

Supplementary Information

Superionic Conduction in a Mg²⁺-Containing Covalent Organic Framework at Intermediate Temperature

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Synthesis of 28-Bromo-2,5,8,11,14,17,20,23,26-nonaoxaocacosane (mPEG9-Br)

mPEG9-Br was synthesized according to a previous report.¹ 2,5,8,11,14,17,20,23,26-nonaoxaocacosan-28-ol (15.8 g, 37.0 mmol) was dissolved in dehydrated dichloromethane (185 mL) in a two-necked flask under N₂. After it was cooled to 0 °C, triphenylphosphine (14.5 g, 44.4 mmol) was added and the solution was stirred for 30 minutes at 0 °C. After that, carbon tetrabromide (18.3 g, 55.5 mmol) was added and it was stirred for 30 minutes at 0 °C. The temperature was then raised to room temperature (RT) with continuous stirring and kept it overnight. After evaporation, diethyl ether (90 mL) was added and it was then kept in refrigerator for 15 minutes. The mixture was filtered and the filtrate was evaporated again. This process was repeated 3 times. After that, the target compound was obtained by column chromatography (dichloromethane : methanol = 50 : 1) (yellow oil, 9.19 g (18.7 mmol), yield: 51%). ¹H NMR (500 MHz, CDCl₃) δ 3.81 (t, 2H), 3.66 (m, 30H), 3.55 (m, 2H), 3.47 (t, 2H), 3.38 (s, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 71.9, 71.2, 70.6, 70.5, 70.5, 70.4, 59.0, 30.3.

(Ref. 1) G. Zhang, Y.-I. Hong, U. Nishiyama, S. Bai, S. Kitagawa, S. Horike, *J. Am. Chem. Soc.*, 2019, **141**, 1227–1234.

Synthesis of 2,5-bis(nonaethylene glycol)oxy-1,4-dibenzaldehyde (PEO-9)

PEO-9 was synthesized according to a previous report.² 2,5-dihydroxyterephthalaldehyde (0.83 g, 5.00 mmol) and mPEG9-Br (7.38 g, 15.00 mmol) was dissolved in dehydrated DMF (30 mL) in a two-necked flask under N₂. Potassium carbonate (4.15 g, 30 mmol) was added and the mixture was stirred at 80 °C overnight. The mixture was diluted with water (250 mL) and extracted with hot ethyl acetate. The organic

layer was dried by adding Na_2SO_4 and filtered. The filtrate was then evaporated. After that, the target compound was obtained by column chromatography (ethyl acetate : methanol = 40:1) (yellow oil, 2.00 g (2.02 mmol), yield: 40%). ^1H NMR (500 MHz, CDCl_3) δ 10.52 (s, 2H), 7.46 (s, 2H), 4.27 (t, 4H), 3.90 (t, 4H), 3.72–3.63 (m, 60H), 3.55 (m, 4H), 3.38 (s, 6H); ^{13}C NMR (500 MHz, CDCl_3) δ 189.2, 155.2, 129.5, 112.2, 71.9, 70.9, 70.6, 70.5, 70.5, 70.2, 69.4, 68.9, 59.0.

(Ref. 2) Y. Okada, M. Sugai, K. Chiba, *J. Org. Chem.*, 2016, **81**, 10922–10929.

Synthesis of TPB-PEO-9-COF

TPB-PEO-9-COF was synthesized according to a previous report.¹ 1,3,5-tri(4-aminophenyl)benzene (35 mg, 0.1 mmol) and PEO-9 (148 mg, 0.15 mmol) were put in a Pyrex tube. A mixed solvent of 1,4-dioxane (1.0 mL) and mesitylene (3.0 mL) was added to the Pyrex tube and it was sonicated for 5 minutes. After that, 6 M aqueous solution of acetic acid (0.4 mL) was added and it was sonicated for 5 minutes. The Pyrex tube was sealed after freeze-degassing of the mixture. The sealed glass tube was heated at 120 °C for 3 days. The precipitate was collected by centrifugation. It was immersed in THF for washing. The yellow powder was collected by centrifugation and dried under vacuum. (1.04 g (for ten times synthesis), yield: 58%). Elemental analysis. calcd (for $\{\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{N})_3\}_2\{\text{C}_6\text{H}_2(\text{C}_{38}\text{H}_{78}\text{O}_{20})(\text{CH})_2\}_3(\text{H}_2\text{O})_{3.6}$): C 61.70%, H 7.88%, N 2.32%; found: C 61.41%, H 7.68%, N 2.50%.

Synthesis of TPB-PEO-9-COF-Mg ($\{\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{N})_3\}_2\{\text{C}_6\text{H}_2(\text{C}_{38}\text{H}_{78}\text{O}_{20})(\text{CH})_2\}_3\{\text{Mg}(\text{TFSI})_2\}_{2.1}$)

TPB-PEO-9-COF (200 mg) was immersed in 1 M THF solution of magnesium bistrifluoromethanesulfonylimide ($\text{Mg}(\text{TFSI})_2 \cdot 8\text{H}_2\text{O}$) at RT for 12 hours. After filtration, the precipitate was washed with THF during suction filtration and it was dried under vacuum.

Preparation of TPB-PEO-9-COF-recovered

TPB-PEO-9-COF-Mg (30 mg) was immersed in 0.5 M THF solution (30 mL) of 18-crown-6-ether at RT overnight. After filtration, the precipitate was corrected by filtration and washed with THF. It was then dried under vacuum.

Physical measurements

X-ray powder diffraction (XPRD) measurements were performed using MiniFlex600 ($\lambda = 1.54059 \text{ \AA}$; $\text{Cu-K}\alpha$) (Rigaku, Inc.) at RT. Fourier transformed Infrared (IR) spectroscopy was performed through a attenuated total reflection (ATR) method using FT/IR4600 (JASCO, Inc.) at RT. Adsorption isotherms were evaluated using TriStar II 3020 (Micromeritics, Inc.). Before the adsorption measurements, the samples were dried at 130 °C under vacuum overnight. Thermogravimetry (TG) curves were recorded

using Thermo Plus Evo2 TG-DTA8122 (Rigaku, Inc.) under N₂ flow (100 mL min⁻¹) with the heating rate of 5 °C min⁻¹. Differential scanning calorimetry (DSC) was performed using DSC-3500 (NETZSCH, Inc.) with the temperature range from -100 to 200 °C (heating or cooling rate is 10 °C min⁻¹). The samples were kept at 200 °C before the measurements. ¹H and ¹³C NMR spectra were recorded with a JNM-ECA500 II (JEOL, Inc.) spectrometer at RT. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed using SPS3520UV instrument (SII Nanotechnology, Inc.). Ionic conductivity was evaluated using Solartron 1260/1296A impedance analyzer under N₂ gas condition. Powder sample was pelletized and it was then sandwiched by porous Au electrodes in a home-made sealed cell connecting to a gas line (pure N₂). The measurement cell was put in an incubator (SU-222, Espec, Inc.) to control the temperature. Resistance of the samples was determined by a semicircle fitting of Nyquist plots or from the real part of the impedance on the intersection of Z'-axis with the electrode-sample resistance. Before the measurements, the sample was dried at 130 °C under N₂ flow overnight. Transport number of Mg²⁺ ($t_{\text{Mg}^{2+}}$) was estimated by dc polarization of the cell, Mg|TPB-PEO-9-COF-Mg|Mg, according to previous reports³. The sample was pelletized and it was sandwiched by magnesium foils under Ar in a glove bag (The sample was preliminarily dehydrated by under vacuum at 130 °C overnight.). The current at the applied voltage 0.3 V at 160 °C was recorded using a potentiostat-galvanostat (Vertex 10A, IVIUM Technologies, Inc.). The transport number was calculated by Bruce-Vincent method according to the results of impedance measurements of the cell⁴.

(Ref. 3) M. Saito, H. Ikuta, Y. Uchimoto, M. Wakihara, S. Yokoyama, T. Yabe, M. Yamamoto, *J. Electrochem. Soc.*, 2003, **150**, A477.

(Ref. 4) P. G. Bruce, C. A. Vincent, *J. Electroanal. Chem.*, 1987, **225**, 1–17.

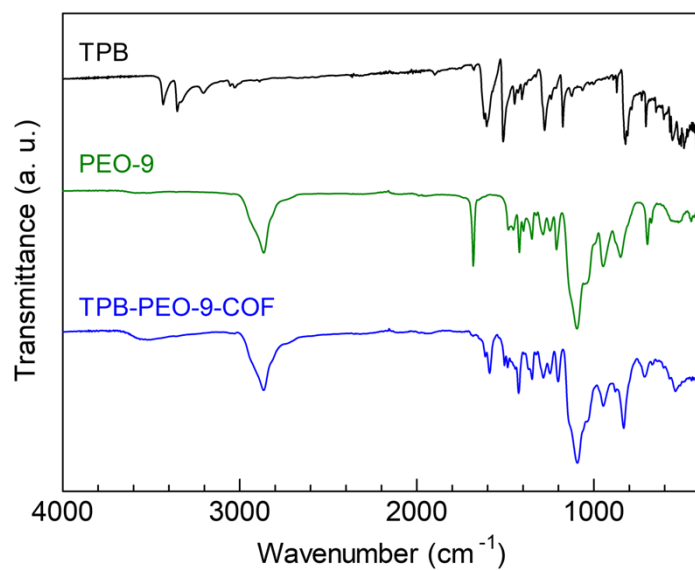


Figure S1. IR spectra of TPB, PEO-9 and TPB-PEO-9-COF.

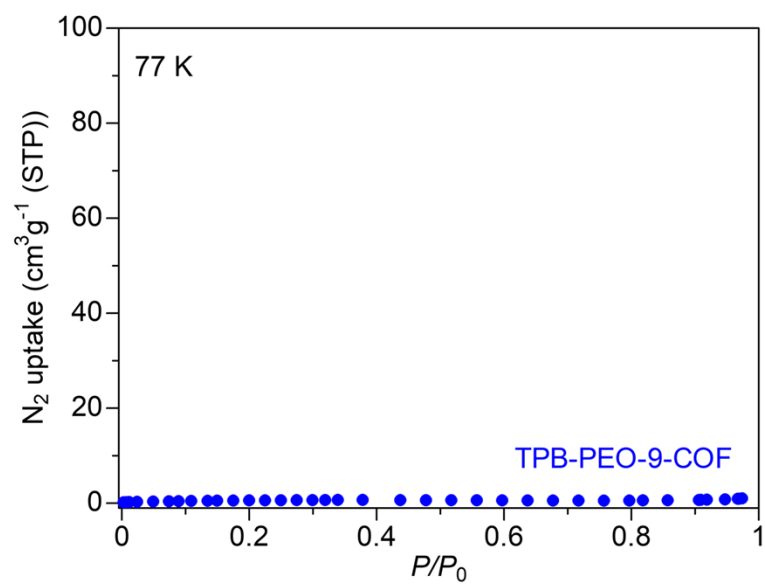


Figure S2. N₂ adsorption isotherms of TPB-PEO-9-COF at 77 K.

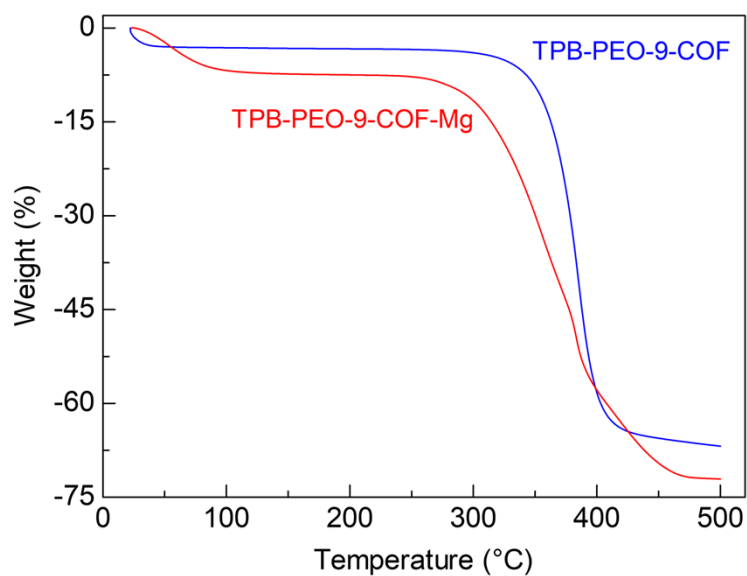


Figure S3. TG curves of TPB-PEO-9-COF and TPB-PEO-9-COF-Mg.

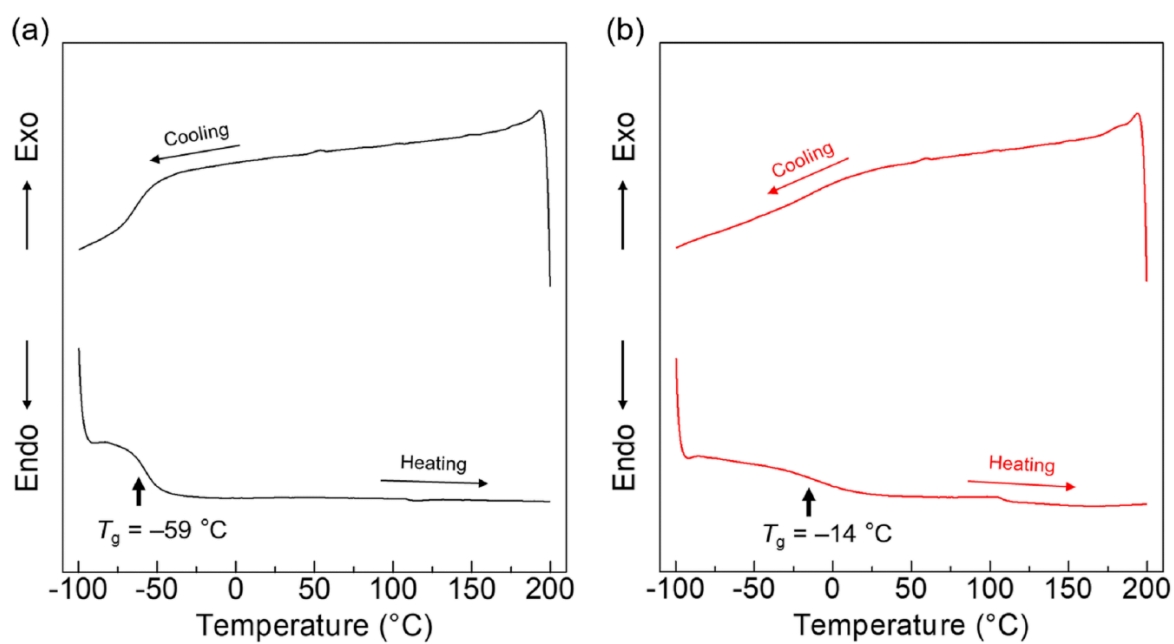


Figure S4. DSC profiles of (a) TPB-PEO-9-COF and (b) TPB-PEO-9-COF-Mg.

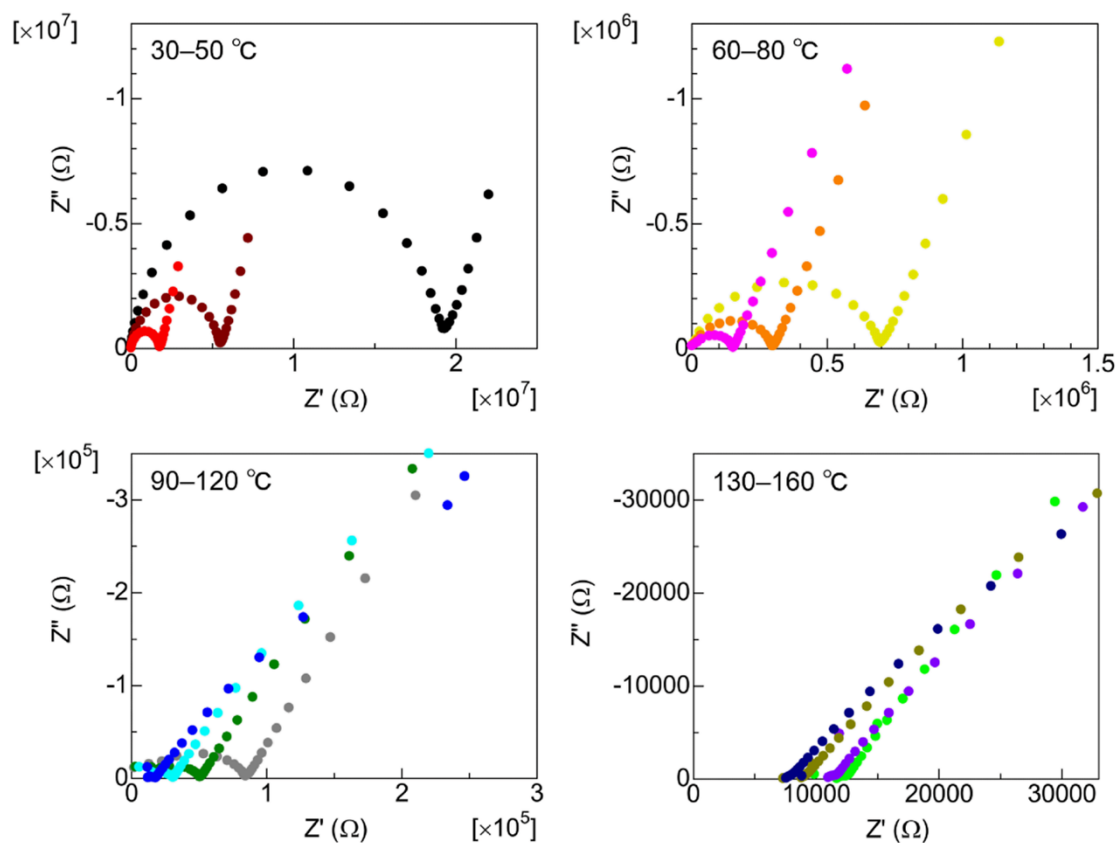


Figure S5. Nyquist plots of TPB-PEO-9-COF-Mg at 30 (black), 40 (brown), 50 (red), 60 (yellow), 70 (orange), 80 (pink), 90 (gray), 100 (green), 110 (light blue), 120 (blue), 130 (light green), 140 (purple), 150 (olive), and 160 °C (dark blue).

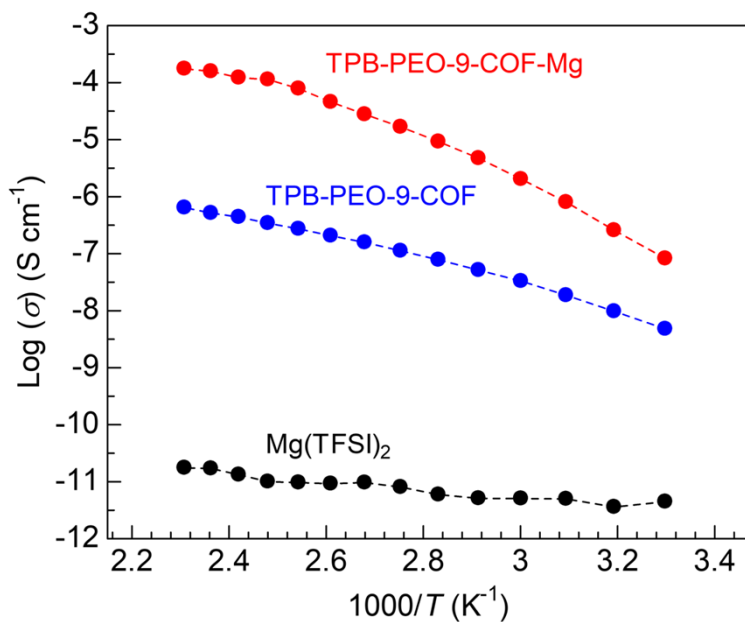


Figure S6. Comparison of ionic conductivity among TPB-PEO-9-COF-Mg, TPB-PEO-9-COF, and Mg(TFSI)₂.

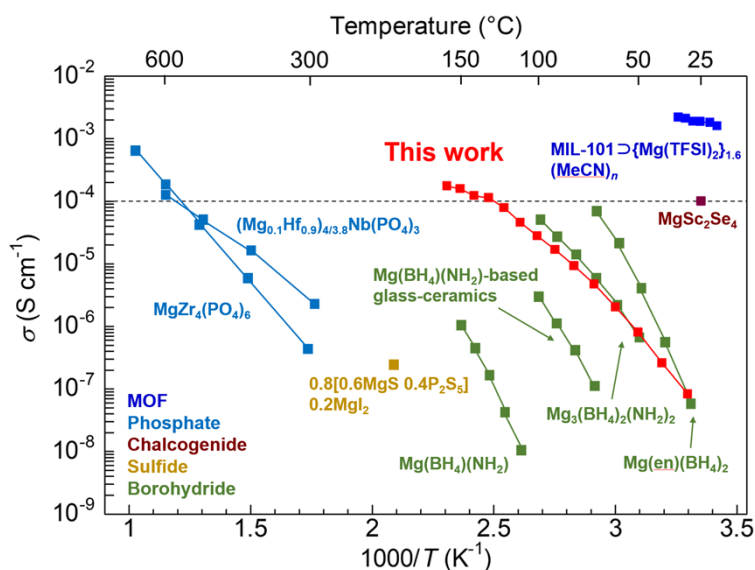


Figure S7. Comparison of ionic conductivity among Mg^{2+} -containing crystalline solids.^{5–13}

(Ref. 5) Y. Yoshida, T. Yamada, Y. Jing, T. Toyao, K. Shimizu and M. Sadakiyo, *J. Am. Chem. Soc.*, 2022, **144**, 8669–8675.

(Ref. 6) P. Canepa, S. Bo, G. S. Gautam, B. Key, W. D. Richards, T. Shi, Y. Wang, J. Li and G. Ceder, *Nature Commun.*, 2017, **8**, 1759.

(Ref. 7) S. Ikeda, M. Takahashi, J. Ishikawa, K. Ito, *Solid State Ionics*, 1987, **23**, 125–129.

(Ref. 8) S. Tamura, M. Yamane, Y. Hoshino, N. Imanaka, *J. Solid State Chem.*, 2016, **235**, 7–11.

(Ref. 9) T. Yamanaka, A. Hayashi, A. Yamauchi, M. Tatsumisago, *Solid State Ionics*, 2014, **262**, 601–603.

(Ref. 10) S. Higashi, K. Miwa, M. Aoki and K. Takechi, *Chem. Commun.*, 2014, **50**, 1320–1322.

(Ref. 11) R. L. Ruyet, R. Berthelot, E. Salager, P. Florian, B. Fleutot and R. Janot, *J. Phys. Chem. C*, 2019, **123**, 10756–10763.

(Ref. 12) R. L. Ruyet, B. Fleutot, R. Berthelot, Y. Benabed, G. Hautier, Y. Filinchuk and R. Janot, *ACS Appl. Energy Mater.*, 2020, **3**, 7, 6093–6097.

(Ref. 13) E. Roedern, R. Kuhnelt, A. Remhof and C. Battaglia, *Sci. Rep.*, 2017, **7**, 46189.

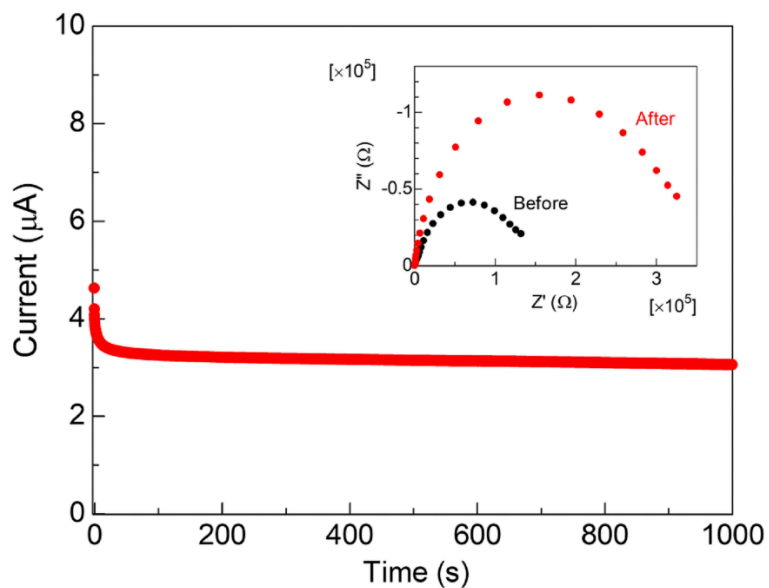


Figure S8. Dc polarization curve of Mg|TPB-PEO-9-COF-Mg|Mg (0.3 V, 160 °C). The inset shows the Nyquist plots of the cell before and after the polarization.