Article

Synthesis of Dicarboxylic Acids Comprising an Ether Linkage and Cyclic Skeleton and Its Further Application for High-Performance Aluminum Electrolyte Capacitors

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ABSTRACT: Aluminum electrolytic capacitors are essential components in all electronic devices, and it is known that their longevity depends on the performance of their electrolytes. We synthesized dicarboxylic acids having ether bonds showing the good solubility in ethylene glycol as a solvent and simultaneously developed a complete halogen removal method, which is strictly prohibited in capacitors. Moreover, the incorporation of bulky α-substituents and cyclic structures dramatically improved their heat resistance and can withstand high voltage, i.e., 764 V.
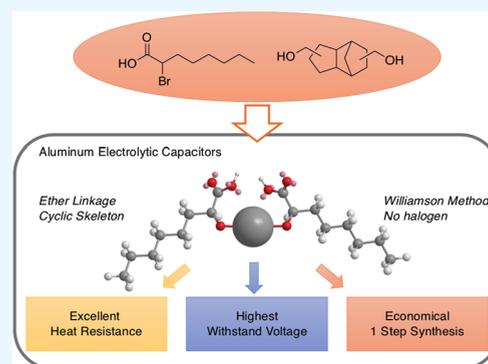
INTRODUCTION

Aluminum electrolytic capacitors (AECs) are essential and important components of all electronic equipment such as personal computers, televisions, automobiles, electric vehicles, and inverter equipment.[1] For example, in power conversion inverters for solar and wind power generation, AECs are connected between the rectifier and the inverter (smoothing circuit section) and are used to smooth out fluctuations in the direct current output from the rectifier.[2] In general, AECs consists of oxidized Al-electrode foil, electrolyte, and separator (Scheme 1a). Especially, an electrolyte is the most important component that controls the electrical performance in AECs.[3] The electrolyte is usually composed of (1) solvents such as ethylene glycol (EG) or γ-butyrolactone and water, (2) dicarboxylic acids, (3) bases for neutralization, and (4) additives. Among them, the dicarboxylic acids significantly change the characteristics of the capacitor such as heat resistance and withstand voltage, and optimization of their structure is important in achieving high performance. Moreover, the electrolyte should be nontoxic, free of halogens, and nonreactive with the electrode. Additionally, since the development of high-performance AECs enables significant miniaturization and performance improvements in general industrial equipment, energy-saving equipment, power electronics equipment, and also contributes to strengthening international competitiveness, there is an ongoing effort to develop AECs with higher heat resistance and withstand voltage by electronic component manufacturers around the world. As a consequence, it is inevitable that innovative development will be needed to achieve high-performance AECs to satisfy recent eco-energy issues.

In conventional AECs, sebacic acids and decane-1,6-dicarboxylic acids (1,6-DDA) are mainly used as dicarboxylic acids (Scheme 1b). However, these diacids are generally known to be degraded by esterification with EG or amidation with ammonia causing undesired side reactions, resulting in an increase in resistivity variation and a decrease in withstand voltage. Their performance is limited to "550 V, 3000 h at 105 °C" for withstand voltage and lifetime. Therefore, in order to achieve higher power efficiency for next-generation industrial equipment, it is necessary to realize the AECs performance with a durability of "700 V, 5000 h at 105 °C", surpassing conventional capacitors. For this purpose, the structural design of AECs, enabling high heat resistance with high voltage is strongly required.

On the other hand, we have started to collaborate with NICHICON Corporation to explore new chemical structure of dicarboxylic acids for the development of next-generation AECs. We reported in 2016 that dicarboxylic acids derived

Scheme 1. Background of AEC

(a) Aluminum Electrolytic Capacitor

①: Al-electrode foil, ②: Electrolyte, ③: Separator
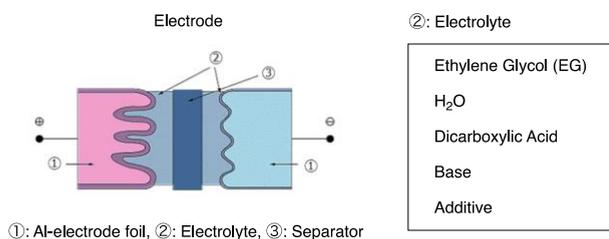
(b) Conventional Dicarboxylic Acids

Sebacic Acid   1,6-DDA

550V, 3000 h at 105 °C

(c) Previous Work (2016)

Methyl Ricinolate   Dicarboxylic Acid

✔ Heat Resistance   ✘ Low Solubility
✔ 510-710 V Withstand Voltage   ✘ 3 to 8 Steps Synthesis

(d) This Work

Williamson Synthesis

✔ Excellent Heat Resistance! ✔ 764V Withstand Voltage! ✔ 1 step Synthesis!
✔ Complete Halogen Removal! ✔ Good Solubility
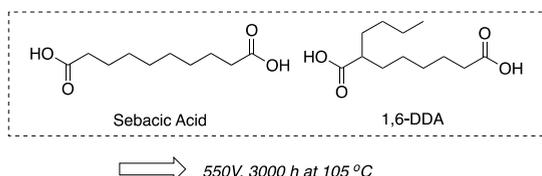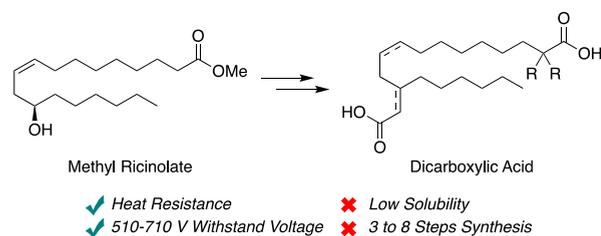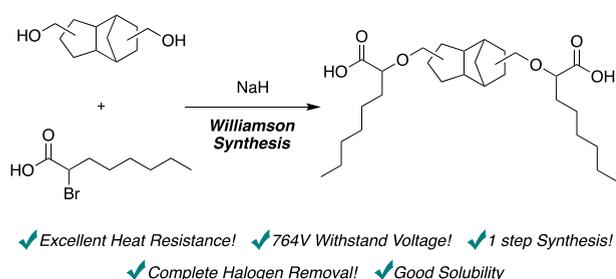
from ricinoleic acid showed good heat resistance and withstand higher voltage compared with sebacic acid and 1,6-DDA for AEC (Scheme 1c).[4] The solubility of these compounds in EG is, however, still a problem. Additionally, synthesis process, which requires a total of three to eight steps, is also a problematic issue in terms of cost.

Williamson ether synthesis is the classic reaction for the synthesis of ethers from alcohols and alkyl halides.[5] In this reaction, the alcohol is treated with a base such as a sodium hydride, and the resulting alkoxide reacts with the alkyl halide in the S_N2 reaction to afford the ether. Therefore, primary halides react easily, and stereochemical inversion of products occurs.

Herein, we found new types of dicarboxylic acids incorporating ether moieties could overcome this problem. Furthermore, we developed a complete halogen removal procedure using sodium methyl mercaptan (MeSNa) aqueous solution in which halogen atoms are strictly forbidden in capacitors because they cause corrosion of aluminum and lead to increased leakage current and malfunction of pressure valves. Also, excellent heat resistance and high withstand

voltage (i.e., 764 V) were achieved by using dicarboxylic acids with bulky substituents and cyclic structures that could be synthesized using only one step (Scheme 1d).

■ RESULTS AND DISCUSSION

To solve the problem of electrolyte solubility in EG, we initially designed a new class of dicarboxylic acids with ether moieties. We devised a simple synthetic procedure from commercially available compounds, namely the Williamson synthesis using inexpensive materials. The reaction was carried out using ethyl lactate 1a and bistosylate 2, which were prepared from diols and TsCl,[6] in the presence of sodium hydride (NaH) and 18-crown-6, and results are shown in Table 1. When a tosylate 2a derived from 1,4-butanediol was

Table 1. Syntheses of Dicarboxylic Acids 4
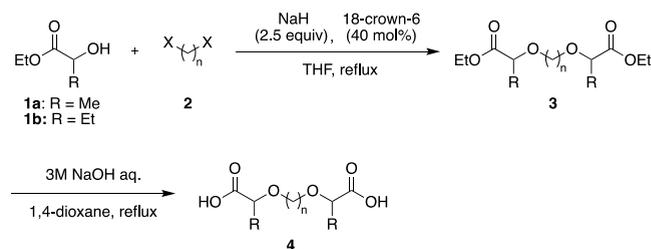
entry	1	X	n	2	3	yield (%)	4	yield (%)
1	1a	TsO	4	2a	3a	36	4a	94
2	1a	TsO	6	2b	3b	42	4b	95
3	1a	TsO	10	2c	3c	30	4c	98
4	1a	TsO	12	2d	3d	19	4d	84
5	1a	TsO	14	2e	3e	39	4e	71
6	1a	TsO	16	2f	3f	40	4f	93
7	1b	TsO	10	2c	3g	50	4g	94
8	1a	MsO	10	2c′	3c	34		
9	1a	MsO	12	2d′	3d	25		

used, the reaction proceeded to give the desired diester 3a in 36% yield, followed by hydrolysis under basic conditions to yield the desired dicarboxylic acid 4a in 94% yield (entry 1).[7] Gratifyingly, all other reactions using various types of tosylate 2 afforded the corresponding dicarboxylic acids 4b−f in moderate-to-good yields (entries 2−6). In addition, substrate 1b having the bulkier ethyl group also provided the diacid 4g in good yield (entry 7).

However, during the syntheses of these compounds, we had a problematic issue. These carboxylic acids 4 included a large amount of halogen contamination derived from TsCl in the first step. For an AEC product, halogen contamination is strictly forbidden due to its corrosion and harmful effect on its performance. We next investigated by decreasing the amount of halogen. In order to achieve less halogen content, recrystallization was performed on the crude product. We examined using crude product 4c including 58.0 ppm of halogen content, and the results are summarized in Table 2. The halogen content was analyzed by TOX-100 and TOX-2100H. Recrystallization from EtOH, toluene, AcOEt, and H₂O could not remove the halogen (entries 2−5), while reprecipitation and purification with hexane and AcOEt reduced the halogen content to 27.6 ppm (entry 6). Finally, when dehalogenation was performed with a 15% NaSMe aqueous solution, the halogen content was completely removed to 0 ppm (entry 7). In cases of halogen-free 4c and

Table 2. Examination of Halogen Removal for Compounds 4

entry	compound	conditions	halogen (ppm)
1	4c-0		58.0
2	**4c-A**	EtOH	50.6
3	**4c-B**	toluene	44.9
4	**4c-C**	AcOEt	61.5
5	**4c-D**	H$_2$O	58.1
6	**4c-E**	hexane	27.6
7	**4c-F**	15% MeSNa aq	0.0
8	**4c**	halogen free	10.3
9	**4d**	halogen free	1.3

4d, which were prepared from bismesylates **2c′** and **2d′** using Ms$_2$O (Table 1, entries 8 and 9), they showed low halogen content (10.3 and 1.3 ppm) (Table 2, entries 8 and 9).

The mechanism of halogen removal by sodium methyl mercaptan is proposed in Scheme 2. The substitution of

Scheme 2. Plausible Mechanism of Halogen Removal
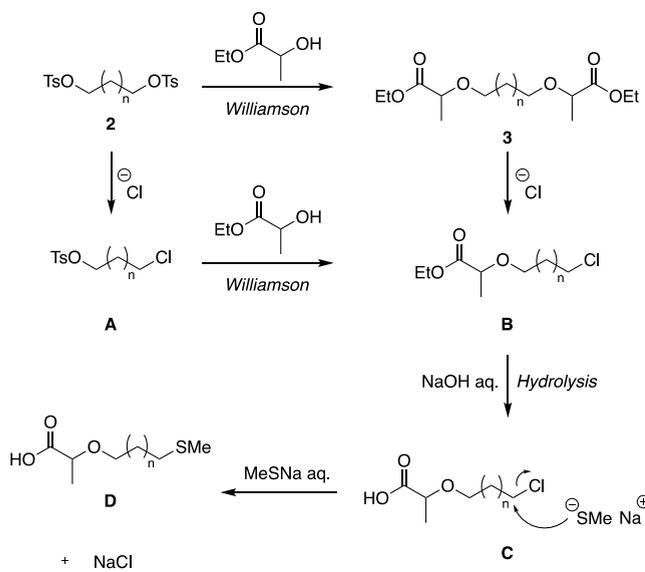
chloride to tosylate **2** or diester **3** leads to the corresponding chloride **A** or **B**. After transformation to carboxylic acid **C**, then sodium methyl mercaptan reacted to afford the compound **D** with the precipitation of sodium chloride.

Having developed for complete halogen removal, the initial electrical characteristics of these compounds for solubility and resistivity in AEC were investigated (Table 3). Electrolytes were used as diammonium salt with 28% aqueous ammonia solution, and each solution was prepared as 0.134 mol/kg EG solution including 2 wt % H$_2$O (See Supporting Information in detail). The conventional electrolytes such as sebacic acid and 1,6-DDA were also prepared as benchmark for the comparison (entries 8 and 9). Regarding the solubility in EG, substrates **4a−d** were satisfactory, while in the case of the longer alkyl chains such as **4e−g**, the solubility gradually deteriorated (entries 1−7). These results indicated that the ether moiety led improvement effectively for the solubility in EG; however, the balance between the number of ethers and the length of the alkyl chain was likely to be important. The heat resistance of electrolytes was next examined. The evaluation was performed on the electrolyte solution at 105 °C in an ampule tube for 250

Table 3. Electrical Characteristics and Heat Resistance Evaluation for Compound 4[a]

			resistivity/Ωcm[c]	
entry	substrate	solubility[b]	0 h	250 h
1	**4a**	○	873	1104 (+26%)
2	**4b**	○	861	1045 (+21%)
3	**4c**	○	883	1141 (+29%)
4	**4d**	○		
5	**4e**	△		
6	**4f**	×		
7	**4g**	△	817	1006 (+23%)
8	sebacic acid	○	680	1324 (+95%)
9	1,6-DDA	○	772	1047 (+36%)

[a]Electrolytes were used as diammonium salt with 28% aqueous ammonia solution, and each solution was prepared as 0.134 mol/kg EG solution including 2 wt % H$_2$O. [b]○: Excellent, △: Good, × : Poor. [c]Increased variation percentage was shown in the parentheses.

h, and the resistivity variation was measured comparing with that of 0 h. The variation rates of electrolytes **4a−g** after 250 h were minimized better than that of conventional sebacic acid and 1,6-DDA (21−29 vs 36−95%). These results suggest that all the electrolytes of compound **4** could inhibit side reactions such as an esterification with EG or an amidation with ammonia in the electrolyte solution due to the presence of their α-substituents derived from ethyl lactate.

The product breakdown characteristics were also investigated, and the results are shown in Figure 1. When
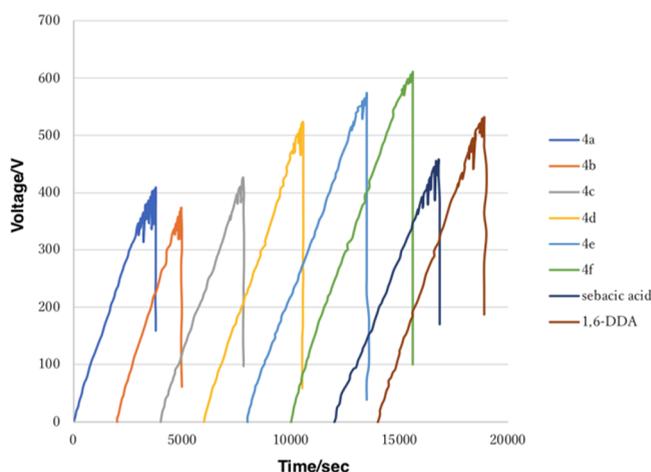
Figure 1. Evaluation of withstand voltage for **4**.

dicarboxylic acids derived from short carbon chains **4a−c** were used, low breakdown voltage (390−440 V) was shown compared with those of sebacic acid and 1,6-DDA (450 and 530 V). On the other hand, dicarboxylic acids derived from the longer alkyl chain **4d−4f** indicated good breakdown voltage (520−610 V). Although electrolyte **4f** showed a high voltage over 600 V, it was insoluble in EG. From these results, we consider that dicarboxylic acids with ether moieties have the potential for electrolytes.

In order to realize the further improvement of heat resistance, we next designed new dicarboxylic acids **7** and the only one-step synthesis using the Williamson method, which introduced bulky alkyl substituents at the α-position of the carboxyl group. After the optimization of reaction

conditions, we finally succeeded in the synthesis of compound **7a** in 33% yield; the reaction was carried out by the Williamson ether synthesis of 2-bromohexanoic acid **5a** with 1,4-butanediol in the presence of NaH for 48 h, followed by treatment with NaSMe solution for halogen removal (Scheme 3). Various dicarboxylic acids **7b−e** could be synthesized in

1,4-butanediol and 1,6-hexanediol showed extremely low heat resistance of 6 and 7% (entries 1 and 2). Furthermore, the electrolyte of compound **7f** showed the best heat resistance of 20% at 1000 h in electrolyte properties (entry 6). This is an extremely excellent result for an electrolyte for AEC.

Finally, the withstand voltage evaluation was performed, and the results are summarized in Figure 2. In comparison with

Scheme 3. Syntheses of Dicarboxylic Acids 7

[a]2.3 equivs of **5** was used.
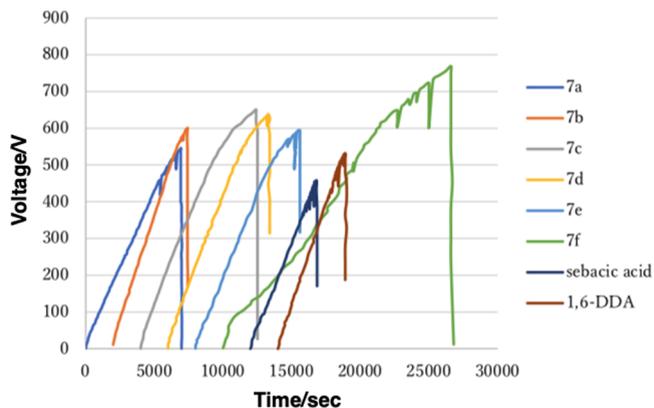
Figure 2. Evaluation of withstand voltage for **7**.

good-to-high yield, and the amount of halogen was also at an extremely low level that did not affect their characteristics. A dicarboxylic acid with bulkier α-substituents and rigid cyclic skeletons could also be synthesized with a similar approach. Tricyclodecanedimethanol reacted with 2-bromooctanoic acid **5b** to afford the desired product **7f** in 72% yield. A reaction mechanism is proposed such that the dialkoxide deprotonated by NaH attacks α-lactone derived from **5** to give the dicarboxylic acid product **7**.

For the evaluation of these compounds **7**, electrolytes were prepared and their initial property characteristics were evaluated, respectively, as shown in Table 4. Fortunately, most of electrolytes were found to be soluble in EG, and extending the side chain length did not affect their solubility (entries 1−5). In the case of **7f**, although solubility in EG was not excellent, it was sufficient for use as a product (entry 6).[8] Regarding heat resistance from their evaluation, sterically bulkier α-substituent increased the stability of molecules, and the variation rates after 250 h were suppressed considerably as we expected. In particular, compounds **7a** and **7b** derived from

sebacic acid and 1,6-DDA, all electrolytes displayed good-to-high voltage withstand capabilities. It should be noted that electrolyte **7f** showed the highest withstand voltage of 764 V, indicating that this compound is most suitable for use as an electrolyte. It is known that breakdown voltage occurs due to discharge from small defects present on the surface of aluminum oxide.[9] In light of this result, we hypothesize that this electrolyte dissolves in EG as ammonium salts and forms a micelle that is capable of covering defects and thereby forming an adsorption layer. Due to its rigid cyclic structures, it is capable of repairing them on the surface and forming thicker layers so as to achieve the high withstand voltage.[10] Although there are still some issues to be overcome, such as the fact that scintillation is observed from around 550 V, and the solubility in EG is slightly inferior, we concluded that the incorporation of hindered α-substituents led to excellent heat resistance and rigid ring skeletons improved the withstand voltage.[4] The details of the correlation between molecular rigidity and withstand voltage are currently under research.

Table 4. Electrical Characteristics and Heat Resistance Evaluation for 7[a]

			resistivity/Ωcm[c]			
entry	substrate	solubility[b]	0 h	250 h	500 h	1000 h
1	**7a**	○	831	880 (+6%)		
2	**7b**	○	1178	1259 (+7%)		
3	**7c**	○	1088	1433 (+32%)		
4	**7d**	○	854	1009 (+18%)		
5	**7e**	○	839	1055 (+26%)		
6	7f	△	913		1004 (+10%)	1096 (+20%)
7	**sebacic acid**	○	680	1324 (+95%)	1564 (+130%)	1890 (+178%)
8	1,6-DDA	○	772	1047 (+36%)	1158 (+50%)	1282 (+66%)

[a]Electrolytes were used as diammonium salt with 28% aqueous ammonia solution, and each solution was prepared as 0.134 mol/kg EG solution including 2 wt % H$_2$O. [b]○: Excellent, △: Good. [c]Increased variation percentage is shown in the parentheses.

CONCLUSIONS

In summary, we developed a novel type of dicarboxylic acids that have ether moieties in molecules, and they showed good solubility to EG. We also developed a complete halogen removal method using NaSMe solution. In addition, by introducing bulky substituents at α-position, the heat resistance of the electrolyte could be improved, preventing esterification or amidation in a capacitor. Furthermore, incorporating cyclic skeletons in the molecule significantly improved the withstand voltage. These compounds can be synthesized by Williamson synthesis in only one step, and it is expected to be an effective method in terms of cost and industrialization.[11]

EXPERIMENTAL SECTION

General Information. Infrared spectra were determined on a JASCO FT/IR-460 plus spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded with a JEOL ECX-400P, or a JEOL A-500 spectrometer using tetramethylsilane as an internal standard. Mass spectra (High-resolution mass spectra) were recorded on a JEOL MS-700D system equipped with EI high-resolution mass spectrometers. Halogen content was analyzed by TOX-100 and TOX-2100H. Tetrahydrofuran (THF) was purified by a Glass Contour Organic Solvent Purification System of Nikko Hansen & Co., Ltd. 1,4-Dioxane was distilled from calcium hydride and stored over sodium. Toluene was dried over calcium chloride, distilled, and stored over Molecular Sieves 4 Å. Hexane was distilled and stored over sodium. All of the other anhydrous solvents were obtained from commercial sources. Purification of products was performed by column chromatography on silica gel (Kanto Silica Gel 60N) and/or preparative TLC on silica gel (Merck Kiesel Gel GF254 or Wako Gel B-5F). For reactions that require heating, oil bath is used as the heat source. The heat resistance was measured with HIOKI 3522 LCR meter. The breakdown voltage was measured with TAKASAGO TMK 1.0−50 as a DC power supply, HIOKI DIFFERENTIAL PROBE 9322 and HIOKI MR8870.

Butane-1,4-diyl Bis(4-methylbenzenesulfonate) (2a). In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar and a rubber septum, NaOH (14.1 g, 353 mmol) and H_2O (50 mL) were added, respectively.[12] The reaction mixture was cooled to 0 °C and butane-1,4-diol (9.01 g, 100 mmol) in THF (40 mL) and TsCl (41.9 g, 220 mmol) in THF (100 mL) were added to this reaction mixture. The mixture was stirred for 20 h at 0 °C. The pH was adjusted to 5−6 with 2 M H_2SO_4 solution to quench the reaction. The mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic phases were washed with H_2O (3 × 30 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product, which was recrystallized from ethyl acetatete/ methanol (1:1) to give the titled compound **2a** (29.9 g, 75%).

Diethyl 2,2′-[Butane-1,4-diylbis(oxy)]dipropionate (3a). In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 6.60 g, 165 mmol) and THF (50 mL) were added, respectively. The reaction mixture was cooled to 0 °C, and 18-crown-6 (3.96 g, 15.0 mmol) in THF (20 mL) and ethyl 2-hydroxypropanoate (19 mL, 165 mmol) in THF (35 mL) were added to this reaction mixture. The mixture was stirred for 1 h at 0 °C; then, butane-1,4-diyl bis(4-methylbenzenesulfonate) **2a** (29.9 g, 75.0 mmol) within

THF (55 mL) was added to the reaction mixture. The reaction mixture was warmed to reflux and stirred for 6 h. The pH was adjusted to 7 with 2 M H_2SO_4 solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate = 2:1) to give the title compound **3a** (7.81 g, 36%). Yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.25−4.17 (m, 4H), 3.99−3.89 (m, 2H), 3.63−3.57 (m, 2H), 3.44−3.36 (m, 2H), 1.73−1.67 (m, 4H), 1.41−1.37 (m, 6H), 1.32−1.27 (m, 6H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 173.6, 75.0, 69.9, 69.9, 60.7, 26.3, 26.3, 18.6, 14.2; IR (neat) 2984, 2939, 2906, 2873, 1746, 1448, 1372, 1269, 1197, 1147, 1122, 755 cm^{-1}; HRMS (EI) *m/z*: $[M-C_3H_5O_2]^+$ calcd for $C_{11}H_{21}O_4$ 217.1440, found 217.1439.

2,2′-[Butane-1,4-diylbis(oxy)]dipropionic Acid (4a). In a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, diester **3a** (2.64 g, 9.08 mmol), 1,4-dioxane (20 mL), and NaOH aq (10 wt %, 20 mL) were added, respectively. The reaction mixture was warmed to reflux and stirred for 14.5 h. The pH was adjusted to 1 with 5 M H_2SO_4 solution to quench the reaction. The whole mixture was extracted with ethyl acetate (5 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate/acetic acid = 7:3:0.1) to give the title compound **4a** (1.99 g, 94%). Yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.00 (q, *J* = 6.8 Hz, 2H), 3.65−3.59 (m, 2H), 3.56−3.50 (m, 2H), 1.78−1.69 (m, 4H), 1.45 (d, *J* = 6.8 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 175.8, 175.6, 74.7, 74.6, 70.1, 69.9, 26.3, 26.3, 18.0, 17.9; IR (neat) 3460, 2987, 2943, 2880, 1727, 1452, 1234, 1118, 920, 744 cm^{-1}; HRMS (EI) *m/z*: $[M-CHO_2]^+$ calcd for $C_9H_{17}O_4$ 189.1127, found 189.1120.

Hexane-1,6-diyl Bis(4-methylbenzenesulfonate) (2b). In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar and a rubber septum, NaOH (14.1 g, 353 mmol) and H_2O (50 mL) were added, respectively.[13] The reaction mixture was cooled to 0 °C and hexane-1,6-diol (11.8 g, 100 mmol) in THF (40 mL) and TsCl (41.9 g, 220 mmol) in THF (100 mL) were added to this reaction mixture. The mixture was stirred for 21 h at 0 °C. The pH was adjusted to 5−6 with 2 M H_2SO_4 solution to quench the reaction. The mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic phases were washed with H_2O (3 × 30 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product, which was recrystallized from ethyl acetate/ methanol (1:1) to give the titled compound **2b** (18.5 g, 43%).

Diethyl 2,2′-[Hexane-1,6-diylbis(oxy)]dipropionate (3b). In a 100-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 2.68 g, 67.1 mmol), and THF (27 mL) were added, respectively. The reaction mixture was cooled to 0 °C and 18-crown-6 (1.77 g, 6.71 mmol) in THF (12 mL) and ethyl 2-hydroxypropanoate (9.2 mL, 80.6 mmol) in THF (22 mL) were added to this reaction mixture. The mixture was stirred for 1 h at 0 °C then hexane-1,6-diyl bis(4-methylbenzenesulfonate) **2b** (11.5 g, 26.9 mmol) with in THF (12 mL) was added to the reaction mixture. The reaction mixture was warmed to reflux and stirred

for 24 h. The pH was adjusted to 7 with 2 M H_2SO_4 solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate = 2:1) to give the title compound **3b** (3.55 g, 42%). Yellow oil; ^{1}H NMR (500 MHz, CDCl3) δ 4.28−4.12 (m, 4H), 3.93 (q, *J* = 7.0 Hz, 2H), 3.55 (dt, *J* = 6.7, 9.0 Hz, 2H), 3.37−3.33 (m, 2H), 1.64−1.57 (m, 4H), 1.41−1.37 (m, 10H including doublet at 1.39 ppm, *J* = 6.7 Hz, 6H), 1.29 (t, *J* = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 173.6, 75.0, 70.2, 60.7, 29.6, 25.8, 18.6, 14.2; IR (neat) 2934, 2869, 1735, 1459, 1215, 1159, 1132, 1045, 748 cm^{-1}; HRMS (EI) *m/z*: $[M-C_3H_5O_2]^+$ calcd for $C_{13}H_{25}O_4$ 245.1753, found 245.1745.

2,2′-[Hexane-1,6-diylbis(oxy)]dipropionic Acid (4b). In a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, diester **3b** (1.30 g, 4.07 mmol), 1,4-dioxane (10 mL), and NaOH aq (15 wt %, 10 mL) were added, respectively. The reaction mixture was warmed to reflux and stirred for 13 h. The pH was adjusted to 1 with 5 M H_2SO_4 solution to quench the reaction. The whole mixture was extracted with ethyl acetate (5 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate/acetic acid = 7:3:0.1) to give the title compound **4b** (1.01 g, 95%). Colorless oil; ^{1}H NMR (500 MHz, CDCl3) δ 4.00 (q, *J* = 7.0 Hz, 2H), 3.57 (dt, *J* = 6.7, 9.0 Hz, 2H), 3.49 (dt, *J* = 6.7, 9.0 Hz, 2H), 1.68−1.60 (m, 4H), 1.45 (d, *J* = 7.0 Hz, 6H), 1.43−1.38 (m, 4H); ^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 177.2, 177.1, 74.6, 70.3, 29.5, 25.6, 25.6, 18.1; IR (neat) 3629, 3160, 2993, 2942, 1710, 1455, 1225, 1119, 769, 732 cm^{-1}; HRMS (EI) *m/z*: $[M-CHO_2]^+$ calcd for $C_{11}H_{21}O_4$ 217.1440, found 217.1437.

Decane-1,10-diyl Bis(4-methylbenzenesulfonate) (2c).[14] In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, decane-1,10-diol (6.97 g, 40 mmol) in pyridine (27 mL) and TsCl (18.7 g, 98.0 mmol) were added, respectively. After stirring for 1 h at 0 °C, ice water (50 mL) was added to quench the reaction and filtered with the Büchner funnel washing with ice water (50 mL) and cooled hexane (50 mL) to give a crude product, which was recrystallized from ethyl acetate/hexane (3:1) to give the titled compound **2c** (11.7 g, 61%).

Diethyl 2,2′-[Decane-1,10-diylbis(oxy)]dipropionate (3c). In a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 2.33 g, 58.3 mmol) and THF (23 mL) were added, respectively. The reaction mixture was cooled to 0 °C and 18-crown-6 (2.41 g, 9.12 mmol) in THF (11 mL) and ethyl 2-hydroxypropanoate (8.0 mL, 69.9 mmol) in THF (19 mL) were added to this reaction mixture. The mixture was stirred for 1 h at 0 °C then decane-1,10-diyl bis(4-methylbenzenesulfonate) **2c** (11.3 g, 23.3 mmol) within THF (11 mL) was added to the reaction mixture. The reaction mixture was warmed to reflux and stirred for 21 h. The pH was adjusted to 7 with 5 M H_2SO_4 solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with brine

(20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate = 2:1) to give the title compound **3c** (2.63 g, 30%). Yellow oil; ^{1}H NMR (500 MHz, CDCl3) δ 4.27−4.14 (m, 4H), 3.93 (q, *J* = 7.1 Hz, 2H), 3.55 (dt, *J* = 6.7, 9.0 Hz, 2H), 3.35 (dt, *J* = 6.7, 9.0 Hz, 2H), 1.61−1.57 (m, 4H), 1.39 (d, *J* = 7.1 Hz, 6H), 1.35−1.27 (m, 18H including triplet at 1.29 ppm, *J* = 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, CDCl3) δ 173.6, 75.0, 70.4, 60.7, 29.7, 29.4, 29.4, 26.0, 18.6, 14.2; IR (neat) 2985, 2930, 2858, 1739, 1455, 1372, 1263, 1200, 1132, 751 cm^{-1}; HRMS (EI) *m/z*: $[M-C_3H_5O_2]^+$ calcd for $C_{17}H_{33}O_4$ 301.2379, found 301.2364.

2,2′-[Decane-1,10-diylbis(oxy)]dipropionic Acid (4c). In a 100-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, diester **3c** (1.80 g, 4.80 mmol), 1,4-dioxane (10 mL), and NaOH aq (3M, 10 mL) were added, respectively. The reaction mixture was warmed to reflux and stirred for 17 h. The pH was adjusted to 1 with 5 M H_2SO_4 solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate/acetic acid = 7:3:0.1) to give the title compound **4c** (1.50 g, 98%). White solid; mp 68−70 °C; ^{1}H NMR (400 MHz, CDCl3) δ 10.2 (brs, 2H), 4.00 (q, *J* = 6.9 Hz, 2H), 3.59 (dt, *J* = 2.0, 6.8 Hz, 1H), 3.57 (dt, *J* = 2.0, 6.8 Hz, 1H), 3.48−3.42 (m, 2H), 1.61 (ddt, *J* = 6.8, 6.8, 6.8 Hz, 4H), 1.46 (d, *J* = 6.9 Hz, 6H), 1.38−1.26 (m, 12H); ^{13}C{^{1}H} NMR (101 MHz, CDCl3) δ 178.3, 178.3, 74.5, 70.5, 29.6, 29.4, 29.2, 29.2, 25.9, 18.2; IR (neat) 3501, 2973, 2857, 2850, 1714, 1461, 1240, 1125, 918, 754 cm^{-1}; HRMS (EI) *m/z*: $[M-CHO_2]^+$ calcd for $C_{15}H_{29}O_4$ 273.2066, found 273.2058.

Dodecane-1,12-diyl Bis(4-methylbenzenesulfonate) (2d). In a 2-L three-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, dodecane-1,12-diol (189 g, 933 mmol) in pyridine (825 mL), and TsCl (433 g, 2.28 mol) were added, respectively.[15] After stirring for 12 h at 0 °C, ice water (1.0 L) was added to quench the reaction and filtered with the Büchner funnel washing with ice water (300 mL) and cooled hexane (300 mL) to give a crude product, which was recrystallized from ethyl acetate/methanol (1:1) to give the titled compound **2d** (220 g, 46%).

Diethyl 2,2′-[Dodecane-1,12-diylbis(oxy)]dipropionate (3d). In a 2-L three-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 40.8 g, 1.02 mol), and THF (200 mL) were added, respectively. The reaction mixture was cooled to 0 °C and 18-crown-6 (27.0 g, 102 mmol) in THF (100 mL) and ethyl 2-hydroxypropanoate (112 mL, 980 mmol) in THF (250 mL) were added to this reaction mixture. The mixture was stirred for 1 h at 0 °C then dodecane-1,12-diyl bis(4-methylbenzenesulfonate) **2d** (200 g, 392 mmol) within THF (550 mL) was added to the reaction mixture. The reaction mixture was warmed to reflux and stirred for 16 h. The pH was adjusted to 7 with 2 M H_2SO_4 solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 50 mL). The combined organic phases were washed with brine (200 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica

gel (*n*-hexane/ethyl acetate = 5:1) to give the title compound **3d** (30.4 g, 19%). Yellow oil; ^{1}H NMR (400 MHz, CDCl$_3$) δ 4.27−4.16 (m, 4H), 3.93 (q, *J* = 6.9 Hz, 2H), 3.55 (dt, *J* = 6.7, 8.9 Hz, 2H), 3.35 (dt, *J* = 6.7, 8.9 Hz, 2H), 1.63−1.55 (m, 4H), 1.39 (d, *J* = 6.9 Hz, 6H), 1.35−1.24 (m, 22H including triplet at 1.29 ppm, *J* = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 173.6, 75.0, 70.4, 60.7, 29.7, 29.6, 29.6, 29.4, 26.0, 18.7, 14.2; IR (neat) 2978, 2928, 2857, 1742, 1456, 1368, 1268, 1186, 1133, 756 cm^{-1}; HRMS (EI) *m/z*: $[M-C_3H_5O_2]^+$ calcd for $C_{19}H_{37}O_4$ 329.2692, found 329.2706.

*2,2′-[Dodecane-1,12-diylbis(oxy)]dipropionic Acid (**4d**).* In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, diester **3d** (1.78 g, 4.42 mmol), 1,4-dioxane (13 mL), and NaOH aq (3M, 13 mL) were added, respectively. The reaction mixture was warmed to reflux and stirred for 9 h. The pH was adjusted to 1 with 2 M H$_2$SO$_4$ solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H$_2$O (20 mL), dried (with Na$_2$SO$_4$), and concentrated in vacuo to give a crude product. The crude product was recrystallized by ethyl acetate/hexane (3:1) to give the title compound **4d** (1.28 g, 84%). White powder; mp 72−74 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.67 (brs, 2H), 3.99 (q, *J* = 6.9 Hz, 2H), 3.59 (dt, *J* = 2.4, 6.6 Hz, 1H), 3.56 (dt, *J* = 2.4, 6.6 Hz, 1H), 3.49−3.44 (m, 2H), 1.65−1.58 (m, 4H), 1.46 (d, *J* = 6.9 Hz, 6H), 1.39−1.25 (m, 16H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 178.1, 178.0, 74.5, 74.5, 70.5, 29.6, 29.6, 29.4, 29.2, 29.2, 25.9, 25.9, 18.2, 18.2; IR (neat) 3434, 2992, 2926, 2854, 1705, 1463, 1372, 1240, 1124, 1073, 720 cm^{-1}; HRMS (EI) *m/z*: $[M-CHO_2]^+$ calcd for $C_{17}H_{33}O_4$ 301.2379, found 301.2364.

*Tetradecane-1,14-diyl Bis(4-methylbenzenesulfonate) (**2e**).* In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, tetradecane-1,14-diol (15.2 g, 66.0 mmol) in pyridine (150 mL), and TsCl (32.7 g, 172 mmol) were added, respectively.[16] After stirring for 12 h at 0 °C, ice water (100 mL) was added to quench the reaction and filtered with the Büchner funnel washing with ice water (50 mL) and cooled hexane (50 mL) to give a crude product, which was recrystallized from toluene to give the titled compound **2e** (31.6 g, 89%).

*Diethyl 2,2′-[Tetradecane-1,14-diylbis(oxy)]dipropionate (**3e**).* In a 500-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 7.76 g, 194 mmol), and THF (80 mL) were added, respectively. The reaction mixture was cooled to 0 °C and 18-crown-6 (10.2 g, 38.7 mmol) in THF (50 mL) and ethyl 2-hydroxypropanoate (23 mL, 196 mmol) in THF (50 mL) were added to this reaction mixture. The mixture was stirred for 1 h at 0 °C then tetradecane-1,14-diyl bis(4-methylbenzenesulfonate) **2e** (31.6 g, 58.7 mmol) within THF (120 mL) was added to the reaction mixture. The reaction mixture was warmed to reflux and stirred for 17 h. The pH was adjusted to 7 with 2 M H$_2$SO$_4$ solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (with Na$_2$SO$_4$), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate = 6:1) to give the title compound **3e** (9.74 g, 39%). Colorless oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.25−4.15 (m, 4H), 3.93 (q, *J* = 6.9 Hz, 2H),

3.55 (dt, *J* = 6.6, 9.3 Hz, 2H), 3.36 (dt, *J* = 6.6, 9.3 Hz, 2H), 1.63−1.56 (m, 4H), 1.38 (d, *J* = 6.9 Hz, 6H), 1.36−1.25 (m, 26H including triplet at 1.29 ppm, *J* = 7.3 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 173.1, 74.6, 69.9, 60.2, 29.4, 29.2, 29.2, 29.2, 29.0, 25.6, 18.2, 13.8; IR (neat) 2983, 2926, 2854, 1749, 1457, 1371, 1268, 1194, 1141, 1026, 752 cm^{-1}; HRMS (EI) *m/z*: $[M-C_3H_5O_2]^+$ calcd for $C_{21}H_{41}O_4$ 357.3005, found 357.3021.

*2,2′-[Tetradecane-1,14-diylbis(oxy)]dipropionic Acid (**4e**).* In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, diester **3e** (9.43 g, 21.9 mmol), 1,4-dioxane (70 mL), and NaOH aq (3M, 70 mL) were added, respectively. The reaction mixture was warmed to reflux and stirred for 10 h. The pH was adjusted to 1 with 2 M H$_2$SO$_4$ solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H$_2$O (20 mL), dried (with Na$_2$SO$_4$), and concentrated in vacuo to give a crude product. The crude product was recrystallized by ethyl acetate to give the title compound **4e** (5.85 g, 71%). White powder; mp 78−80 °C; ^{1}H NMR (400 MHz, CDCl$_3$) δ 3.99 (q, *J* = 6.8 Hz, 2H), 3.58−3.49 (m, 4H), 1.68−1.56 (m, 4H), 1.45 (d, *J* = 6.8 Hz, 6H), 1.38−1.25 (m, 20H); ^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ 177.3, 74.5, 74.5, 70.6, 29.6, 29.5, 29.5, 29.4, 29.2, 25.9, 18.1; IR (neat) 3041, 2994, 2917, 2850, 1705, 1471, 1288, 1243, 1158, 1125, 913, 732 cm^{-1}; HRMS (EI) *m/z*: $[M-CHO_2]^+$ calcd for $C_{19}H_{37}O_4$ 329.2692, found 329.2701.

*Hexadecane-1,16-diyl Bis(4-methylbenzenesulfonate) (**2f**).* In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, hexadecane-1,16-diol (16.7 g, 64.8 mmol) in pyridine (130 mL), and TsCl (32.1 g, 168 mmol) were added, respectively.[16] After stirring for 12 h at 0 °C, ice water (100 mL) was added to quench the reaction and filtered with the Büchner funnel washing with ice water (50 mL) and cooled hexane (50 mL) to give a crude product, which was recrystallized from toluene to give the titled compound **2f** (25.1 g, 68%).

*Diethyl 2,2′-[Hexadecane-1,16-diylbis(oxy)]dipropionate (**3f**).* In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 5.28 g, 132 mmol), and THF (28 mL) were added, respectively. The reaction mixture was cooled to 0 °C and 18-crown-6 (7.01 g, 26.6 mmol) in THF (7.0 mL) and ethyl 2-hydroxypropanoate (14 mL, 120 mmol) in THF (35 mL) were added to this reaction mixture. The mixture was stirred for 1 h at 0 °C then hexadecane-1,16-diyl bis(4-methylbenzenesulfonate) **2f** (23.9 g, 42.1 mmol) within THF (44 mL) was added to the reaction mixture. The reaction mixture was warmed to reflux and stirred for 13.5 h. The pH was adjusted to 7 with 5 M H$_2$SO$_4$ solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (with Na$_2$SO$_4$), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate = 10:1) to give the title compound **3f** (7.79 g, 40%). Yellow oil; ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.27−4.15 (m, 4H), 3.93 (q, *J* = 6.8 Hz, 2H), 3.55 (dt, *J* = 6.7, 9.0 Hz, 2H), 3.36 (dt, *J* = 6.7, 9.0 Hz, 2H), 1.63−1.56 (m, 4H), 1.39 (d, *J* = 6.8 Hz, 6H), 1.33−1.24 (m, 30H); ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$) δ 173.6, 75.0, 70.4, 60.7, 29.7, 29.6,

29.6, 29.5, 29.4, 26.0, 18.7, 14.2; IR (neat) 2983, 2925, 2854, 1750, 1460, 1371, 1268, 1194, 1142, 755 cm^{-1}; HRMS (EI) m/z: $[M-C_3H_5O_2]^+$ calcd for $C_{23}H_{45}O_4$ 385.3318, found 385.3307.

2,2′-[Hexadecane-1,16-diylbis(oxy)]dipropionic Acid (4f). In a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, diester **3f** (5.26 g, 11.5 mmol), 1,4-dioxane (20 mL), and NaOH aq (3M, 23 mL) were added, respectively. The reaction mixture was warmed to reflux and stirred for 12 h. The pH was adjusted to 1 with 2 M H_2SO_4 solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. In a 1000-mL one-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, crude product, EtOH (35 mL), and MeSNa aq (15 wt %, 10 mL) were added, respectively. The reaction mixture was warmed to 40 °C and stirred for 44 h. After the reaction, reaction mixture was concentrated in vacuo, and the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was recrystallized by ethyl acetate to give the title compound **4f** (4.31 g, 93%). White powder; mp 80−82 °C; ^1H NMR (500 MHz, CDCl$_3$) δ 4.00 (q, J = 6.7 Hz, 2H), 3.58−3.49 (m, 4H), 1.65−1.58 (m, 4H), 1.46 (d, J = 6.7 Hz, 6H), 1.39−1.25 (m, 24H); $^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$) δ 176.4, 74.6, 74.5, 70.6, 29.6, 29.4, 29.4, 29.2, 25.9, 17.9; IR (neat) 3678, 2917, 2849, 1705, 1471, 1245, 1158, 1126, 1076, 1019, 914, 739 cm^{-1}; HRMS (EI) m/z: $[M-CHO_2]^+$ calcd for $C_{21}H_{41}O_4$ 357.3005, found 357.3006.

Diethyl 2,2′-[Decane-1,10-diylbis(oxy)]dibutyrate (3g). In a 200-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 2.98 g, 74.6 mmol), and THF (16 mL) were added, respectively. The reaction mixture was cooled to 0 °C and 18-crown-6 (3.94 g, 14.9 mmol) in THF (4.0 mL) and ethyl 2-hydroxybutanoate (8.96 g, 67.8 mmol) in THF (20 mL) were added to this reaction mixture. The mixture was stirred for 1 h at 0 °C then decane-1,10-diyl bis(4-methylbenzenesulfonate) **2c** (11.5 g, 23.8 mmol) within THF (25 mL) was added to the reaction mixture. The reaction mixture was warmed to reflux and stirred for 14 h. The pH was adjusted to 7 with 5 M H_2SO_4 solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate = 10:1) to give the title compound **3g** (4.75 g, 50%). Yellow oil; ^1H NMR (500 MHz, CDCl$_3$) δ 4.28−4.14 (m, 4H), 3.73 (dd, J = 5.1, 7.4 Hz, 2H), 3.57 (dt, J = 6.6, 9.2 Hz, 2H), 3.32 (dt, J = 6.6, 9.2, 2H), 1.81−1.69 (m, 4H), 1.62−1.56 (m, 6H), 1.33−1.25 (m, 16H including triplet at 1.29 ppm, J = 7.0 Hz, 6H), 0.97 (t, J = 7.5 Hz, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$) δ 173.2, 80.4, 70.7, 60.6, 29.6, 29.4, 29.3, 26.2, 26.0, 14.2, 9.7; IR (neat) 2931, 2857, 1751, 1462, 1371, 1340, 1294, 1262, 1191, 1138, 1026, 948 cm^{-1}; HRMS (EI) m/z: $[M-C_3H_5O_2]^+$ calcd for $C_{19}H_{37}O_4$ 329.2692, found 329.2700.

2,2′-[Decane-1,10-diylbis(oxy)]dibutyric Acid (4g). In a 50-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, diester **3g** (3.20 g, 7.96 mmol), 1,4-dioxane (16 mL), and NaOH aq (3M, 16 mL) were added, respectively. The reaction mixture was warmed to reflux and stirred for 12.5 h. The pH was adjusted to 1 with 2 M H_2SO_4 solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. In a 200-mL one-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, crude product, EtOH (10 mL), and MeSNa aq (15 wt %, 5.0 mL) were added, respectively. The reaction mixture was warmed to 40 °C and stirred for 1 h. After the reaction, reaction mixture was concentrated in vacuo, and the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give the title compound **4g** (2.58 g, 94%). Yellow oil; ^1H NMR (400 MHz, CDCl$_3$) δ 7.88 (brs, 2H), 3.82 (dd, J = 4.9, 7.1 Hz, 2H), 3.62 (dt, J = 1.9, 6.7, 1H), 3.59 (dt, J = 1.9, 6.7 Hz, 1H), 3.44−3.38 (m, 2H), 1.89−1.74 (m, 4H), 1.65−1.57 (m, 4H), 1.38−1.26 (m, 12H), 1.00 (t, J = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (101 MHz, CDCl$_3$) δ 177.5, 177.5, 79.7, 79.7, 70.9, 29.5, 29.4, 29.2, 29.2, 25.9, 25.7, 9.4; IR (neat) 3440, 2930, 2859, 1722, 1459, 1333, 1225, 1133, 925, 730 cm^{-1}; HRMS (EI) m/z: $[M-CHO_2]^+$ calcd for $C_{17}H_{33}O_4$ 301.2379, found 301.2376.

Decane-1,10-diyl Dimethanesulfonate (2c′). In a 100-mL three-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, decane-1,10-diol (10.2 g, 58.6 mmol) in pyridine (42 mL), and Ms_2O (25.0 g, 144 mol) were added, respectively.[16] After stirring for 13.5 h at 0 °C, ice water (50 mL) was added to quench the reaction and filtered with the Büchner funnel washing with ice water (30 mL) and cooled hexane (30 mL) to give a crude product, which was recrystallized from ethyl acetate/methanol (1:1) to give the titled compound **2c′** (7.42 g, 38%).

Diethyl 2,2′-[Decane-1,10-diylbis(oxy)]dipropionate (3c). In a 100-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 2.27 g, 56.8 mmol), and THF (12 mL) were added, respectively. The reaction mixture was cooled to 0 °C and 18-crown-6 (2.99 g, 11.3 mmol) in THF (5.0 mL) and ethyl 2-hydroxypropanoate (5.9 mL, 51.5 mmol) in THF (12 mL) were added to this reaction mixture. The mixture was stirred for 1 h at 0 °C then decane-1,10-diyl dimethanesulfonate **2c′** (5.68 g, 17.2 mmol) within THF (21 mL) was added to the reaction mixture. The reaction mixture was warmed to reflux and stirred for 14 h. The pH was adjusted to 5−6 with 2 M H_2SO_4 solution to quench the reaction. The whole mixture was extracted with diethyl ether (3 × 30 mL). The combined organic phases were washed with H_2O (3 × 30 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate = 6:1) to give the title compound **3c** (2.17 g, 34%).

Dodecane-1,12-diyl Dimethanesulfonate (2d′). In a 300-mL three-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, dodecane-1,12-diol (11.9 g, 58.8 mmol) in pyridine (120 mL) and Ms_2O (25.0 g, 144 mol) were added, respectively.[16] After stirring for 18.5 h at 0 °C, ice water (200 mL) was added to quench the reaction and filtered with the Büchner funnel

washing with ice water (100 mL) and cooled hexane (100 mL) to give a crude product, which was recrystallized from ethyl acetate (1:1) to give the titled compound **2d′** (16.9 g, 80%).

Diethyl 2,2′-[Dodecane-1,12-diylbis(oxy)]dipropionate (3d). In a 500-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 7.36 g, 184 mmol), and THF (50 mL) were added, respectively. The reaction mixture was cooled to 0 °C and 18-crown-6 (9.91 g, 37.5 mmol) in THF (60 mL) and ethyl 2-hydroxypropanoate (19 mL, 167 mmol) in THF (50 mL) were added to this reaction mixture. The mixture was stirred for 1 h at 0 °C then dodecane-1,12-diyl dimethanesulfonate **2d′** (16.9 g, 47.1 mmol) within THF (120 mL) was added to the reaction mixture. The reaction mixture was warmed to reflux and stirred for 22 h. The pH was adjusted to 7 with 2 M H_2SO_4 solution to quench the reaction. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with brine (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate = 5:1) to give the title compound **3d** (4.74 g, 25%).

2,2′-[Butane-1,4-diylbis(oxy)]dihexanoic Acid (7a). In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 6.92 g, 173 mmol), and THF (60 mL) were added, respectively. The reaction mixture was stirred and butane-1,4-diol (2.60 g, 28.8 mmol) in THF (60 mL) was added. The reaction mixture was warmed to reflux and stirred for 18 h. Then, the reaction mixture was cooled to 0 °C and 2-bromohexanoic acid **5a** (8.5 mL, 60.2 mmol) was added slowly to this reaction mixture. The reaction mixture was warmed to reflux and stirred for 48 h. After the reaction, the reaction mixture was cooled to 0 °C and ice water (100 mL) was added to quench the reaction. The whole mixture was extracted with H_2O (5 × 10 mL). Then, the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. In a 100-mL one-necked round-bottomed flask equipped with a magnetic stirring bar and a rubber septum, crude product, EtOH (20 mL), and MeSNa aq (15 wt %, 20 mL) were added, respectively. The reaction mixture was warmed to 40 °C and stirred for 24 h. After the reaction, the reaction mixture was concentrated in vacuo and extracted with H_2O (5 × 10 mL). Then, the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate/acetic acid = 7:3:0.1) to give the title compound **7a** (3.05 g, 33%). Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 3.87 (dd, J = 4.9, 7.3 Hz, 2H), 3.68–3.60 (m, 2H), 3.52–3.45 (m, 2H), 1.82–1.69 (m, 8H), 1.44–1.31 (m, 8H), 0.91 (t, J = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 177.3, 177.1, 78.8, 78.8, 70.6, 70.5, 32.2, 32.1, 27.1, 27.1, 26.3, 26.3, 22.3, 13.8; IR (neat) 3450, 2952, 2930, 2870, 1704, 1466, 1423, 1246, 1213, 1142, 929, 739 cm^{-1}; HRMS (EI) *m/z*: [M-$C_6H_{11}O_3$]$^+$ calcd for $C_{10}H_{19}O_3$ 187.1334, found 187.1333.

2,2′-[Hexane-1,6-diylbis(oxy)]dihexanoic Acid (7b). In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 6.92 g, 173 mmol), and THF (30 mL) were added, respectively. The reaction mixture was stirred, and hexane-1,6-diol (3.40 g, 28.8 mmol) in THF (30 mL) was added. The reaction mixture was warmed to reflux and stirred for 12 h. Then, the reaction mixture was cooled to 0 °C and 2-bromohexanoic acid **5a** (9.3 mL, 66.2 mmol) was added slowly to this reaction mixture. The reaction mixture was warmed to reflux and stirred for 48 h. After the reaction, the reaction mixture was cooled to 0 °C ice water (100 mL) was added to quench the reaction. The whole mixture was extracted with H_2O (5 × 10 mL). Then, the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. In a 100-mL one-necked round-bottomed flask equipped with a magnetic stirring bar and a rubber septum, crude product, EtOH (20 mL), and MeSNa aq (15 wt %, 20 mL) were placed, respectively. The reaction mixture was warmed to 40 °C and stirred for 24 h. After the reaction, the reaction mixture was concentrated in vacuo and extracted with H_2O (5 × 10 mL). Then, the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give the title compound **7b** (7.76 g, 78%). Yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ 3.86 (dd, J = 4.9, 7.3 Hz, 2H), 3.60 (dt, J = 6.5, 9.1 Hz, 2H), 3.42 (dt, J = 6.5, 9.1 Hz, 2H), 1.82–1.73 (m, 4H), 1.66–1.60 (m, 4H), 1.45–1.32 (m, 12H), 0.91 (t, J = 7.1 Hz, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$) δ 177.6, 78.8, 70.9, 32.2, 29.5, 27.1, 25.7, 25.7, 22.3, 13.8; IR (neat) 3451, 3037, 2953, 2935, 2865, 1721, 1463, 1335, 1210, 1102, 1026, 929, 731 cm^{-1}; HRMS (EI) *m/z*: [M-$C_6H_{11}O_3$]$^+$ calcd for $C_{12}H_{23}O_3$ 215.1647, found 215.1645.

2,2′-[Octane-1,8-diylbis(oxy)]dihexanoic Acid (7c). In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 6.44 g, 161 mmol), and THF (60 mL) were added, respectively. The reaction mixture was stirred, and octane-1,8-diol (3.92 g, 26.8 mmol) in THF (30 mL) was added. The reaction mixture was warmed to reflux and stirred for 12 h. Then, the reaction mixture was cooled to 0 °C and 2-bromohexanoic acid **5a** (7.91 mL, 56.3 mmol) was added slowly to this reaction mixture. The reaction mixture was warmed to reflux and stirred for 48 h. After the reaction, the reaction mixture was cooled to 0 °C and ice water (100 mL) was added to quench the reaction. The whole mixture was extracted with 1 M NaOH (5 × 10 mL). Then, the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate/acetic acid = 7:3:0.1) to give the title compound **7c** (5.78 g). In a 100-mL one-necked round-bottomed flask equipped with a magnetic stirring bar and a rubber septum, product **7c**, EtOH (15 mL), and MeSNa aq (15 wt %, 15 mL) were added, respectively. The reaction mixture was warmed to 40 °C and stirred for 24 h. After the reaction, the reaction mixture was

concentrated in vacuo, and the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give the title compound **7c** (5.41 g, 54%). Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.86 (dd, J = 4.8, 7.1 Hz, 2H), 3.59 (dt, J = 6.5, 9.4 Hz, 2H), 3.49−3.37 (m, 2H), 1.82−1.72 (m, 4H), 1.65−1.56 (m, 4H), 1.46−1.29 (m, 16H), 0.91 (t, J = 7.0 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 177.5, 78.8, 71.0, 32.2, 29.5, 29.1, 27.1, 25.8, 22.3, 13.8; IR (neat) 3424, 2952, 2866, 1643, 1459, 1383, 1279, 1207, 1128, 926, cm^{-1}; HRMS (EI) m/z: [M-CHO$_2$]$^+$ calcd for $C_{19}H_{37}O_4$ 329.2692, found 329.2692.

2,2′-[Nonane-1,9-diylbis(oxy)]dihexanoic Acid (7d). In a 200-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 6.24 g, 156 mmol), and THF (30 mL) were added, respectively. The reaction mixture was stirred, and nonane-1,9-diol (4.17 g, 26.0 mmol) in THF (30 mL) was added. The reaction mixture was warmed to reflux and stirred for 12 h. Then, the reaction mixture was cooled to 0 °C, and 2-bromohexanoic acid **5a** (7.63 mL, 54.6 mmol) was added slowly to this reaction mixture. The reaction mixture was warmed to reflux and stirred for 48 h. After the reaction, the reaction mixture was cooled to 0 °C and ice water (100 mL) was added to quench the reaction. The whole mixture was extracted with 1 M NaOH (5 × 10 mL). Then, the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. In a 100-mL one-necked round-bottomed flask equipped with a magnetic stirring bar and a rubber septum, crude product, EtOH (20 mL), and MeSNa aq (15 wt %, 20 mL) were added, respectively. The reaction mixture was warmed to 40 °C and stirred for 24 h. After the reaction, the reaction mixture was concentrated in vacuo, and the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give the crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate/acetic acid = 7:3:0.1) to give the title compound **7d** (5.41 g, 54%). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.13 (brs, 2H), 3.86 (dd, J = 4.9, 7.6 Hz, 2H), 3.66−3.58 (m, 2H), 3.39 (t, J = 7.6 Hz, 1H), 3.37 (t, J = 7.6 Hz, 1H), 1.83−1.73 (m, 4H), 1.65−1.57 (m, 4H), 1.46−1.28 (m, 18H), 0.91 (t, J = 7.2 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 178.8, 78.6, 70.9, 32.3, 29.5, 29.3, 29.1, 27.2, 25.8, 22.2, 13.7; IR (neat) 3451, 3146, 2931, 2859, 1721, 1467, 1335, 1284, 1208, 1130, 1102, 987, 730 cm^{-1}; HRMS (EI) m/z: [M-CHO$_2$]$^+$ calcd for $C_{20}H_{39}O_4$ 343.2848, found 343.2850.

2,2′-[Dodecane-1,12-diylbis(oxy)]dihexanoic Acid (7e). In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 5.56 g, 139 mmol), and THF (30 mL) were added, respectively. The reaction mixture was stirred, and dodecane-1,12-diol (4.69 g, 23.2 mmol) in THF (30 mL) was added. The reaction mixture was warmed to reflux and stirred for 12 h. Then, the reaction mixture was cooled to 0 °C, and 2-bromohexanoic acid **5a** (6.8 mL, 48.7 mmol) was added slowly to this reaction mixture. The reaction

mixture was warmed to reflux and stirred for 48 h. After the reaction, the reaction mixture was cooled to 0 °C and ice water (100 mL) was added to quench the reaction. The whole mixture was extracted with 1 M NaOH (5 × 10 mL). Then, the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. In a 100-mL one-necked round-bottomed flask equipped with a magnetic stirring bar and a rubber septum, crude product, EtOH (30 mL), and MeSNa aq (15 wt %, 30 mL) were added, respectively. The reaction mixture was warmed to 40 °C and stirred for 24 h. After the reaction, the reaction mixture was concentrated in vacuo, and the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give the crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate/acetic acid = 7:3:0.1) to give the title compound **7e** (6.08 g, 61%). Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.56 (brs, 2H), 3.86 (t, J = 6.1 Hz, 2H), 3.61 (dt, J = 7.0, 7.0 Hz, 2H), 3.39 (dt, J = 7.0, 7.0 Hz, 2H), 1.82−1.72 (m, 4H), 1.65−1.57 (m, 4H), 1.45−1.25 (m, 24H), 0.91 (t, J = 7.1 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 178.4, 178.3, 78.7, 71.0, 32.3, 29.5, 29.4, 29.2, 29.2, 27.2, 25.9, 25.8, 22.3, 13.8; IR (neat) 3443, 3097, 2927, 2857, 1720, 1467, 1335, 1283, 1244, 1129, 1103, 928, 728 cm^{-1}; HRMS (EI) m/z: [M-CHO$_2$]$^+$ calcd for $C_{23}H_{45}O_4$ 385.3318, found 385.3305.

2,2′-{Tricyclo[5.2.1.0^{2,6}]decane-bis(methyleneoxy)}-dihexanoic Acid (7f). In a 300-mL two-necked round-bottomed flask equipped with a magnetic stirring bar, a rubber septum and an argon balloon, NaH (60% dispersion in mineral oil, 4.80 g, 120 mmol), and THF (50 mL) were added, respectively. The reaction mixture was stirred and tricyclo-[5.2.1.0^{2,6}]decanedimethanol (3.93 g, 20.0 mmol) in THF (70 mL) was added. The reaction mixture was warmed to reflux and stirred for 12 h. Then, the reaction mixture was cooled to 0 °C, and 2-bromooctanoic acid **5b** (7.3 mL, 42.0 mmol) was added slowly to this reaction mixture. The reaction mixture was warmed to reflux and stirred for 48 h. After the reaction, the reaction mixture was cooled to 0 °C and ice water (100 mL) was added to quench the reaction. The whole mixture was extracted with 1 M NaOH (5 × 10 mL). Then, the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give a crude product. In a 100-mL one-necked round-bottomed flask equipped with a magnetic stirring bar and a rubber septum, crude product, EtOH (30 mL), and MeSNa aq (15 wt %, 50 mL) were added, respectively. The reaction mixture was warmed to 40 °C and stirred for 24 h. After the reaction, the reaction mixture was concentrated in vacuo, and the pH was adjusted to 1 with 2 M H_2SO_4 solution. The whole mixture was extracted with diethyl ether (5 × 10 mL). The combined organic phases were washed with H_2O (20 mL), dried (with Na_2SO_4), and concentrated in vacuo to give the crude product. The crude product was purified by flash column chromatography on silica gel (*n*-hexane/ethyl acetate/acetic acid = 7:3:0.1) to give the title compound **7f** (6.88 g, 72%). Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.87−3.82 (m, 2H), 3.52−3.12 (m, 4H), 2.54−1.96

(m, 6H), 1.93−1.17 (m, 28H), 0.88 (t, J = 6.6 Hz, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, CDCl$_3$) δ 178.3, 177.9, 177.9, 177.8, 177.8, 79.9, 79.0, 78.9, 78.9, 78.8, 78.8, 78.7, 77.4, 76.4, 76.3, 75.4, 75.3, 75.3, 75.2, 75.2, 75.2, 75.1, 50.1, 45.5, 45.1, 45.1, 45.0, 45.0, 44.9, 44.7, 44.7, 44.6, 44.0, 43.9, 43.3, 43.1, 42.9, 42.4, 42.1, 42.0, 42.0, 41.6, 41.6, 41.5, 40.9, 40.9, 40.7, 40.6, 40.5, 40.4, 40.4, 39.9, 39.8, 39.5, 39.3, 39.1, 38.9, 35.1, 35.0, 35.0, 34.9, 34.3, 33.0, 32.6, 32.5, 32.4, 31.6, 30.9, 29.0, 28.9, 28.9, 27.5, 25.2, 25.1, 25.0, 25.0, 24.8, 24.7, 24.6, 24.6, 22.5, 20.8, 14.0; IR (neat) 3407, 2931, 2864, 1713, 1459, 1277, 1229, 1128, 1036, 932, 721 cm^{-1}; HRMS (EI) m/z: [M-CHO$_2$]$^+$ calcd for C$_{27}$H$_{47}$O$_4$ 435.3474, found 435.3479.

The Heat-Resistance Evaluation. The heat-resistance evaluation was performed with the electrolyte solutions enclosed in an ampule tube at 105 °C conditions for a certain period of aging duration (5−10 min). The aged electrolyte solutions were placed in a platinum-measuring cell with two aluminum electrodes. The resistivity of each aged electrolyte solutions was measured by using a LCR meter (1 kHz) for every period of time, e.g., 250, 500, and 1000 h at 30 ± 0.5 °C.

Measurement of the Breakdown Voltage (the Sparking Voltage Measurement). The breakdown voltage was evaluated by using the practical electrolyte capacitor which is made out of anode (Al$_2$O$_3$)- and cathode−electrode foils and the developed electrolyte solution as the impregnant (see Scheme 1a). The dc 1000 V was applied to the capacitor anode−electrode at 105 °C with the conditions of constant dc current of 2.5 mA. Since the capacity of the measuring sample was so large, the anode voltage increases quite slowly with voltage application time, resulting in the scintillation and then sudden voltage drop as the breakdown voltage. The breakdown voltage measurements can be recorded as the voltage−time characteristics with the constant flowing current.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c09089.

Initial electrolyte properties, and 1H and 13C NMR spectra for all new compounds (PDF)

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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