Electronic Supplementary Material (ESI) for Materials Advances.

Electronic Supplemental Information

for

A proton conductive hydrogen-bonded framework incorporating 18-crown-6-ether and dicarboxy-*o*-terphenyl moieties

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Contents.

1. General

Materials. All the chemicals used as starting materials, reagents and solvents were purchased from commercial suppliers and used as received without further purification. Analytical thin layer chromatography (TLC) was carried out on aluminum sheets coated with silica gel (Kieselgel 60F_{254}, Merck). Column chromatographic purifications were performed using silica gel (63-200 μm, Merck and 64-210 μm, Wakosil.). Unless stated otherwise, reported yields refer to analytically pure samples.

Spectroscopy. Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ on AV 400 MHz JEOL ECX-400 NMR spectrometers. Chemical shifts are reported in δ ppm relative to solvent peak (^{1}H NMR: δ 7.26 ppm and 2.50 ppm for $CDCl_3$ and DMSO-d_6, respectively; ^{13}C NMR: δ 77.16 ppm and 39.52 ppm for $CDCl_3$ and DMSO-d_6, respectively) with peak multiplicities described as singlet (s), broad singlet (br. s), doublet (d), triplet (t), quartet (q) and multiplet (m) in ^{1}H NMR spectra.

Thermal Stability. Thermogravimetric analysis (TGA) was conducted using a Rigaku Thermo Plus TG8120 with a heating rate of 5 K/min under nitrogen.

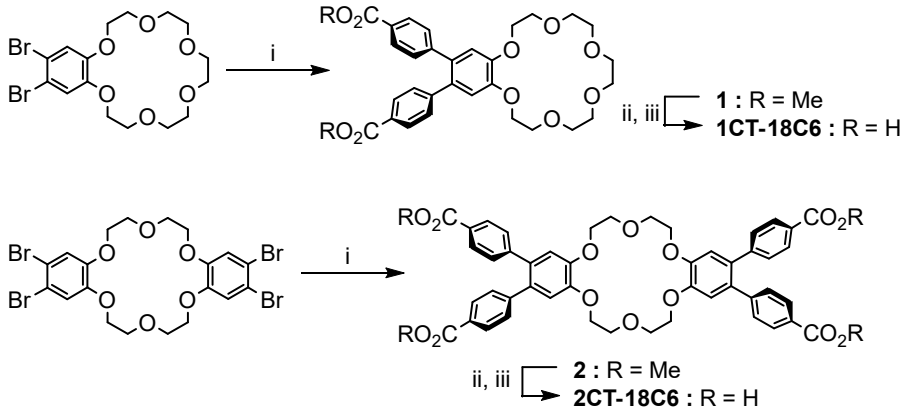
Powder X-Ray Diffraction Patterns (PXRD). PXRD were measured with a Rigaku RINT2100 in the 2θ region of 5 - 50°. The measurements were performed with Cu K_α radiation (λ = 1.5418 Å) at scanning rate of 1.2° · min^{-1} under an applied electric voltage and current of 40 KV and 40 mA, respectively.

Crystal Structure Determination. Single crystalline X-ray diffraction data was collected by Rigaku MicroMax-007HF diffractometer with a Pilatus 200K detector and Cu K_α radiation (λ = 1.54184 Å) at 223 K. Analytical and multi-scan absorption corrections were applied to the reflection data. A single crystal was mounted on MicroMounts^{TM} tip (MiTeGen) with Paratone$^{®}$ 8277 (Hampton Research). Data collection, cell refinement, and data reduction were carried out with Crysalis ^{PRO} (Rigaku Oxford Diffraction, 2017). The initial structure was solved by using SHELXT, and structural refinement was performed by using full-matrix least-squares techniques on F^2 using Crystal structure software (Rigaku). Anisotropic refinement was applied to all atoms except for hydrogens. SQUEEZE function equipped in the PLATON program was used to remove severely disordered solvent molecules in voids. These data are provided free of charge in The Cambridge Crystallographic Data Centre (CCDC-2057700, 2078832, 2078834, 2078835).

Impedance Spectroscopy under humid condition. Frequency-dependent impedance spectra were measured using an impedance analyzer 4294A (Agilent) with four-probe AC impedance method at a frequency range from $10^{2.5}$ to 10^6 Hz. The crystalline sample was powdered with agate milk stick and pelletized with a shaper. Gold paste (No. 8556, Tokuriki Chemical Research Co., Ltd.) and 30 μm ϕ gold wires (Nilaco Corp.) were used for electrical contacts between sample and electrical wire from the device. Temperature was controlled by water bath with pipe heater (AW-1105, Hakko Electric

Co.,Ltd) and temperature controller (TC-3000A, As One). The impedance was measured in a closed glass cell containing a saturated KCl solution and humidity was monitored by humidity sensor (SHT31-DIS, Senserion). Data fitting is carried out by using EIS Spectrum Analyser.

Section 2. Synthesis of compounds



Scheme S1. Synthesis of **1CT-18C6** and **2CT-18C6**. Reaction conditions: i) 4-(methoxycarbonyl)phenylboronic acid, $Pd(PPh_3)_4$, K_2CO_3, THF, water, reflux; ii) $NaOH_{aq.}$ THF, iii) HCl.

4,5-Dibromodibenzo-18-crown-6.[S1] Benzo[18]crown-6 ether (2.00 g, 6.40 mmol) was dissolved in acetic acid (80 ml). Bromine (5.00 g, 31.3 mmol) was added to the solution, and the mixture was stirred for 12 h at 85 ˚C. After cooling the solution, the orange powder was filtered and washed with water, $Na_2S_2O_3$(aq), MeOH (two times for each) to give 4,5-Dibromodibenzo-18-crown-6 (2.43 g, 81%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (s, 2H), 4.12 (d, J = 5.7 Hz, 4H), 3.92 (d, J = 5.6 Hz, 4H), 3.77 (d, J = 6.0 Hz, 4H), 3.76-3.64 (m, 8H); ^{13}C NMR: (100 MHz, $CDCl_3$): δ 148.56, 118.17, 115.37, 70.93, 70.74, 70.69, 69.40, 69.24 ppm.

4,5-Dibenzoic ester benzo-18-crown-6 derivative 1. 4,5-dibromobenzo-18-crown-6 (0.80 g, 1.7 mmol), K_2CO_3 (0.71 g, 5.1 mmol) and $Pd(PPh_3)_4$ (0.13 g, 0.11 mmol) were dissolved in THF (100 ml) and stirred for 15 min. 4-methoxycarbonylphenyl boronic acid (0.92 g, 5.1 mmol), dissolved in methanol (30 ml), was added to the solution and stirred for 48 h under reflux condition. After being cooled to the room temperature, the mixture was concentrated in a rotary evaporator, extracted with chloroform, washed with water and dried over anhydrous $MgSO_4$. The product was purified with column chromatography (silica gel, chloroform) to give **1** (0.71 g, 72%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (d, *J* = 8.4 Hz, 4H), 7.13 (d, *J* = 8.4 Hz, 4H), 6.93 (s, 2H), 4.27-4.20 (m, 4H), 3.98-3.89 (m, 4H), 3.88 (s, 6H), 3.82-3.66 (m, 12H) ppm; ^{13}C NMR: (100 MHz, $CDCl_3$): δ 166.99, 148.60, 145.84, 132.58, 129.99, 129.41, 128.24, 115.60, 69.91, 69.10, 52.15.

1CT-18C6. To a solution of **1** (0.70 g, 1.2 mmol) dissolved in THF (20 ml) was added 10% $NaOH_{aq}$ (10 ml). After stirred at 65 ºC for 48 h, 6 M HCl aqueous solution was added to the organic layer until it became neutral. The product was collected by centrifugation, washed with water for three time, and dried in vacuo to give **1CT-18C6** (0.51 g, 77 %) as a white solid.
^{1}H NMR(400 MHz, DMSO): δ 7.74 (d, *J* = 7.9 Hz, 4H), 7.17 (d, *J* = 7.9 Hz, 4H), 7.00 (s, 2H), 4.21-4.14 (m, 4H), 3.75 (d, *J* = 5.9 Hz, 4H) , 3.60-3.56 (m, 4H) , 3.53 (d, *J* = 5.9 Hz, 4H) , 3.50 (s, 4H) ppm; ^{13}C NMR: (100 MHz, DMSO-*d*$_6$) δ 167.7, 148.4, 145.7, 132.0, 130.5, 129.6, 129.4, 115.3, 70.29, 70.25, 69.1, 68.6 ppm; ESI-MS *m/z* calc. for $[M]^+$ $C_{30}H_{32}O_{10}$: 552.19; found: 552.20.

4,4',5,5'-Tetrabromodibenzo-18-crown-6.[S1] Dibenzo[18]crown-6 ether (1.61 g, 4.47 mmol) was dissolved in acetic acid (50 ml). Bromine (5.00 g, 31.3 mmol) was added to the solution, and the mixture was stirred for 12 h at 85 ˚C. After cooling the solution, the orange powder was filtered and washed with water, $Na_2S_2O_3$(aq), MeOH (two times for each) to give 4,4',5,5'-tetrabromodibenzo-18-crown-6 (2.61 g, 86%) as white residue.
^{1}H NMR (400 MHz, $CDCl_3$): 7.03 (s, 4H), 4.08 (s, 8H), 3.96 (s, 8H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.67, 117.95, 115.21, 69.72, 69.08 ppm.

4,4',5,5'-Terabenzoic ester dibenzo-18-crown-6 derivative 2. 4,4',5,5'-tetrabromodibenzo-18-crown-6 (4.05 g, 5.99 mmol), K_2CO_3 (4.16 g, 30.10 mmol) and $Pd(PPh_3)_4$ (0.47 g, 0.41 mmol) were dissolved in THF (100 ml) and stirred for 15 min. 4-methoxycarbonylphenyl boronic acid (5.39 g, 30.0 mmol), dissolved in methanol (50 ml), was added to the solution and stirred for 48 h under reflux condition. After being cooled to the room temperature, the mixture was concentrated in a rotary evaporator, extracted with chloroform, washed with water and dried over anhydrous $MgSO_4$. The product was purified with column chromatography (silica gel, chloroform) to give **2** (4.11 g, 76%) as a white solid.
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 8.4 Hz, 8H), 7.13 (d, *J* = 8.4 Hz, 8H), 6.94 (s, 4H), 4.26 (t, *J* = 4.5 Hz, 8H), 4.07 (t, *J* = 4.6 Hz, 8H), 3.88 (s, 12H) ppm; ^{13}C NMR: (100 MHz, $CDCl_3$) δ 167.02, 148.71, 145.82, 132.71, 130.00, 129.44, 128.27, 115.97, 70.03, 69.31, 52.19 ppm.

2CT-18C6. To a solution of **2** (1.07 g, 1.19 mmol) dissolved in THF (30 ml) was added 10 % $NaOH_{aq}$ (10 ml). After stirred at 60 ºC for 48 h, 6 M HCl aqueous solution was added to the organic layer until it became neutral. The product was collected by centrifugation, washed with water for three time, and dried in vacuo to give **2CT-18C6** (0.73 g, 73 %) as a white solid.
^{1}H NMR(400 MHz, DMSO-*d*$_6$): δ 7.75 (d, *J* = 7.9 Hz, 8H), 7.19 (d, *J* = 7.9 Hz, 8H), 7.00 (s, 4H), 4.22-

4.14 (m, 8H), 3.89-3.85 (m, 8H) ppm; ^{13}C NMR: (100 MHz, DMSO-d_6) δ 167.67, 147.93, 145.76, 131.89, 130.52, 129.60, 129.23, 114.43, 69.13, 68.09 ppm; ESI-MS *m/z* calc. for $[M+Na]^+$ $C_{48}H_{40}O_{14}$: 840.22; found: 840.24.

Section 3. Crystallography

Table S1. Crystallographic parameters of **1CT-18C6** and **2CT-18C6.**

	1CT-18C6-I	**2CT-18C6-I**	**2CT-18C6-II**	**2CT-18C6-III**
Empirical formula	$C_{30}H_{36}O_{13}$	$C_{58.5}H_{64.5}N_{3.5}Na\ O_{17.5}$	$C_{57}H_{60}N_3NaO_{17}$	$C_{48}H_{42}O_{17}$
Guest species	H_2O	Na^+, DMF	Na^+, DMF	H_2O
Formula weight	604.59	1119.62	1082.07	890.81
Temperature/K	223	293	293	298
Crystal system	Monoclinic	triclinic	triclinic	orthorhombic
Space group	$P2_1/n$	P-1	P-1	$Cmc2_1$
a / Å	13.6633(2)	11.3113(2)	13.1094 (8)	27.4687(10)
b / Å	8.2601(1)	13.4267(2)	25.3405(16)	20.3236(8)
c / Å	26.8789(6)	21.7047(4)	26.7457(16)	8.0251(6)
α / °	90	104.103(2)	105.281(5)	90
β / °	90.208(2)	95.2670(10)	90.128(5)	90
γ / °	90	111.048(2)	91.834(5)	90
V / Å^3	3033.54(9)	2924.57(10)	8565.8(9)	4480.1(4)
Z	4	2	6	4
F (000)	1280	1138	3408	1864
F^2	1.029	1.059	0.901	1.034
R_1 [a], wR_2 [b][I > 2σ(I)]	0.059, 0.184	0.061,0.209	0.081, 0.352	0.094, 0.288
CCDC *No*.	2057700	2078832	2078834	2078835

* [a] $R_1 = \sum||F_o| - |F_c|/\sum|Fo|$. [b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

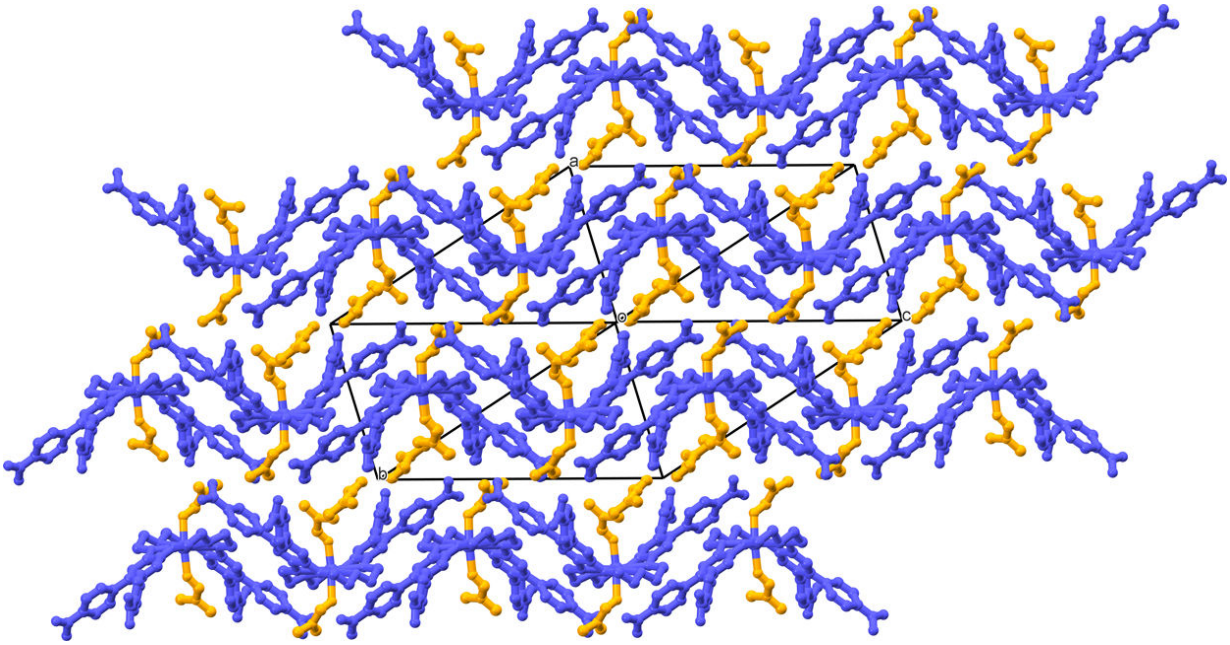


Fig. S1 Crystal structure of **2CT-18C6-II**.

Section 4. Impedance Spectroscopy

Nyquist plots[S2-S4]

1CT-18C6-I

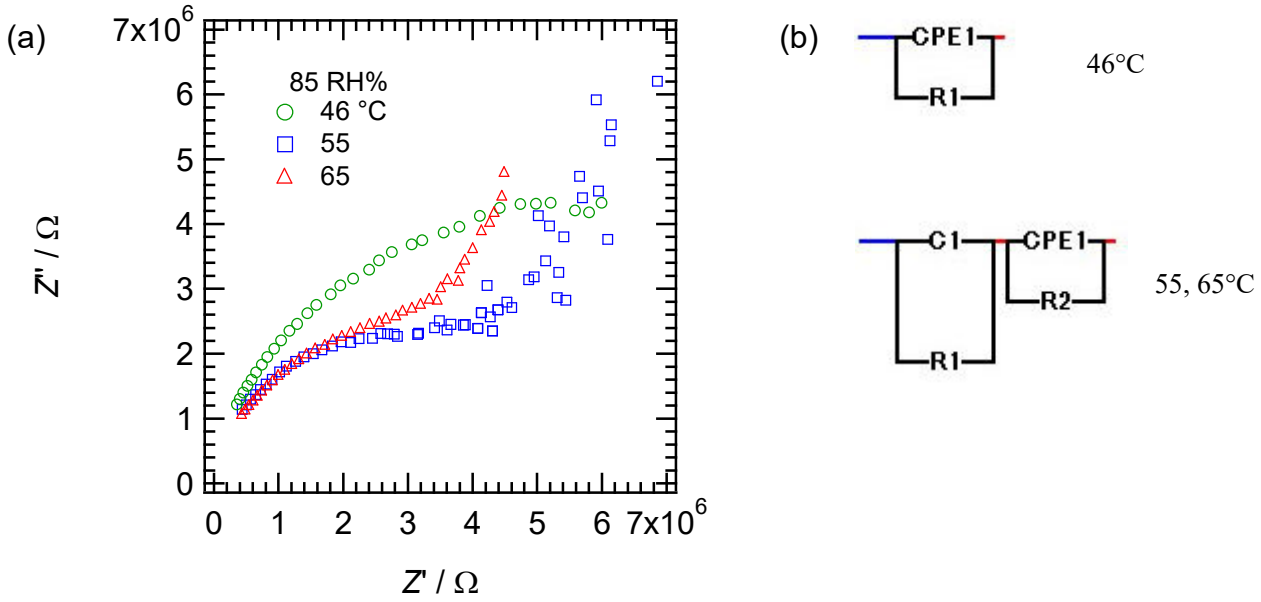


Fig. S2 (a) Nyquist plot for **1CT-18C6-I** at 46, 55, and 65 °C under 85 RH% humidity and (b) equivalent circuit models for the fitting to data of 46 °C (top) and 55 and 65 °C (bottom).

Table S2. Fitting parameters of equivalent circuit model at each temperature for **1CT-18C6-I.**

T / °C	R_1 / Ω	C_1 or CPE_1 / F ^{n1}	n_1	R_2 / Ω	C_2 / F
46	1.148×10^{7}	2.025×10^{-12}	0.822	---	---
55	5.4385×10^{6}	1.639×10^{-12}	0.839	3.297×10^{7}	3.538×10^{-12}
65	4.420×10^{6}	1.329×10^{-12}	0.852	3.718×10^{7}	1.329×10^{-12}

4,4'-Dicarboxy-o-tephenyl (CT)

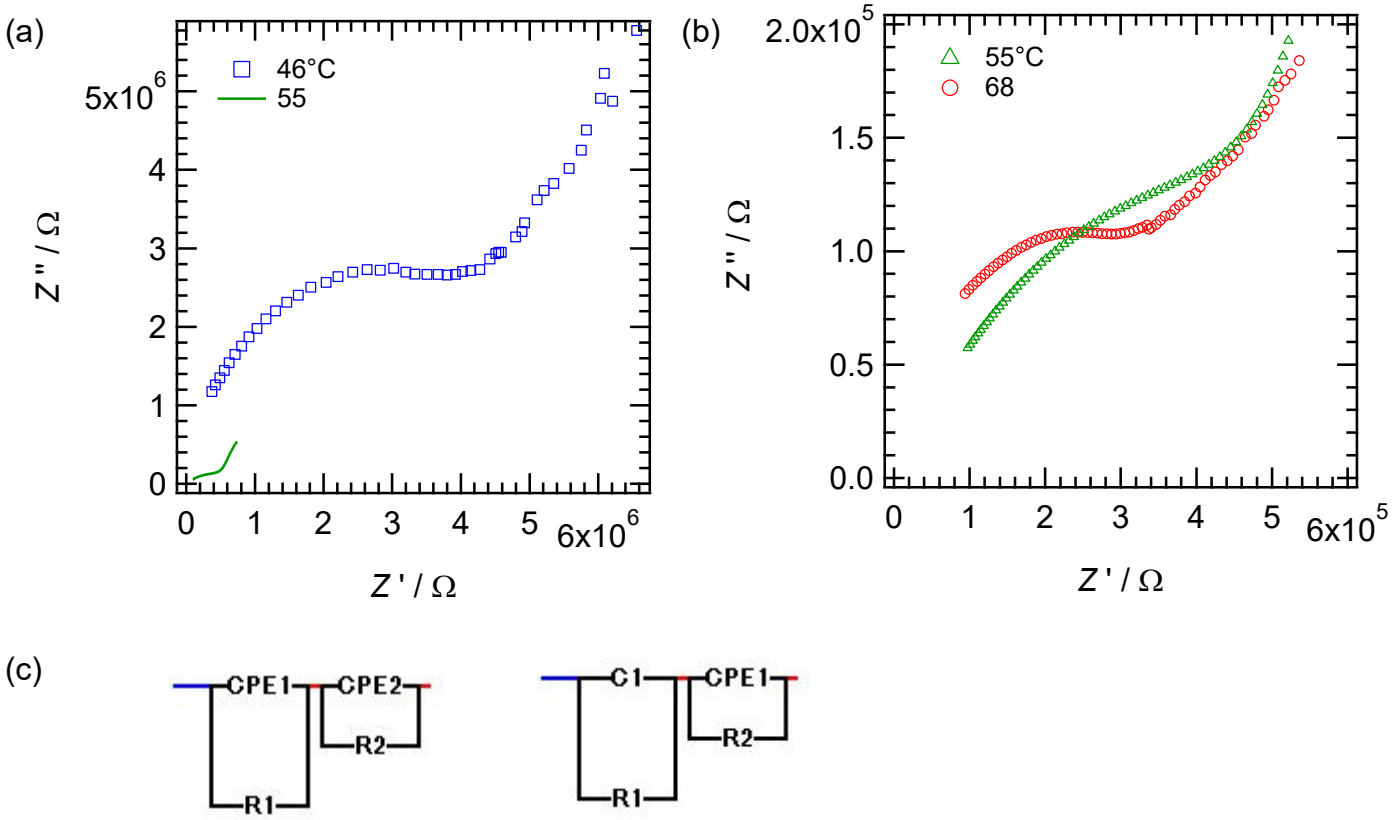


Fig. S3 (a) Nyquist plot for CT at 46, 55, and 68 °C under 85 RH% humidity and (b) equivalent circuit models for the fitting to data of 46 °C (top) and 55 and 68 °C (bottom).

Table S3. Fitting parameters of equivalent circuit model at each temperature for 4,4'-Dicarboxy-o-tephenyl (CT).

T / °C	R_1 / Ω	C_1 or CPE_1 / F ^{n1}	n_1	R_2 / Ω	C_2 or CPE_2 / F ^{n1}	n_2
46	4.594×10^{6}	1.472×10^{-13}	---	1.491×10^{7}	1.604×10^{-12}	---
55	6.584×10^{5}	8.921×10^{-9}	0.433	1.776×10^{6}	9.584×10^{-10}	---
68	2.876×10^{5}	4.026×10^{-10}	0.631	1501×10^{6}	3.793×10^{-8}	0.451

Dibenzo[18]crown-6 (DB18C6)

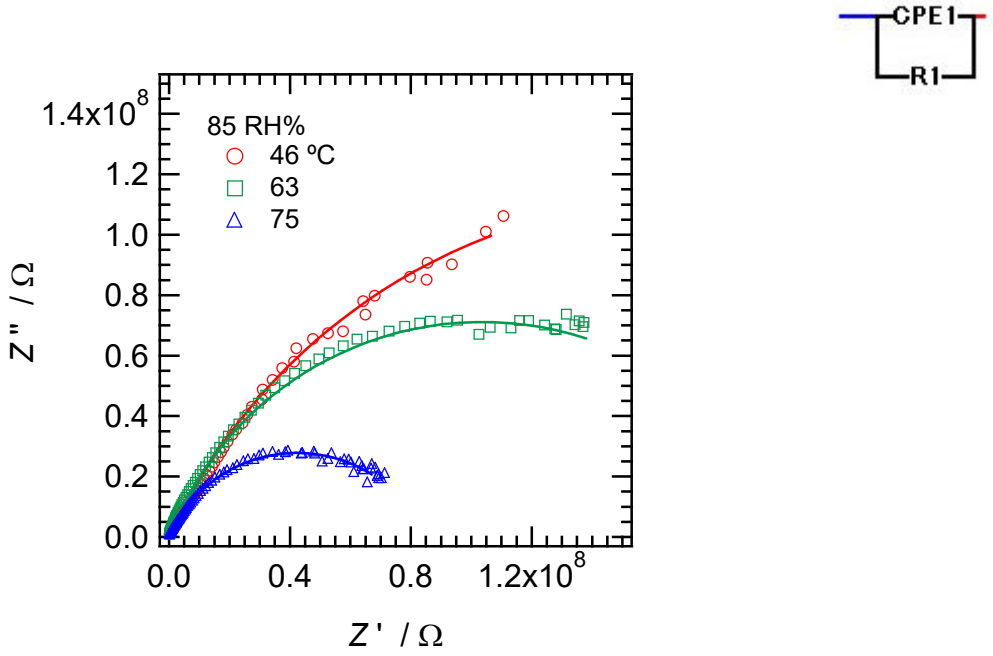


Fig. S4 (a) Nyquist plot for DB18C6 at 46, 63, and 75 °C under 85 RH% humidity and (b) equivalent circuit models for the fitting to data.

Table S4. Fitting parameters of equivalent circuit model at each temperature for DB18C6.

T / °C	R_1 / Ω	CPE_1 / F ^{n1}	n_1
46	3.492×10^{8}	1.231×10^{-11}	0.727
63	2.071×10^{8}	5.191×10^{-12}	0.766
75	8.473×10^{7}	1.124×10^{-11}	0.740

2CT-18C6-III

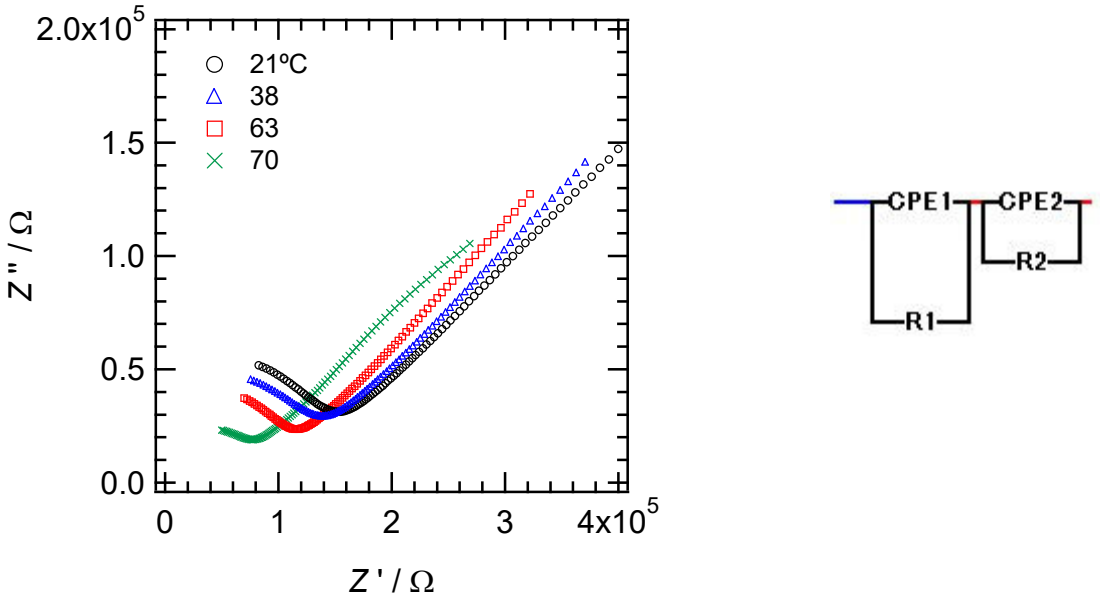


Fig. S5 (a) Nyquist plot for **2CT-18C6-III** at 25, 63, 66, and 75 °C under 85 RH% humidity and (b) equivalent circuit models for the fitting to data.

Table S5. Fitting parameters of equivalent circuit model at each temperature for **2CT-18C6-III**.

T / °C	R_1 / Ω	CPE_1 / F ^{n1}	n_1	R_2 / Ω	CPE_2 / F ^{n1}	n_2
21	1.138×10^{5}	2.591×10^{-11}	0.803	2.818×10^{6}	3.788×10^{-7}	0.312
38	1.040×10^{5}	5.245×10^{-11}	0.764	1.000×10^{10}	4.666×10^{-7}	0.304
66	6.712×10^{4}	3.903×10^{-10}	0.642	6.474×10^{5}	6.876×10^{-8}	0.456
70	6.432×10^{4}	3.940×10^{-10}	0.651	1.895×10^{6}	4.170×10^{-10}	0.346

Activation Energy calculation based on Arrhenius law.

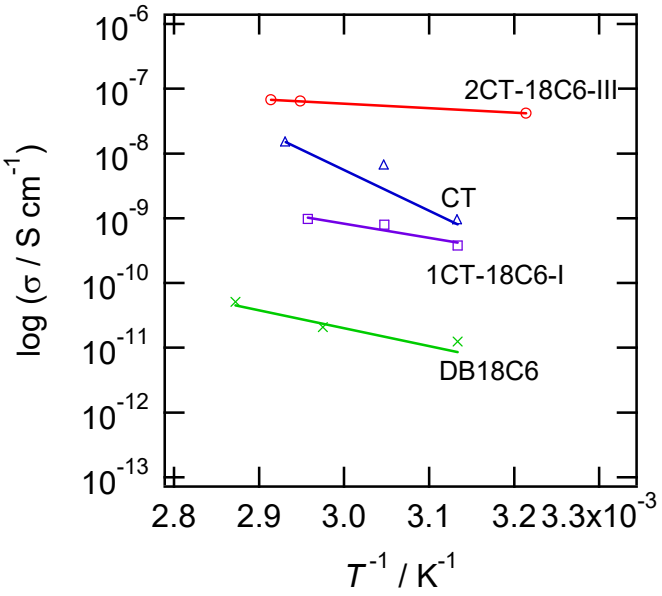


Fig. S6 Arrhenius plot of proton conductivity under 85 RH%.

Table S6. Pre-exponential Factor (σ_0) and activation energies (E_a) of proton conductivity for **1CT-18C6-I**, **2CT-18C6-III**, CT, and DB18C6 under 85 RH%.

	σ_0	E_a / kJ mol^{-1}	E_a / eV
1CT-18C6-I	2.02×10^{-5}	44.8	0.354
2CT-18C6-III	1.66×10^{-2}	13.4	0.140
CT	2.04×10^{-21}	110.9	1.150
DB18C6	1.70×10^{-9}	43.6	0.452

Section 5. ^{1}H and ^{13}C NMR Spectra

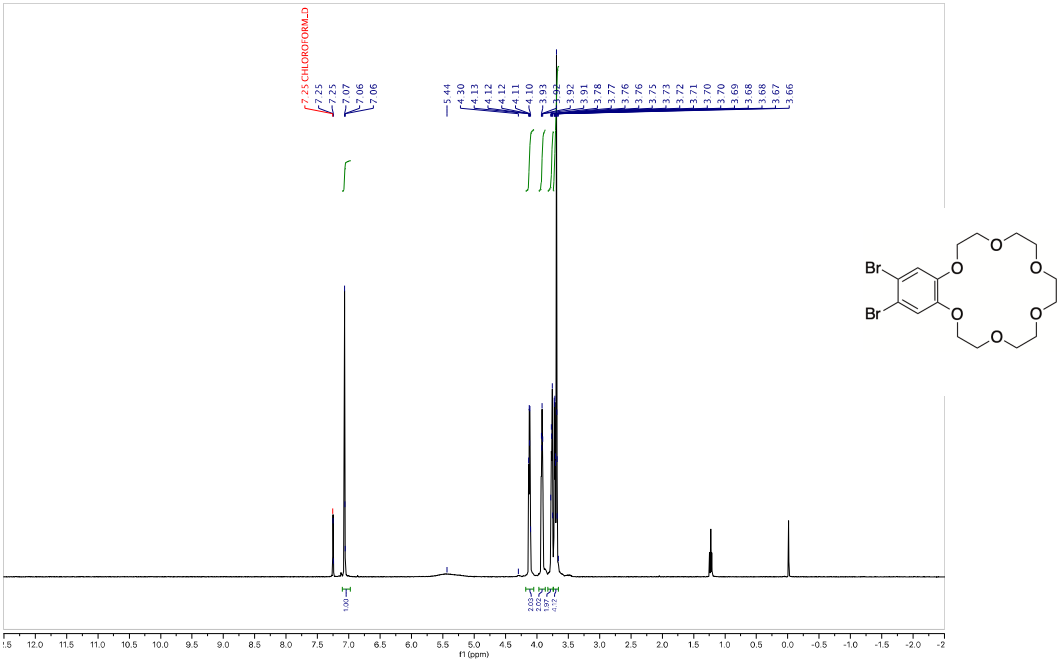


Fig. S7 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4,5-Dibromodibenzo-18-crown-6.

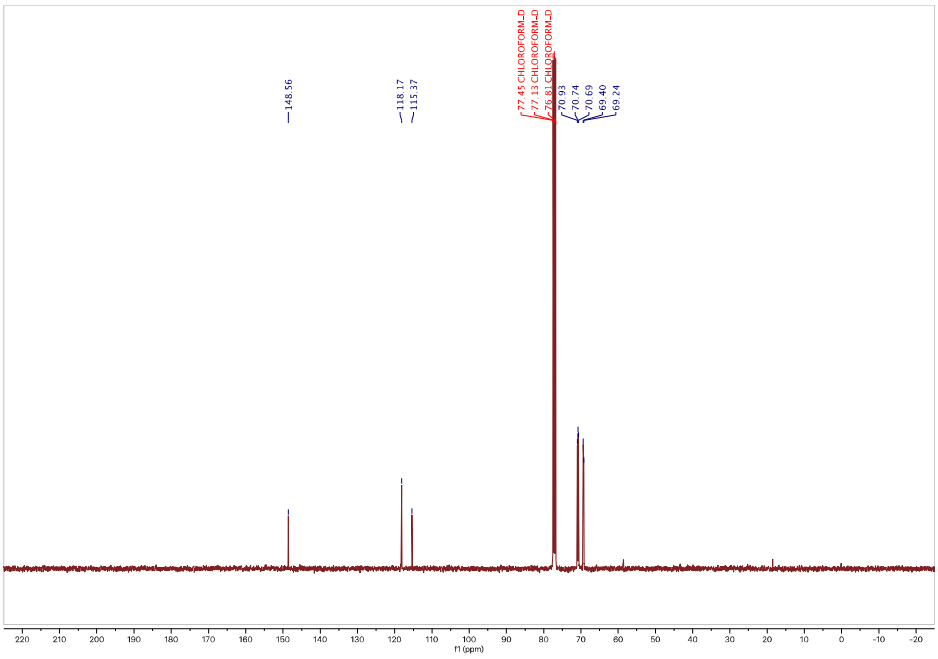


Fig. S8 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4,5-Dibromodibenzo-18-crown-6.

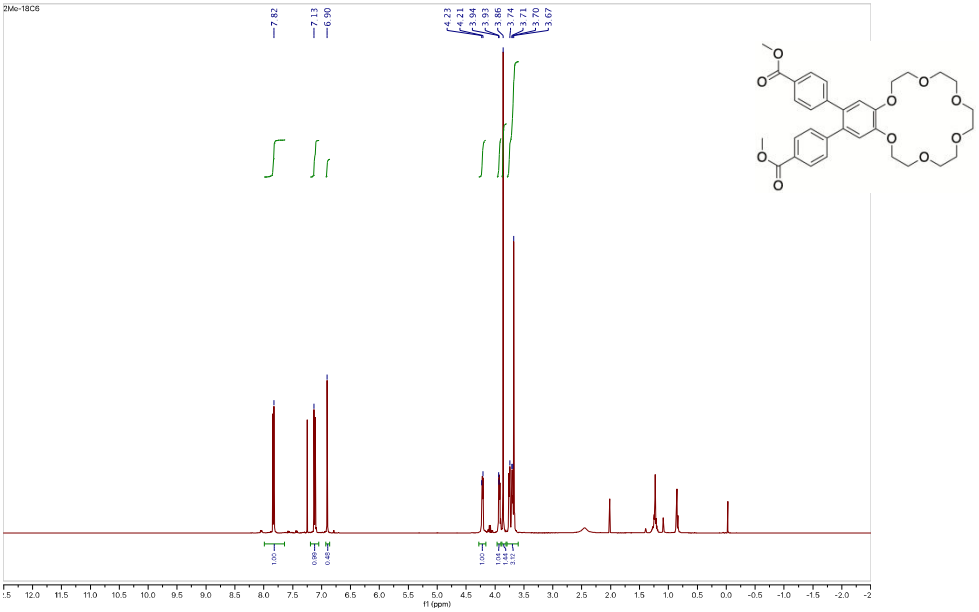


Fig. S9 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1**.

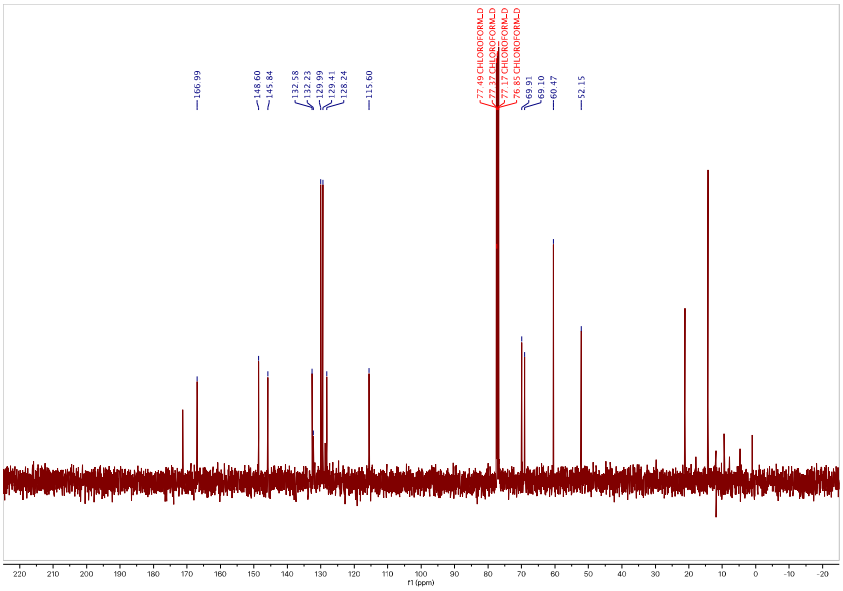


Fig. S10 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **1**.

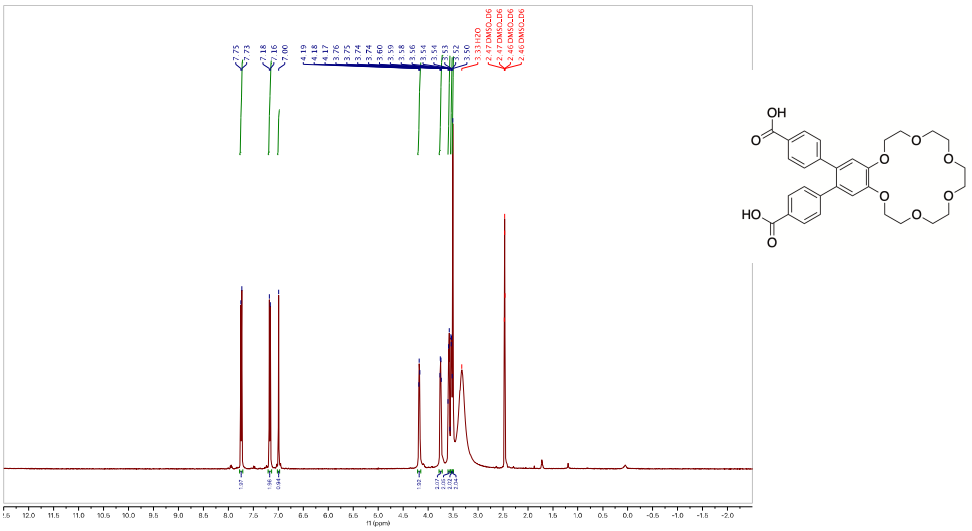


Fig. S11 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **1CT-18C6**.

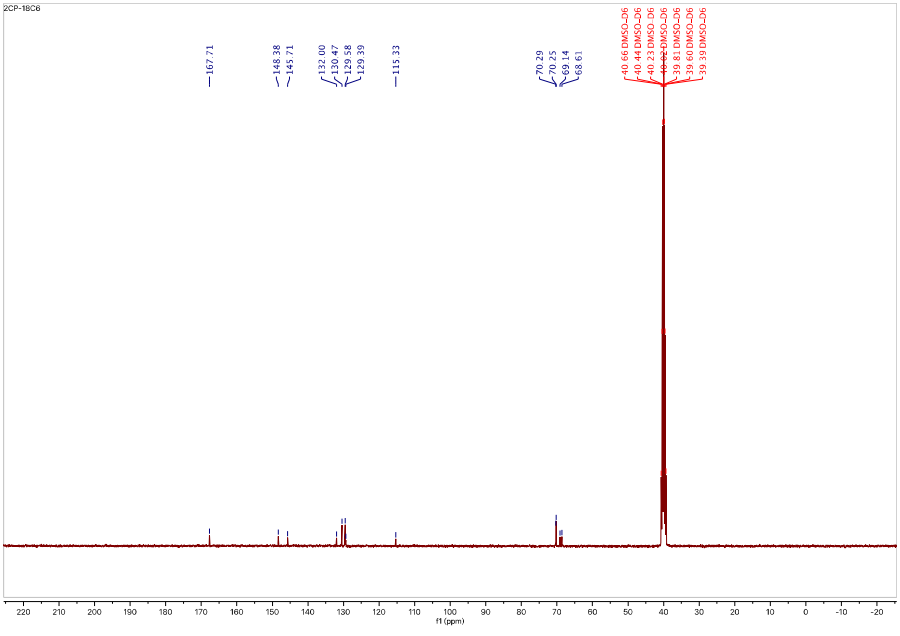


Fig. S12 ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **1CT-18C6**.

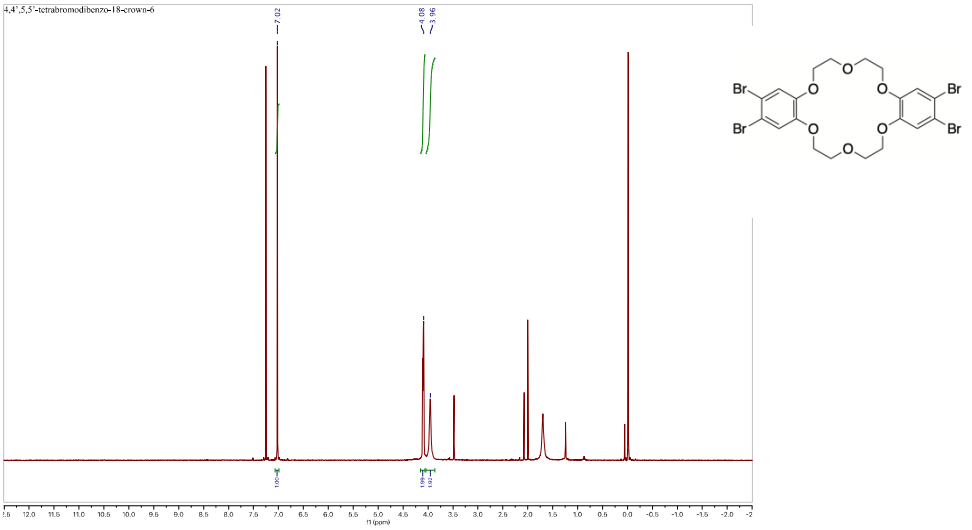


Fig. S13 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 4,4',5,5'-Tetrabromodibenzo-18-crown-6.

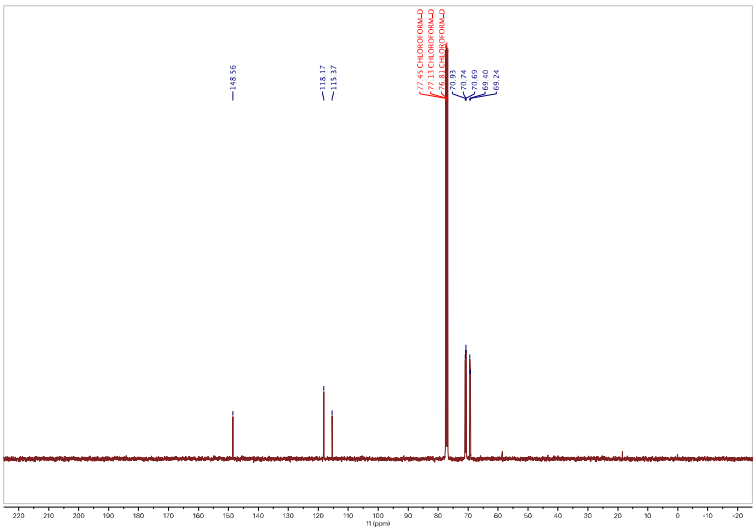


Fig. S14 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of 4,4',5,5'-Tetrabromodibenzo-18-crown-6.

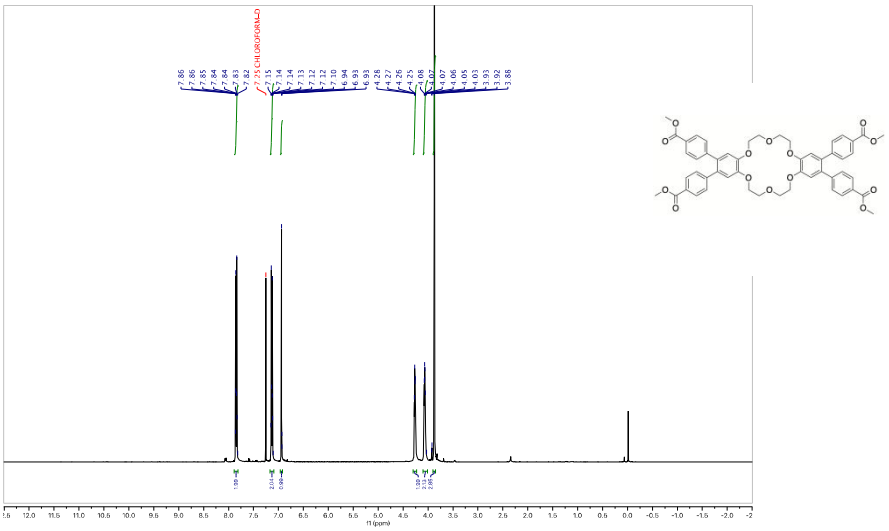


Fig. S15 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2**.

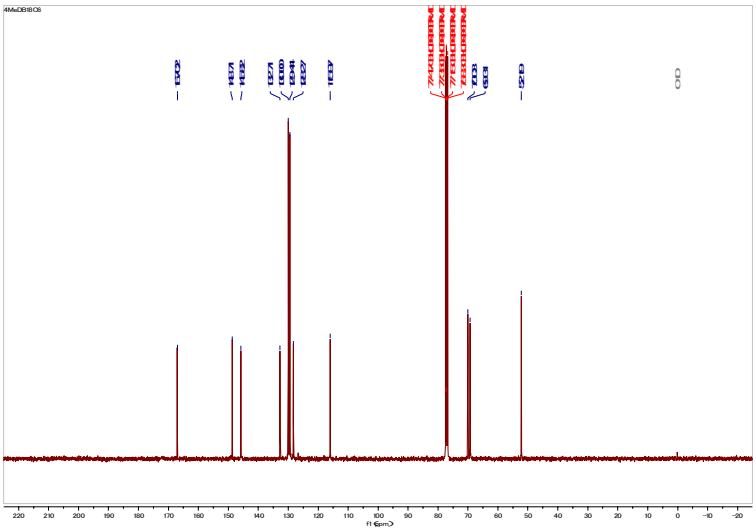


Fig. S16 ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **2**.

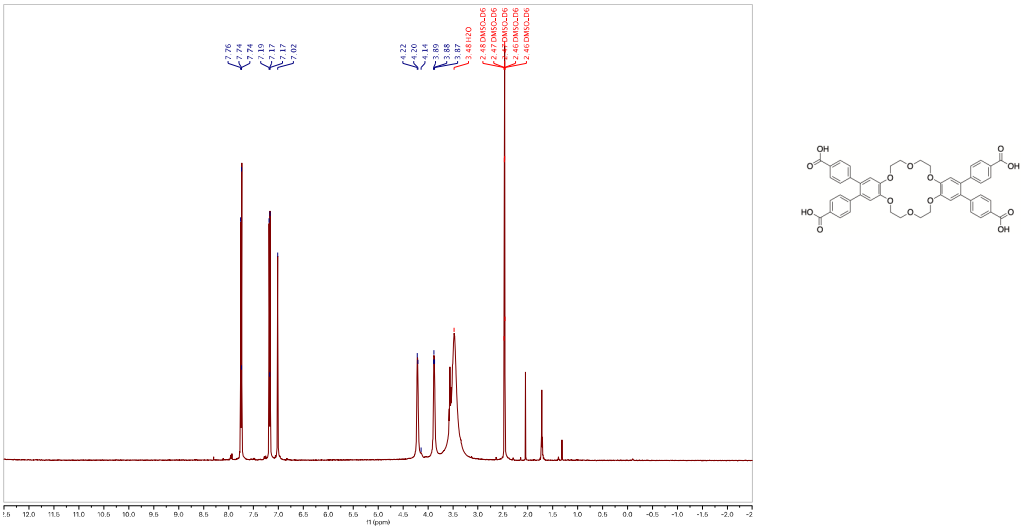


Fig. S17 ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of **2CT-18C6**.

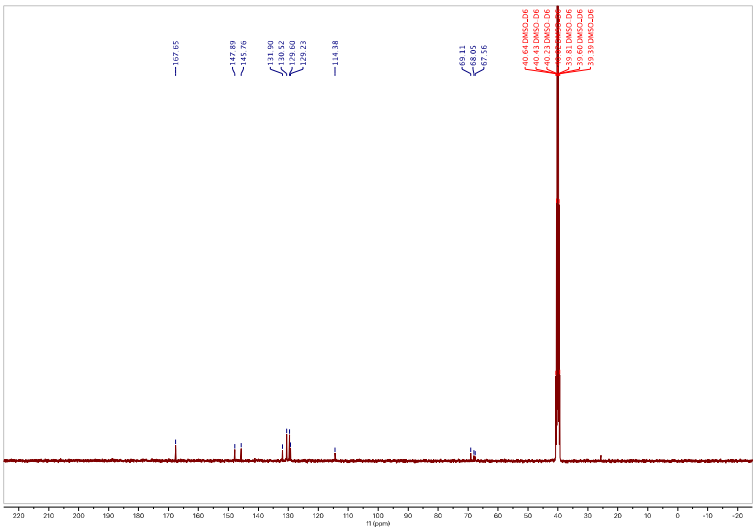


Fig. S18 ^{13}C NMR (100 MHz, DMSO-d_6) spectrum of **2CT-18C6**.

Section 6. References

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