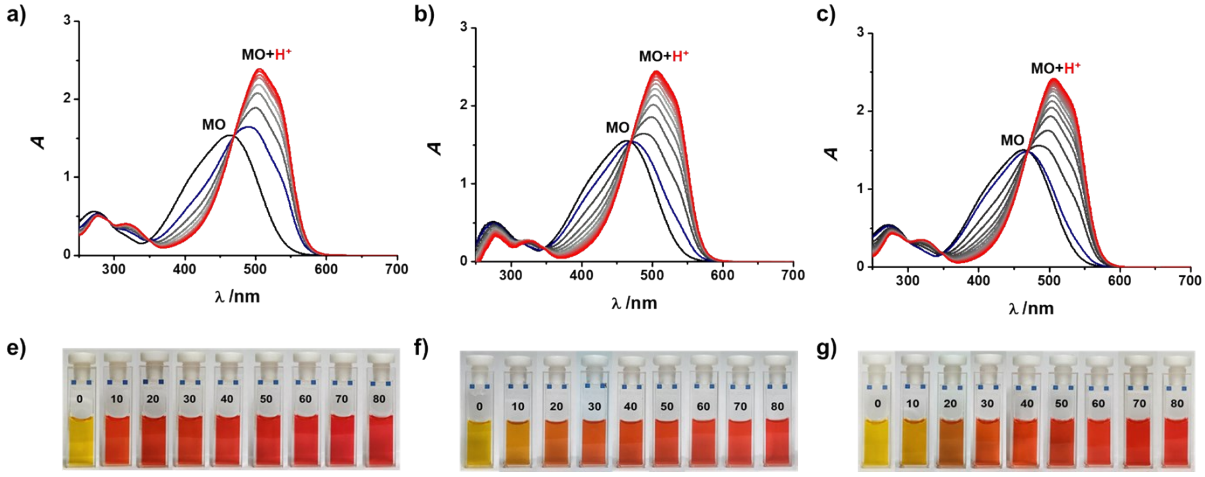
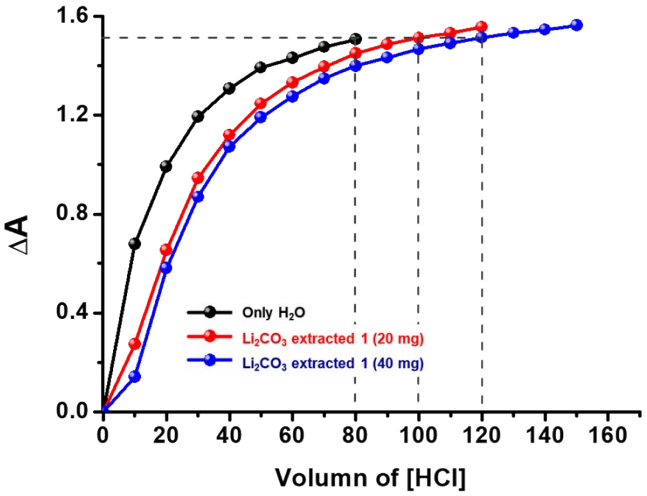



**Figure S14.** UV/Vis spectral titration for methyl orange (**MO**) as a pH indicator using 0.05 M HCl and its photographs: (a) and (e) only deionized water, the solution containing lithium carbonate extracted by (b) and (f) 20 mg of **1**, (c) and (g) 40 mg of **1**.

a)




b)

| Amount of **1** used for solid-liquid extraction | Extracted amount (mg) |
|---|---|
| 20 mg | 0.146 |
| 40 mg | 0.292 |

**Figure S15**. (a) The binding isotherm graph for acid-base titration and (b) the amount of lithium carbonate extracted by **1** was summarized on table.

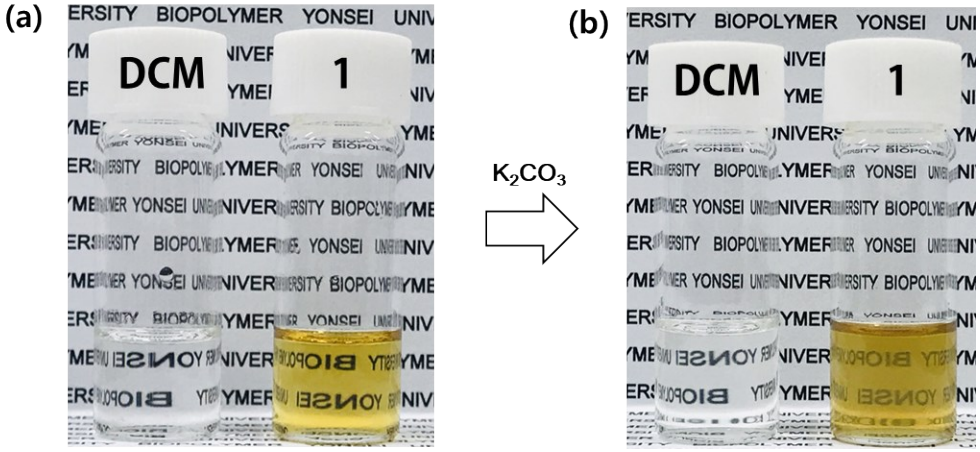



**Figure S16**. $Li_2CO_3$(s) was precipitated by addition of $K_2CO_3$ diluted in methanol into the solution containing **1**•LiCl complex; (a) before addition of $K_2CO_3$ and (b) after addition of $K_2CO_3$.

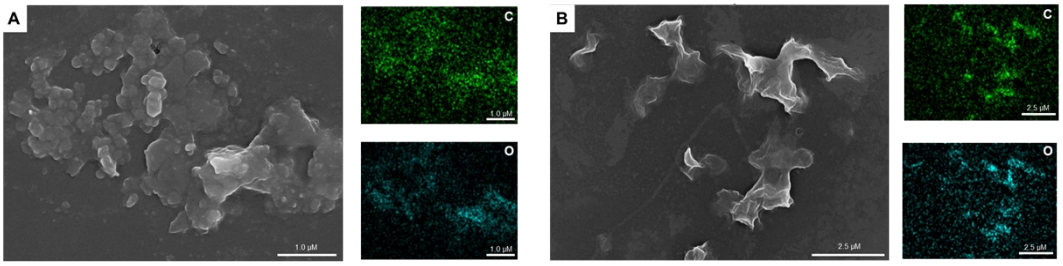



**Figure S17.** The images of SEM/EDS mapping of oxygen and carbon for A) commercial lithium carbonate and B) lithium carbonate extracted by **1**.

## $^{1}H$ and $^{13}C$ NMR spectra of each compounds

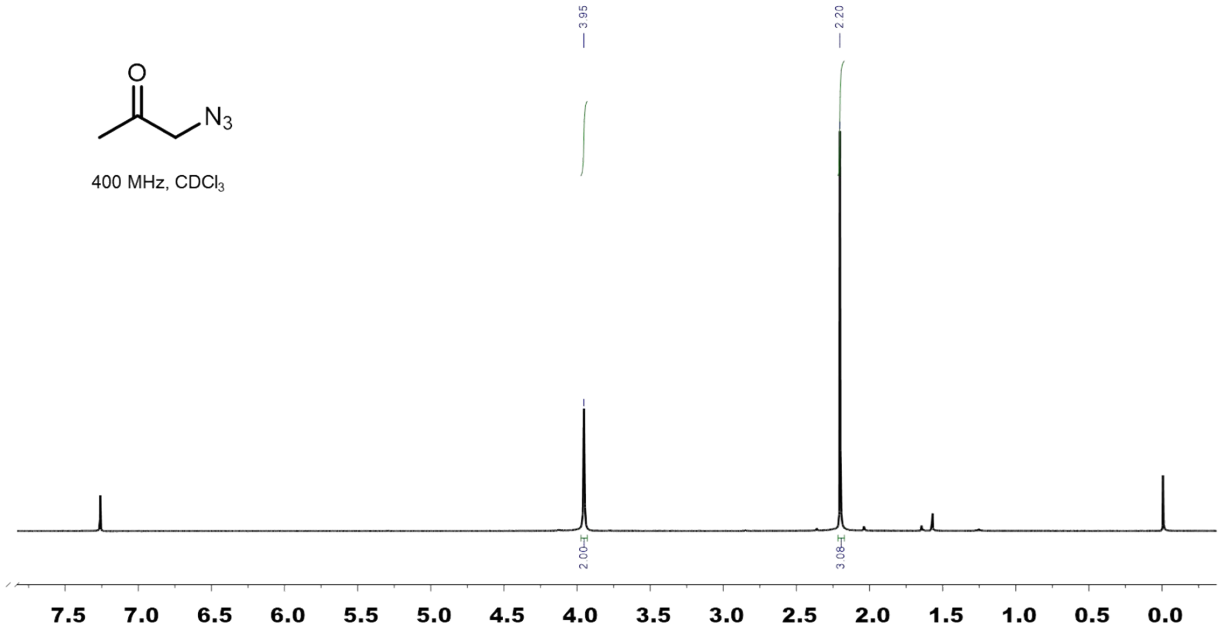



**Figure S18**. $^{1}H$ NMR spectrum of **3**.

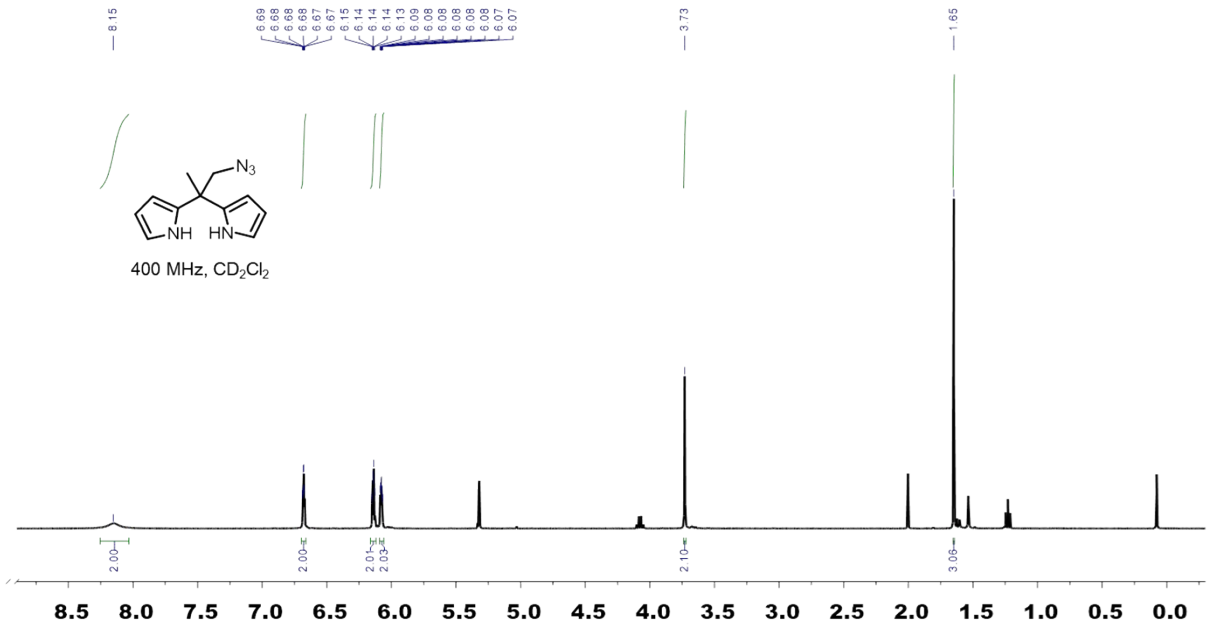



**Figure S19**. $^{1}H$ NMR spectrum of **4.**

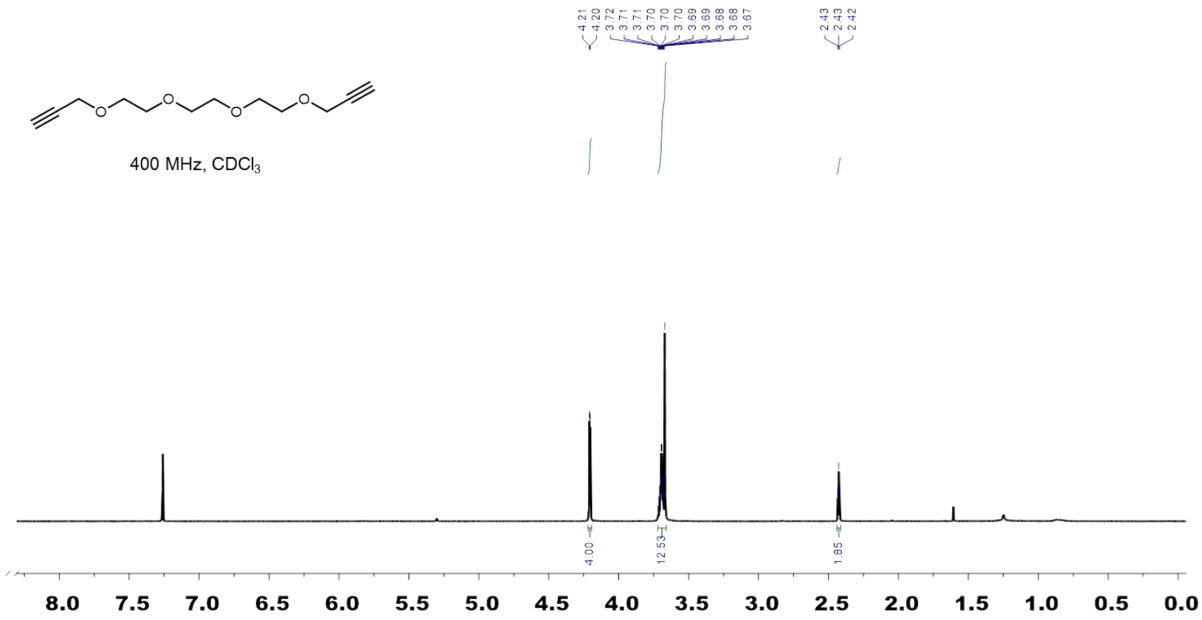



**Figure S20**. [1]H NMR spectrum of **5**.

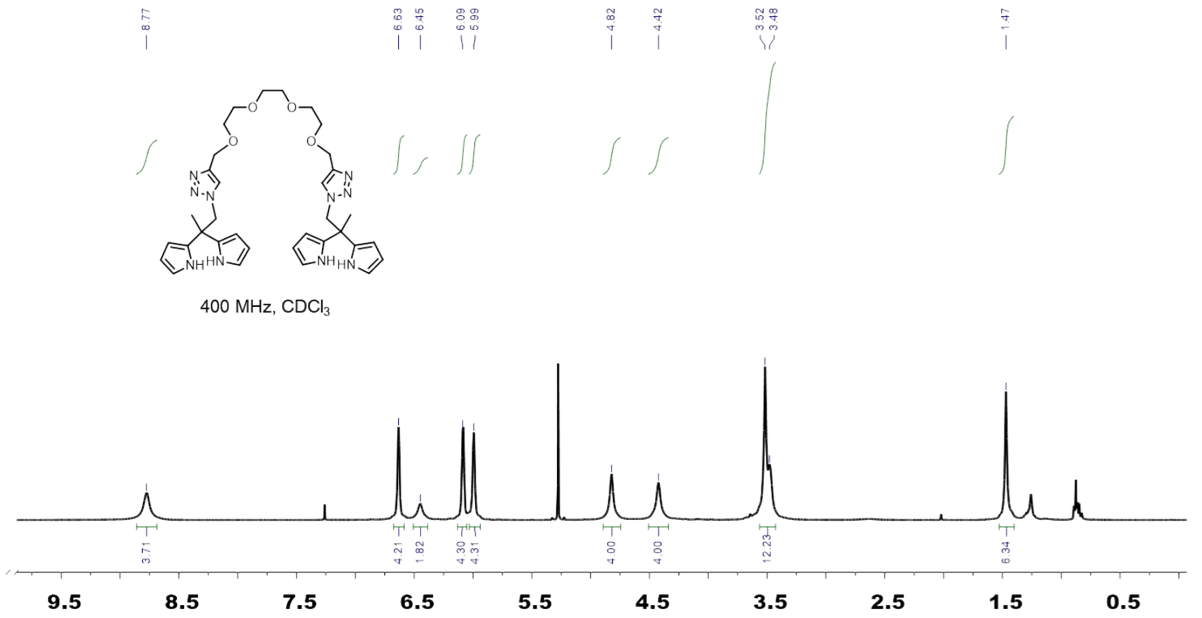



**Figure S21**. [1]H NMR spectrum of **6**.

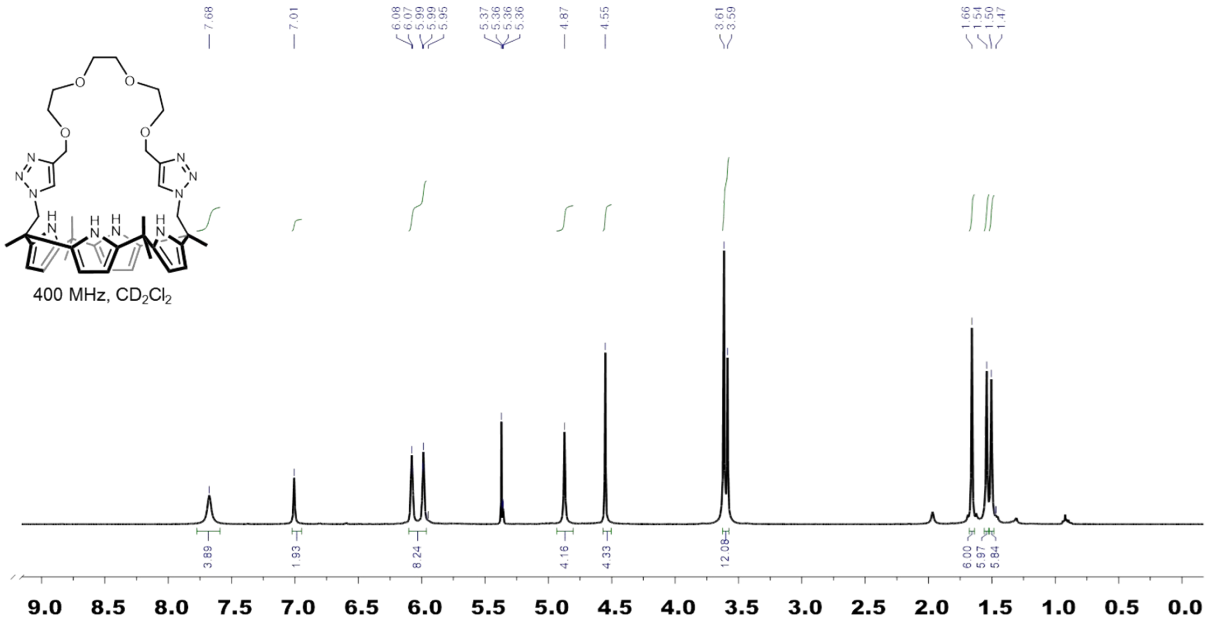



**Figure S22**. $^{1}H$ NMR spectrum of **1**.

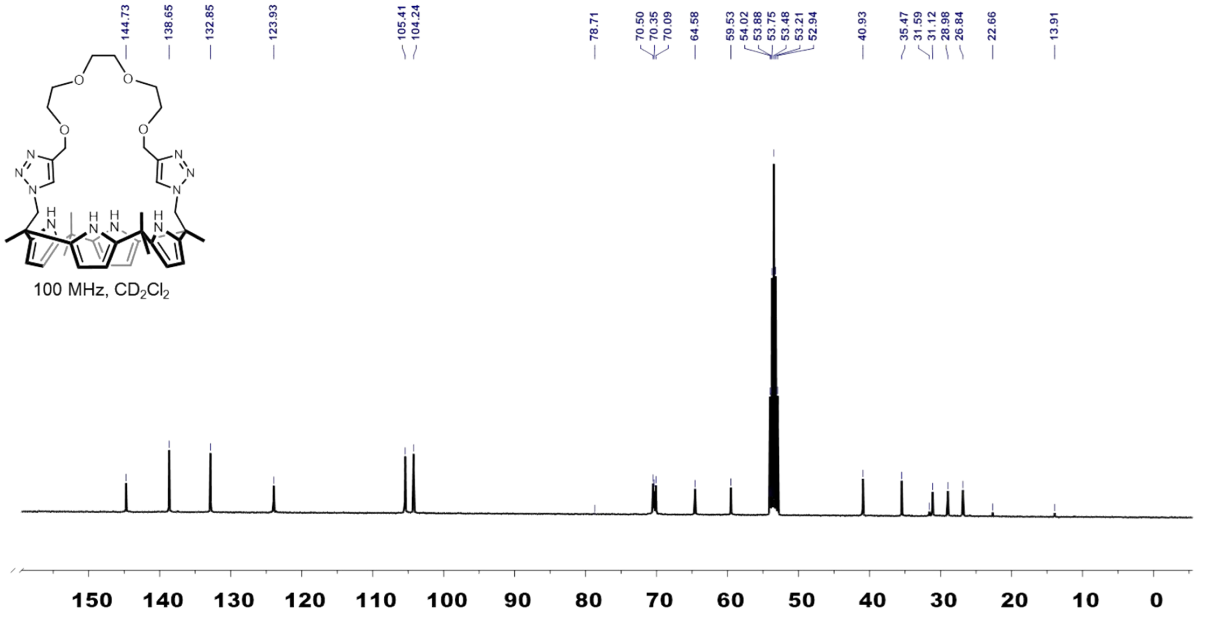



**Figure S23**. $^{13}C$ NMR spectrum of **1**.

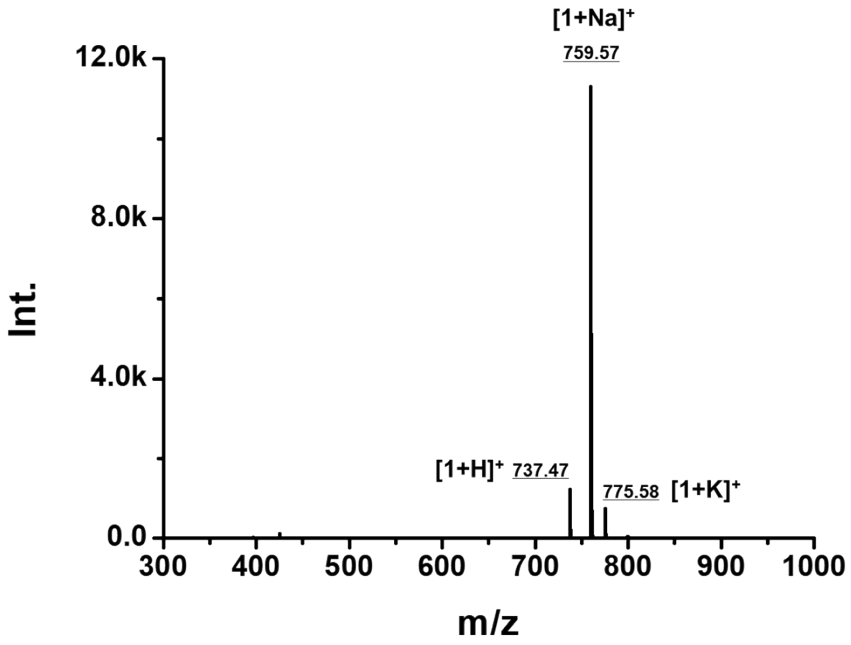



**Figure S24**. MALDI-TOF-MS spectrum of **1**.

**References**

(1) Arvai, A. J.; Nielsen, C. ADSC Quantum-210 ADX Program, Area Detector System Corporation: Poway, CA, USA, 1983.

(2) Otwinowski, Z.; Minor, W. Methods in Enzymology; Carter Jr., C. W. Jr.; Sweet, R. M., Eds.; Academic Press: New York, 1997, vol. 276, part A, pp. 307-326.

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