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ORIGINAL ARTICLE

Sulfonyl-bridged oligo(benzoic acid)s: synthesis, X-ray structures, and properties as metal extractants

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Abstract Sulfonyl-bridged oligo(benzoic acid)s $\mathbf{7}_n$ ($n = 2$–4) are prepared from the corresponding triflate esters ($\mathbf{8}_n$) of sulfur-bridged oligophenols by palladium-catalyzed methoxycarbonylation of the triflate moieties, followed by hydrolysis of the resulting methyl esters, and subsequent oxidation of the sulfur bridges. X-ray analysis reveals that dimer $\mathbf{7_2}$ forms supramolecular zig-zag chains through intermolecular hydrogen bonds between the carboxy groups. As for the crystal of trimer $\mathbf{7_3}$, two molecules are associated through two couples of intermolecular hydrogen bonds between terminal and central carboxy groups to form a cyclic dimer, which connects with two adjacent dimers with the remaining carboxy groups to construct an infinite columnar structure. Tetramer $\mathbf{7_4}$ adopts a monomolecular cyclic structure through intramolecular hydrogen bonds between the terminal carboxy groups, and a molecule connects with each of two adjacent molecules through two couples of intermolecular hydrogen bonds between inner carboxy and sulfonyl groups. Solvent extraction experiments reveal that the oligo(benzoic acid)s exhibit high extractability toward lanthanoid ions (Ln^{3+}); the performance follows the order $\mathbf{7_4} \approx \mathbf{7_3} > \mathbf{7_2}$. Moderate extraction selectivity is observed for the extraction of Pr^{3+}, Gd^{3+}, and Yb^{3+} with $\mathbf{7_2}$. X-ray crystallographic analysis of cluster $[Tb_4L_4(H_2O)_6](Et_3NH)_4$, which was prepared from $\mathbf{7_4}$ (H_4L) and $Tb(NO_3)_3{\cdot}6H_2O$ in the presence of Et_3N, reveals that no sulfonyl oxygens coordinate to the metal centers. This indicates that the high extractability of $\mathbf{7_4}$ originates from the electron-withdrawing nature of the sulfonyl function, which increases the acidity of two adjacent carboxy groups.

Keywords Oligo(benzoic acid) · Sulfonyl group · Solvent extraction · Lanthanoid ion

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Introduction

Recently, many studies have been focused on the development of novel extractants for the separation, purification, and recycling of lanthanoid ions against the background of an increasing demand in high-technology industries [1–3]. Calix[*n*]arenes (e.g., **1**) are a versatile platform for developing metal extractants [4–6]. To capture lanthanoid ions (Ln^{3+}), binding sites such as 2-(dialkylphosphoryl)acetamido [7, 8], phosphono [9, 10], alkoxy(hydroxy)phosphoryl [11], and carboxy groups [12–14] have been introduced either to the hydroxy groups through linking moieties or, alternatively, at the *p*-positions with or without linking moieties. On the other hand, we reported that thiacalixarenes **2** and **3**, and sulfur-oxidized derivatives **4** and **5** exhibit high extractability toward metal ions [15, 16], which is attributed to the coordination of the sulfur atomic groups to metal ions in cooperation with two neighboring phenoxy oxygens, as evidenced by X-ray structural analysis [17]. In agreement with this, extraction selectivity varies depending on the oxidation state of the bridging moieties. For example, thiacalixarenes **2** and **3** extract very well so-called "soft" metal ions in the hard and soft acids and bases (HSAB) principle [18, 19], with the aid of the coordination of the soft sulfur atoms, whereas sulfonylcalixarene **5** prefers "hard" metal ions, including lanthanoid

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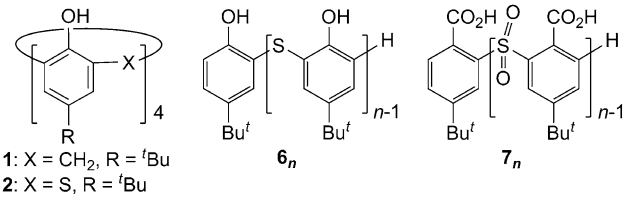
ions, with the aid of the coordination of the hard sulfonyl oxygen [16]. However, compounds **2–5** require high pH and long time for extraction [15, 16]. We assumed that these drawbacks can be improved by replacing the hydroxy groups with more acidic and more metal-affinitive functions such as carboxy, phosphono, and sulfo groups. However, such chemical transformations are difficult even by using transition metal catalysts [20–25], because calixarenes have sterically crowded cyclic structures and possess a number of coordination sites. Recently, Ohba et al. and our group reported that an open-chain analog of thiacalixarene **2** (**6**$_4$) exhibits almost equal extractability to that of compound **2** toward soft metal ions [26, 27]. In addition, linear tetramer **6**$_4$ with reduced steric hindrance allowed to replace the hydroxy groups with carboxy and diphenylphosphino functions [28–30]. In this study, we have synthesized sulfonyl-bridged bis-, tris-, and tetrakis(benzoic acid)s **7**$_n$ (n = 2–4) and examined their metal extraction capability in order to develop efficient extractants for lanthanoid ions [29].



1: X = CH_2, R = ^{t}Bu
2: X = S, R = ^{t}Bu
3: X = S, R = ^{t}Oct
4: X = SO, R = ^{t}Oct
5: X = SO_2, R = ^{t}Oct

6$_n$ **7**$_n$

Experimental section

General methods

Melting points were taken using Stuart SMP3 and are uncorrected. ^{1}H and ^{13}C NMR spectra were measured with tetramethylsilane as an internal standard and $CDCl_3$ as a solvent, unless otherwise noted. Infrared (IR) spectra were recorded on a Shimazu FTIR-8300 spectrometer. Microanalyses were carried out in the Microanalytical Laboratory of the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. HRMS spectra were measured using a Bruker Daltonics APEX III in Research and Analytical Center for Giant Molecules, Graduate School of Science, Tohoku University. Inductively coupled plasma atomic emission spectra (ICP-AES) were measured using a Thermo scientific iCPA6500. Silica gel (63–200 μm) was used for column chromatography and TLC. Water- and air-sensitive reactions were routinely carried out under nitrogen. Toluene was distilled from sodium diphenyl ketyl and stored under nitrogen. DMSO ($CaSO_4$), CH_2Cl_2 (CaH_2), and MeOH (Mg) were distilled from dehydrating agents and stored under nitrogen. Compounds **6**$_n$ was prepared according to the literature procedures [31].

Synthesis

Compound **8**$_2$: To a solution of **6**$_2$ (4.00 g, 12.0 mmol) in CH_2Cl_2 was added pyridine (d = 0.983; 3.9 mL, 48.0 mmol), and the mixture was stirred at room temperature for 30 min. To the mixture was added trifluoromethanesulfonic anhydride (d = 1.719; 4.3 mL, 26.4 mmol), and the resulting mixture was stirred for 2 h. The reaction was quenched with 2 M HCl (5 mL). The resulting mixture was poured into 2 M HCl (60 mL) and extracted with $CHCl_3$. The organic layer was evaporated to leave an oil, which was purified by column chromatography on silica gel with $CHCl_3$-hexane (1:1) as an eluent to give **8**$_2$ (7.10 g, 99 %), mp 120–120.8 °C; FAB-MS 594 (M^+); ^{1}H NMR (400 MHz) δ 1.23 (s, 18H, C(CH_3)$_3$), 7.24 (d, 2H, J = 7.3 Hz, ArH), 7.36 (dd, 2H, J = 7.3, 2.5 Hz, ArH), 7.41 (d, 2H, J = 2.5 Hz, ArH); ^{13}C NMR (100 MHz) δ 31.0, 34.8, 117.0, 120.2, 121.5, 127.0, 127.4, 131.9, 146.9, 152.5; IR (KBr) 2,970, 1,423, 1,215, 1,134 cm^{-1}. Anal. Calcd for $C_{22}H_{24}F_6O_6S_3$: C, 44.44; H, 4.07. Found: C, 44.30; H, 4.07.

Compound **8**$_3$: This compound was prepared by a similar procedure to that used for the preparation of **8**$_2$. Hexane–AcOEt (3:1) was employed for the column chromatography as an eluent. Starting from **6**$_3$ (700 mg), **8**$_3$ (1.08 g, 87 %) was obtained as a colorless powder, mp 101.3–104.0 °C; FAB-MS 907 (M^+); ^{1}H NMR (400 MHz) δ 1.12 (s, 9H, C(CH_3)$_3$), 1.28 (s, 18H, C(CH_3)$_3$), 7.23 (s, 2H, ArH), 7.24–7.26 (m, 2H, ArH), 7.39 (dd, 2H, J = 8.7, 2.4 Hz, ArH), 7.44 (d, 2H, J = 2.4 Hz, ArH); ^{13}C NMR (125 MHz) δ 30.8, 31.2, 35.0, 114.9, 117.5, 120.0, 121.8, 122.6, 127.3, 127.6, 130.0, 131.4, 132.3, 145.5, 147.0, 152.7, 152.8; IR (KBr) 2,970, 1,421, 1,211, 1,141 cm^{-1}. Anal. Calcd for $C_{33}H_{35}F_9O_9S_5$: C, 43.70; H, 3.89. Found: C, 43.66; H, 4.03.

Compound **8**$_4$: This compound was prepared by a similar procedure to that used for the preparation of **8**$_2$. Hexane–$CHCl_3$ (1:1) was employed for the column chromatography as an eluent. Starting from **6**$_4$ (500 mg), **8**$_4$ (786 mg, 89 %) was obtained as a colorless powder, mp 128.2–130.9 °C; FAB-MS 1,218 (M^+); ^{1}H NMR (400 MHz) δ 1.08 (s, 18H, C(CH_3)$_3$), 1.25 (s, 18H, C(CH_3)$_3$), 7.23 (d, 2H, J = 2.4 Hz, ArH), 7.24 (d, 2H, J = 2.4 Hz, ArH), 7.26 (d, 2H, J = 8.7 Hz, ArH), 7.41 (dd, 2H, J = 8.7, 2.4 Hz, ArH), 7.46 (d, 2H, J = 2.4 Hz, ArH); ^{13}C NMR (100 MHz) δ 30.6, 31.0, 34.9, 117.0, 120.2, 121.7, 123.4, 127.2, 127.3, 130.0, 130.1, 131.1, 131.3, 132.2, 145.3, 146.9, 152.7, 152.7; IR (KBr) 2,970, 1,427, 1,211, 1,138 cm^{-1}. Anal. Calcd for $C_{44}H_{46}F_{12}O_{12}S_7$: C, 43.34; H, 3.80. Found: C, 43.15; H, 3.80.

Compound **9**$_2$: To a solution of **8**$_2$ (1.15 g, 1.93 mmol) in DMSO–MeOH (2:1, 45 mL) were added $Pd(OAc)_2$

(86.8 mg, 0.390 mmol), DPPB (319 mg, 0.770 mmol), $^{i}Pr_2NEt$ ($d = 0.742$; 1.5 mL, 7.72 mmol). The mixture was stirred under CO atmosphere (1 atm) at 70 °C for 18 h. After cooling, the reaction was quenched with 2 M HCl (50 mL). The mixture was poured into water (50 mL) and extracted with $CHCl_3$ (100 mL × 3). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography on silica gel with AcOEt–MeOH (2:1) as an eluent to give **9₂** (773 mg, 97 %) as an oil, FAB-MS 414 (M^+); ^{1}H NMR (400 MHz) δ 1.18 (s, 18H, C(C*H*$_3$)$_3$), 3.84 (s, 6H, CO_2CH_3), 7.20 (d, 2H, $J = 1.9$ Hz, Ar*H*), 7.30 (dd, 2H, $J = 8.3$, 1.9 Hz, Ar*H*), 7.85 (d, 2H, $J = 8.3$ Hz, Ar*H*); ^{13}C NMR (100 MHz) δ 30.6, 34.7, 51.8, 123.5, 128.8, 129.7, 130.3, 137.7, 155.4, 166.8; IR (KBr) 1,716 cm^{-1}. Anal. Calcd for $C_{24}H_{30}O_4S$: C, 69.53; H, 7.29. Found: C, 69.46; H, 7.33.

Compound **9₃**: This compound was prepared by a similar procedure to that used for the preparation of **9₂**. Hexane–$CHCl_3$ (3:2) was employed for the column chromatography as an eluent. Starting from **8₃** (1.00 g), **9₃** (574 mg, 83 %) was obtained as an oil, FAB-MS 636 (M^+); ^{1}H NMR (400 MHz) δ 1.12 (s, 18H, C(C*H*$_3$)$_3$), 1.23 (s, 9H, C(C*H*$_3$)$_3$), 3.68 (s, 3H, CO_2CH_3), 3.93 (s, 6H, CO_2CH_3), 6.89 (d, 2H, $J = 1.8$ Hz, Ar*H*), 7.16 (dd, 2H, $J = 8.2$, 1.8 Hz, Ar*H*), 7.62 (s, 2H, Ar*H*), 7.91 (d, 2H, $J = 8.2$ Hz, Ar*H*); ^{13}C NMR (100 MHz) δ 30.9, 31.1, 35.2, 35.2, 52.2, 52.4, 122.1, 124.6, 126.0, 130.9, 131.6, 134.6, 141.6, 143.4, 154.9, 156.0, 166.9, 167.4; IR (KBr) 1,715 cm^{-1}. Anal. Calcd for $C_{36}H_{44}O_6S_2$: C, 67.89; H, 6.96. Found: C, 67.80; H, 7.17.

Compound **9₄**: this compound was prepared by a similar procedure to that used for the preparation of **9₂**. Starting from **8₄** (786 mg), **9₄** (408 mg, 78 %) was obtained as an oil, FAB-MS 858 (M^+); ^{1}H NMR (400 MHz) δ 1.12 (s, 18H, C(C*H*$_3$)$_3$), 1.17 (s, 18H, C(C*H*$_3$)$_3$), 3.81 (s, 6H, CO_2CH_3), 3.93 (s, 6H, CO_2CH_3), 6.87 (d, 2H, $J = 1.8$ Hz, Ar*H*), 7.16 (dd, 2H, $J = 8.3$, 1.8 Hz, Ar*H*), 7.41 (d, 2H, $J = 1.8$ Hz, Ar*H*),7.47 (d, 2H, $J = 1.8$ Hz, Ar*H*), 7.91 (d, 2H, $J = 8.3$ Hz, Ar*H*); ^{13}C NMR (100 MHz) δ 30.8, 30.9, 35.0, 35.1, 52.1, 52.5, 122.0, 124.5, 126.0, 130.8, 130.8, 131.4, 133.0, 133.9, 139.7, 141.6, 154.5, 155.8, 166.8, 167.3; IR (KBr) 1,732 cm^{-1}. Anal. Calcd for $C_{48}H_{58}O_8S_3$: C, 67.10; H, 6.80. Found: C, 66.92; H, 7.02.

Compound **10₂**: A mixture of **9₂** (921 mg, 2.22 mmol) and KOH (1.25 g, 22.2 mmol) in EtOH–H_2O (10:1, 44.0 mL) was refluxed for 2 h. The mixture was cooled in an ice-water bath and acidified with 4 M HCl (100 mL) to liberate the free acid, which was collected by filtration and washed with water to give **10₂** (760 mg, 89 %), mp 275.8–277.1 °C; FAB-MS 386 (M^+); ^{1}H NMR (400 MHz, DMSO-d$_6$) δ 1.13 (s, 18H, C(C*H*$_3$)$_3$), 7.06 (d, 2H, $J = 1.8$ Hz, Ar*H*), 7.40 (dd, 2H, $J = 8.2$, 1.8 Hz, Ar*H*), 7.80 (d, 2H, $J = 8.2$ Hz, Ar*H*); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 30.5, 34.6, 123.9, 129.0, 130.1, 130.2, 136.7, 154.7, 167.7; IR (KBr) 1,697 cm^{-1}. Anal. Calcd for $C_{22}H_{26}O_4S$: C, 68.37; H, 6.78. Found: C, 68.28; H, 6.77.

Compound **10₃**: This compound was prepared by the same procedure as used for the preparation of **10₂**. Starting from **9₃** (574 mg), **10₃** (318 mg, 60 %) was obtained as a colorless powder, mp 269.0–269.3 °C; FAB-MS 594 (M^+); ^{1}H NMR (400 MHz, acetone-d$_6$) δ 1.16 (s, 18H, C(C*H*$_3$)$_3$), 1.33 (s, 9H, C(C*H*$_3$)$_3$), 6.99 (d, 2H, $J = 1.8$ Hz, Ar*H*), 7.28 (dd, 2H, $J = 8.2$, 1.8 Hz, Ar*H*), 7.73 (s, 2H, Ar*H*), 7.98 (d, 2H, $J = 8.2$ Hz, Ar*H*); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 30.5, 30.6, 34.7, 34.7, 121.9, 124.2, 124.9, 129.7, 130.8, 134.1, 140.9, 144.5, 153.8, 155.0, 167.2, 167.7; IR (KBr) 1,684 cm^{-1}. Anal. Calcd for $C_{33}H_{38}O_6S_2$: C, 66.64; H, 6.44. Found: C, 66.31; H, 6.55.

Compound **10₄**: This compound was prepared by the same procedure as used for the preparation of **10₂**. Starting from **9₄** (331 mg), **10₄** (226 mg, 85 %) was obtained as a colorless powder, mp 297.2–300.9 °C; FAB-MS 803 ($[M + 1]^+$); ^{1}H NMR (400 MHz, $CDCl_3$-DMSO-d$_6$ (4:1)) δ 1.12 (s, 18H, C(C*H*$_3$)$_3$), 1.18 (s, 18H, C(C*H*$_3$)$_3$), 6.85 (d, 2H, $J = 1.8$ Hz, Ar*H*), 7.16 (dd, 2H, $J = 8.2$, 1.8 Hz, Ar*H*), 7.45 (d, 2H, $J = 1.8$ Hz, Ar*H*), 7.47 (d, 2H, $J = 1.8$ Hz, Ar*H*), 7.92 (d, 2H, $J = 8.2$ Hz, Ar*H*); ^{13}C NMR (100 MHz, DMSO-d$_6$) δ 30.4, 30.4, 34.6, 34.6, 121.8, 124.1, 124.4, 129.3, 130.0, 130.7, 132.2, 133.2, 141.2, 141.3, 153.5, 154.9, 167.1, 167.7; IR (KBr) 3,427, 1,693 cm^{-1}. Anal. Calcd for $C_{44}H_{52}O_9S_3$ (**10₄**·H_2O): C, 64.36; H, 6.38. Found: C, 64.11; H, 6.12.

Compound **7₂**: To a solution of **10₂** (318 mg, 0.824 mmol) in $CHCl_3$ (5 mL) were added acetic acid (5 mL) and $NaBO_3$·$4H_2O$ (507 mg, 3.30 mmol), and the mixture was refluxed for 24 h. After cooling, the mixture was poured into 2 M HCl (50 mL) and extracted with $CHCl_3$ (50 mL × 3). The combined organic layer was washed with 6 M HCl and evaporated to leave a residue, which was crystallized from acetone–hexane to give **7₂** (318 mg, 92 %), mp 281.3–283.6 °C; FAB-MS 441 ($[M + Na]^+$); ^{1}H NMR (500 MHz, acetone-d$_6$) δ 1.37 (s, 18H, C(C*H*$_3$)$_3$), 7.64 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.79 (dd, 2H, $J = 8.0$, 1.9 Hz, Ar*H*), 8.45 (d, 2H, $J = 1.9$ Hz, Ar*H*); ^{13}C NMR (100 MHz, acetone-d$_6$) δ 31.2, 35.9, 129.5, 129.7, 131.1, 132.3, 140.0, 154.7, 169.1; IR (KBr) 1,711, 1,293 cm^{-1}. Anal. Calcd for $C_{22}H_{26}O_6S_3$: C, 63.14; H, 6.26. Found: C, 62.85; H, 6.18.

Compound **7₃**: This compound was prepared by a similar procedure to that used for the preparation of **7₂**. Starting from **10₃** (220 mg), **7₃** (195 mg, 80 %) was obtained as a colorless powder, mp 309.7–311.6 °C; FAB-MS 681 ($[M + Na]^+$); ^{1}H NMR (400 MHz, acetone-d$_6$) δ 1.35 (s, 18H, C(C*H*$_3$)$_3$), 1.39 (s, 9H, C(C*H*$_3$)$_3$), 7.62 (d, 2H, $J = 8.0$ Hz, Ar*H*), 7.81 (dd, 2H, $J = 8.0$, 1.8 Hz, Ar*H*),

8.32 (d, 2H, $J = 1.8$ Hz, Ar*H*), 8.72 (s, 2H, Ar*H*); ^{13}C NMR (100 MHz, DMSO-d_6) δ 30.3, 30.6, 35.0, 35.4, 127.6, 128.6, 131.4, 131.5, 132.0, 133.2, 137.0, 138.7, 153.1, 153.5, 166.2, 168.9; IR (KBr) 3,200, 1,706, 1,327 cm^{-1}, HRMS calcd for $C_{33}H_{37}O_{10}S_2$ $[M - H]^+$ 657.1834, found 657.1831.

Compound **7$_4$**: This compound was prepared by a similar procedure to that used for the preparation of **7$_2$**. Crystallization was carried out from CH_2Cl_2–hexane. Starting from **10$_2$** (260 mg), **7$_4$** (192 mg, 66 %) was obtained as a colorless powder, mp 249.9–251.3 °C; FAB-MS 921 ($[M + Na]^+$); ^{1}H NMR (400 MHz) δ 1.22 (s, 18H, C(C*H*$_3$)$_3$), 1.46 (s, 18H, C(C*H*$_3$)$_3$), 7.38 (d, 2H, $J = 1.9$ Hz, Ar*H*), 7.78 (dd, 2H, $J = 8.2$, 1.9 Hz, Ar*H*), 7.99 (d, 2H, $J = 8.2$ Hz, Ar*H*), 8.48 (d, 2H, $J = 1.9$ Hz, Ar*H*), 8.57 (d, 2H, $J = 1.9$ Hz, Ar*H*); ^{13}C NMR (100 MHz, DMSO-d_6) δ 30.5, 30.7, 35.6, 36.1, 128.9, 129.4, 131.6, 131.9, 132.1, 133.6, 134.6, 138.7, 139.5, 140.3, 154.5, 154.8, 166.7, 168.7; IR (KBr) 3,568, 1,720, 1,331 cm^{-1}. Anal. Calcd for $C_{44}H_{50}O_{14}S_3$: C, 58.78; H, 5.61. Found: C, 58.70; H, 5.72.

Cluster **11**: To a solution of **7$_4$** (23.0 mg, 25.0 μmol) in methanol–toluene (4:1, 20.0 mL) was added Et_3N ($d = 0.729$; 69 μL, 0.50 mmol), and the mixture was stirred for 30 min. To a mixture was added a solution of $Tb(NO_3)_3 \cdot 6H_2O$ (11.0 mg, 25.0 μmol) in methanol–toluene (4:1, 5.0 mL), and the resulting mixture was refluxed for 3 h. The volatile materials were evaporated to leave a residue, which was dissolved in $CHCl_3$ (10 mL) and washed with water (10 mL × 2). After the organic layer was evaporated, the residue was crystallized from CH_2Cl_2–hexane to give **11** (17.0 mg, 59 %) as a colorless powder. Vapor diffusion of diethyl ether to a solution of **11** in CH_2Cl_2 afforded single crystals.

Solvent extraction

General procedure for the extraction experiment is as follows: An aqueous solution containing indicated concentrations of a metal ion ($[Metal]_{aq,init} = 1.0 \times 10^{-4}$ M), Me_4NCl (0.1 M), and a pH buffer (0.05 M) was prepared; the pH buffer was selected from glycine–NH_3 (pH = 2.5–3.5), succinic acid–NH_3 (pH = 4.0–5.0), MES–NH_3 (pH = 5.5–6.0), PIPES–NH_3 (pH = 6.5–7.0), HEPPSO–NH_3 (pH = 7.5–8.5), and CHES–NH_3 (pH = 9.0–10.0). In case of the extraction of Ag^+, Me_4NCl was not added to avoid the formation of AgCl. The aqueous solution (10 mL) was combined with a solution of an extractant ($[\mathbf{7_2}] = 1.0 \times 10^{-3}$ M, $[\mathbf{7_3}] = 6.7 \times 10^{-4}$ M, $[\mathbf{7_4}] = 5.0 \times 10^{-4}$ M) in 4-methyl-2-pentanone or $CHCl_3$ (10 mL) in a 30 mL vial tube, and the mixture was shaken at 300 strokes min^{-1} at room temperature (~20 °C) for 1 h. After the two layers were separated, $[Metal]_{aq}$ was measured by ICP-AES.

X-ray crystallographic analysis

X-ray crystallographic analysis was performed with a Bruker SMART APEX or APEX II diffractometer (graphite monochrometor, MoKα radiation, $\lambda = 0.71073$ Å). Data integration and reduction were performed with the SAINT and XPREP software [32] and the absorption correction was performed by the semi-empirical method with SADABS [33]. The structure was solved by the direct method using SHELXS-97 [34] and refined by using least-squares methods on F2 with SHELXL-97 [34]. X-ray analysis was undertaken using the free GUI software of Yadokari-XG 2009 [35, 36]. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC 908516–908518 for **7$_2$**, **7$_3$**, and **11** and 908785 for **7$_4$**.

Crystallographic data for **7$_2$**: $C_{22}H_{26}O_6S_4$, fw = 418.49, orthorhombic, *P*bcn, $a = 13.049(2)$ Å, $b = 10.9020(18)$ Å, $c = 14.746(3)$ Å, $V = 2{,}097.9(6)$ Å^3, $Z = 4$, $T = 173(2)$ K, 10,867 reflections measured, 2,395 independent reflections, 2,147 reflections were observed ($I > 2\sigma(I)$), $R_1 = 0.0418$, $wR_2 = 0.1090$ (observed), $R_1 = 0.0459$, $wR_2 = 0.1154$ (all data).

Crystallographic data for **7$_3$**·H_2O·$(CH_3CN)_{0.5}$: $C_{34}H_{41.5}O_{11}S_2$, fw = 697.30, monoclinic, *C*2/c, $a = 31.493(9)$ Å, $b = 11.149(3)$ Å, $c = 25.511(7)$ Å, $\beta = 119.872(4)°$, $V = 7{,}767(4)$ Å^3, $Z = 8$, $T = 173(2)$ K, 20,953 reflections measured, 8,720 independent reflections, 3,710 reflections were observed ($I > 2\sigma(I)$), $R_1 = 0.0872$, $wR_2 = 0.2170$ (observed), $R_1 = 0.2108$, $wR_2 = 0.2991$ (all data).

Crystallographic data for **7$_4$**·CH_2ClCH_2Cl·$(CH_3OH)_{0.5}$·hexane: $C_{52.5}H_{70}Cl_2O_{14.5}S_3$, fw = 1,100.17, monoclinic, $P2_1/c$, $a = 16.506(6)$ Å, $b = 18.365(6)$ Å, $c = 20.401(7)$ Å, $\beta = 109.994(11)°$, $V = 5{,}811(3)$ Å^3, $Z = 4$, $T = 100\,(2)$ K, 26,154 reflections measured, 7,599 independent reflections, 2,652 reflections were observed ($I > 2\sigma(I)$), $R_1 = 0.0956$, $wR_2 = 0.2196$ (observed), $R_1 = 0.2418$, $wR_2 = 0.2643$ (all data).

Crystallographic data for **11**·CH_2Cl_2·$(C_2H_5OC_2H_5)_3$·$(H_2O)_4$: $C_{213}H_{300}Cl_2N_4O_{69}S_{12}Tb_4$, fw = 5,111.87, monoclinic, *C2/c*, $a = 46.801(11)$ Å, $b = 19.028(5)$ Å, $c = 42.374(10)$ Å, $\beta = 121.267(3)°$, $V = 33{,}015(14)$ Å^3, $Z = 4$, $T = 100$ (2) K, 182,210 reflections measured, 37,607 independent reflections, 22,968 reflections were observed ($I > 2\sigma(I)$), $R_1 = 0.0785$, $wR_2 = 0.2212$ (observed), $R_1 = 0.1430$, $wR_2 = 0.2712$ (all data).

Results and discussions

Synthesis

Sulfonyl-bridged oligo(benzoic acid)s **7$_n$** ($n = 2$–4) were readily prepared by using palladium-catalyzed methoxycarbonylation

as a key step (Scheme 1) [37–39]. Thus, the esterification of oligophenols $\mathbf{6}_n$ (n = 2–4) with triflic anhydride gave triflate esters $\mathbf{8}_n$, which were subjected to palladium-catalyzed methoxycarbonylation using MeOH, $Pd(OAc)_2$, dppb, and Hunig's base in DMSO under CO atmosphere (1 atm). The Pd catalyst smoothly replaced all the triflate moieties with methoxycarbonyl functions to give oligo(benzoate ester)s $\mathbf{9}_n$. Hydrolysis of the methyl esters $\mathbf{9}_n$, followed by the oxidation of the bridging sulfur moieties using $NaBO_3{\cdot}4H_2O$ gave sulfonyl-bridged oligo(benzoic acid)s $\mathbf{7_2}$, $\mathbf{7_3}$, and $\mathbf{7_4}$ in total yields of 79, 35, and 39 %, respectively, based on the starting oligophenols $\mathbf{6}_n$.

X-ray structural analysis

The novel sulfonyl-bridged oligo(benzoic acid)s were subjected to single-crystal X-ray analysis. Prerequisite single crystals were obtained by the vapor diffusion of hexane (for $\mathbf{7_2}$ and $\mathbf{7_4}$) or CH_3CN (for $\mathbf{7_3}$) to an acetone solution of $\mathbf{7_2}$ or $\mathbf{7_3}$, or a CH_2ClCH_2Cl solution of $\mathbf{7_4}$.

The crystal of $\mathbf{7_2}$ belongs to the orthorhombic system with *P*bcn space group. The molecule has a C_2 symmetric structure (Fig. 1a). The two carboxy groups adopt *anti* conformation with respect to the plane defined by the sulfur and two adjacent carbon atoms. As a result, the carboxy groups do not form intramolecular hydrogen bonds but connect with other carboxyl groups of neighboring $\mathbf{7_2}$ molecules through intermolecular hydrogen bonds to construct a 2_1-helical zig-zag structure along the c axis (Fig. 1b); the average O–H···O=C distance is 1.785 Å.

The crystal of $\mathbf{7_3}$ belongs to the monoclinic system with *C*2/c space group. The molecule adopts a twisted conformation (Fig. 2a) and the central and a terminal carboxy group connect with a terminal and the central carboxy group of an adjacent molecule, respectively, through intermolecular hydrogen bonds to construct a cyclic dimer structure with C_2 symmetry (Fig. 2b); the average O···O distance is 2.631 Å. Interestingly, the conformation of the dimer is molecularly chiral and two enantiomeric conformers connect alternately through intermolecular hydrogen bonds between the remaining carboxy groups to form an infinite columnar structure along the c-axis (Fig. 2c); the average O–H···O=C distance is 1.767 Å. Further, the columnar structures are arranged parallel to each other along the b-axis to construct a layer (Fig. 2d), and the layers pile up along the a-axis (Fig. 2e). Interestingly, porous channels are created along the b-axis and filled with CH_3CN and H_2O molecules.

The crystal of $\mathbf{7_4}$ belongs to the monoclinic system with $P2_1/c$ space group. The molecule has a cyclic structure with intramolecular hydrogen bonds between the terminal carboxy groups (Fig. 3a). The conformation is chiral and a

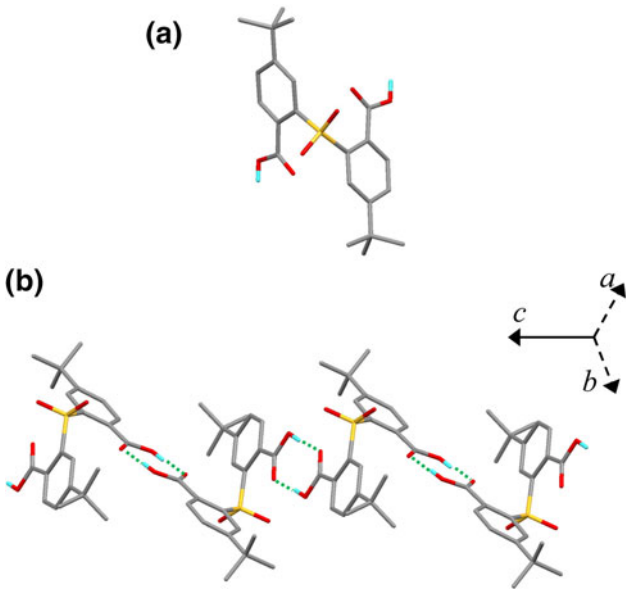
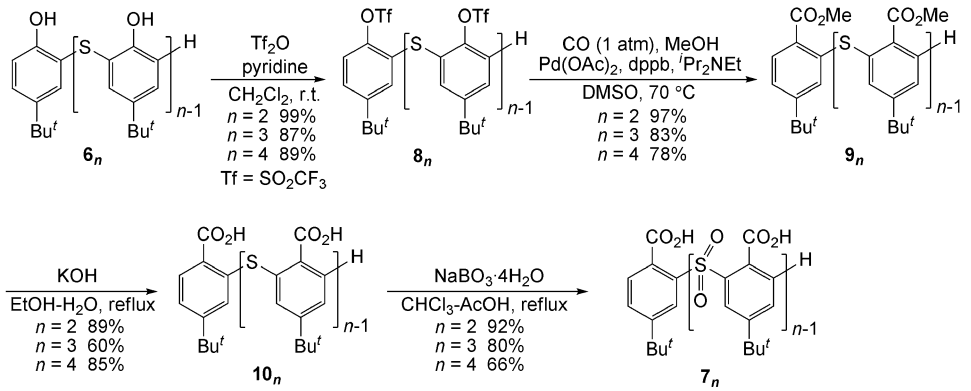


Fig. 1 X-ray structure of $\mathbf{7_2}$: **a** Molecule and **b** hydrogen-bond network viewed along the c-axis. Hydrogen atoms except those of carboxy groups and disordered carbon atoms are omitted for clarity. *Green dotted lines* represent intermolecular hydrogen bonds. (Color figure online)

Scheme 1 Synthesis of $\mathbf{7_2}$, $\mathbf{7_3}$, and $\mathbf{7_4}$



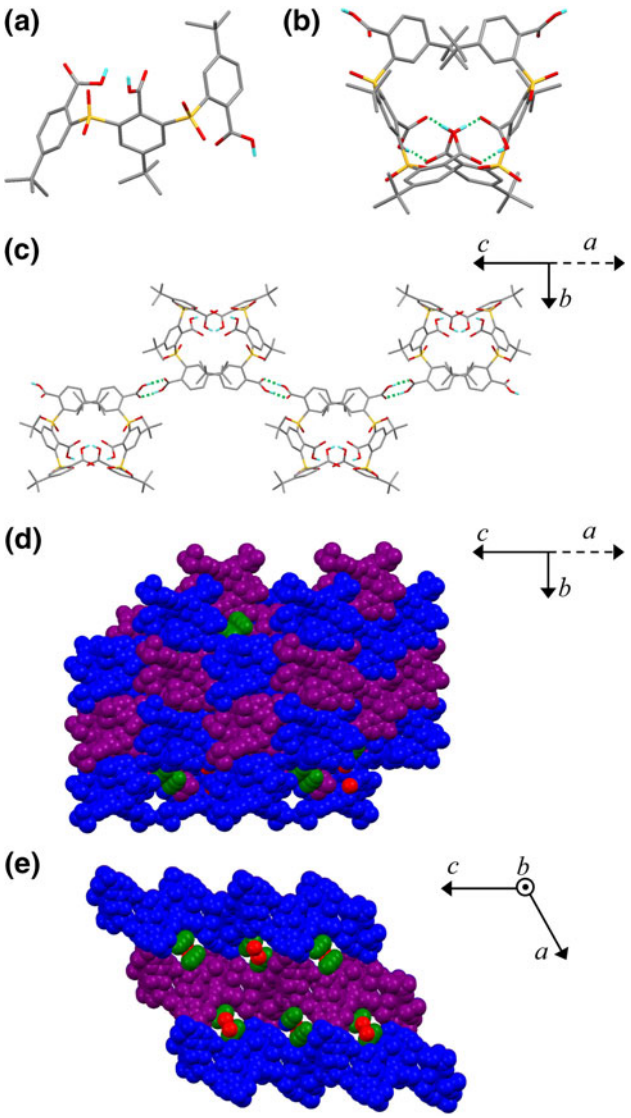


Fig. 2 X-ray structure of $\mathbf{7_3}$: **a** Molecule, **b** dimer, **c** hydrogen-bond network viewed along the *c*-axis, **d** cross-section of crystal packing parallel to the *bc* plane, and **e** cross-section of crystal packing parallel to the *ac* plane. *Green dotted lines* represent intermolecular hydrogen bonds. Hydrogen atoms except those of carboxy groups, disordered carbon atoms, and included solvents (**a**–**c**) are omitted for clarity. Molecules are *color-coded* to clarify the packing structure (**d** and **e**). (Color figure online)

molecule connects with each of two adjacent antipodal conformers through two couples of intermolecular hydrogen bonds between inner carboxy and sulfonyl groups to construct an infinite columnar structure along the *a*-axis (Fig. 3b). The average intramolecular O–H···O=C and intermolecular C(=O)O···O=S distances are 1.819 and 2.661 Å, respectively.

As mentioned above, it was found that the sulfonyl-bridged oligo(benzoic acid)s change their crystal structures depending on the number of monomer unit. The crystal of tri(benzoic acid) $\mathbf{7_3}$, bearing porous channels, has a potential

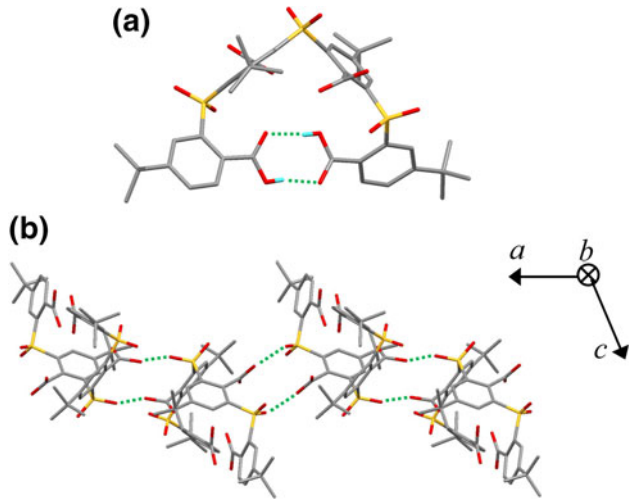


Fig. 3 X-ray structure of $\mathbf{7_4}$: **a** Molecule and **b** hydrogen-bond network viewed along the *a*-axis. *Green dotted lines* represent intermolecular hydrogen bonds. Hydrogen atoms, disordered carbon atoms, and included solvents are omitted for clarity. (Color figure online)

for serving as a supramolecular absorbent, which captures specific molecules in the solid state [40, 41].

Solvent extraction

Solvent extraction was carried out to evaluate the coordination ability of the sulfonyl-bridged oligo(benzoic acid)s $\mathbf{7_n}$ toward lanthanoid ions (Ln^{3+}), as well as several other metal ions. An aqueous solution (10 mL) containing a metal ion (1.0×10^{-4} M), Me_4NCl (0.1 M), and a pH buffer (0.05 M) was combined with the same volume of a solution of an extractant ($[\mathbf{7_2}] = 1.0 \times 10^{-3}$ M, $[\mathbf{7_3}] = 6.7 \times 10^{-4}$ M, $[\mathbf{7_4}] = 5.0 \times 10^{-4}$ M) in MIBK or $CHCl_3$ (10 mL); the concentration of the monomer unit was fixed at 2.0×10^{-3} M for the three extractants. The mixture was vigorously shaken at room temperature for 1 h and the metal ion remained in the aqueous phase was analyzed by ICP-AES. The extraction percent (*E* %) was calculated according to the following equation:

$$E\% = \left([\text{Metal}]_{\text{aq,init}} - [\text{Metal}]_{\text{aq}}\right) / [\text{Metal}]_{\text{aq,init}} \times 100\%$$

where $[\text{Metal}]_{\text{aq,init}}$ and $[\text{Metal}]_{\text{aq}}$ are the concentrations of the metal ion in the aqueous phase before and after extraction. Figures 4 and 5 show the pH dependence of *E* % for Ag^+, Cu^{2+}, Ni^{2+}, Mg^{2+}, Ho^{3+}, and Tb^{3+}. The performance of sulfur-bridged tetrakisphenol $\mathbf{6_4}$, as well as that of tetrakis(benzoic acid) $\mathbf{10_4}$, was also tested for comparison.

A soft metal ion, Ag^+, was extracted only with tetrakisphenol $\mathbf{6_4}$ in a moderate *E* % at pH 6.0 (Fig. 4a). On the other hand, an intermediate metal ion, Cu^{2+}, was

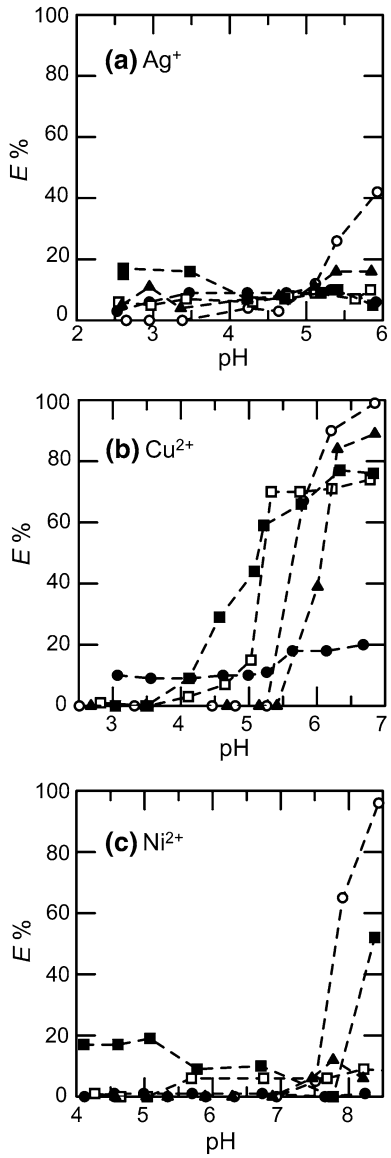


Fig. 4 The pH dependence of *E* % for Ag^{+} (**a**), Cu^{2+} (**b**), and Ni^{2+} (**c**) with $\mathbf{6_4}$ (*open circle*), $\mathbf{7_2}$ (*filled circle*), $\mathbf{7_3}$ (*open square*), $\mathbf{7_4}$ (*filled square*), and $\mathbf{10_4}$ (*filled triangle*). MIBK was used as an organic phase

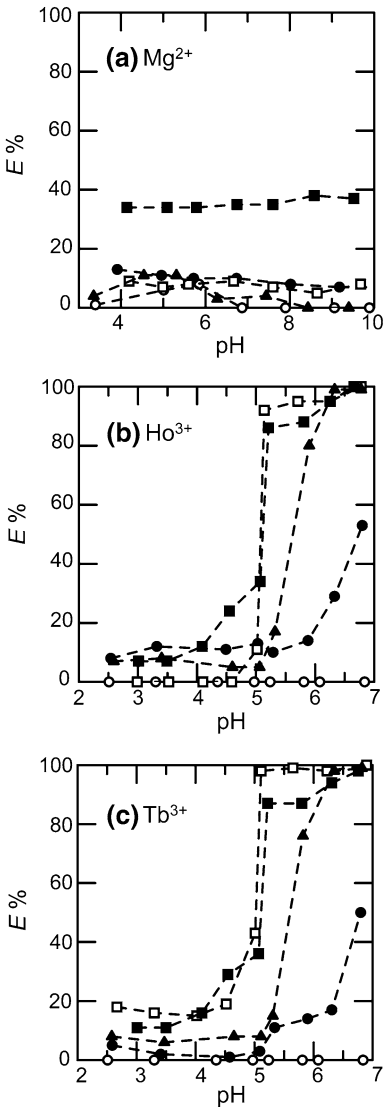


Fig. 5 The pH dependence of *E* % for Mg^{2+} (**a**), Ho^{3+} (**b**), and Tb^{3+} (**c**) with $\mathbf{6_4}$ (*open circle*), $\mathbf{7_2}$ (*filled circle*), $\mathbf{7_3}$ (*open square*), $\mathbf{7_4}$ (*filled square*), and $\mathbf{10_4}$ (*filled triangle*). MIBK was used as an organic phase

extracted with not only $\mathbf{6_4}$ but also $\mathbf{7_3}$, $\mathbf{7_4}$, and $\mathbf{10_4}$ in high *E* % at pH 6.0–7.0 (Fig. 4b). However, another intermediate metal ion, Ni^{2+}, was extracted only with $\mathbf{7_4}$ among $\mathbf{7}_n$ in a moderate *E* % even at pH 8.5, whereas $\mathbf{6_4}$ completely extracted this ion at the same pH (Fig. 4c). As mentioned above, sulfonyl-bridged oligo(benzoic acid)s $\mathbf{7}_n$ was inferior to sulfur-bridged tetrakisphenol $\mathbf{6_4}$ in extractability toward soft to intermediate metal ions. It seems that the replacement of phenolic hydroxy groups with more acidic and more metal-affinitive carboxy groups cannot cover the lack of soft sulfur coordination sites.

A hard metal ion, Mg^{2+}, was extracted only with $\mathbf{7_4}$ in moderate *E* % (Fig. 5a). Interestingly, $\mathbf{7}_n$ and $\mathbf{10_4}$ exhibited high extractability toward lanthanoid ions, Ho^{3+} and Tb^{3+}, which were hardly extracted with $\mathbf{6_4}$ (Fig. 5b, c). The pH dependence of *E* % indicates that $\mathbf{7}_n$, as well as $\mathbf{10_4}$, extracted the metal ions by exchanging their acidic protons. In this mechanism, extraction becomes difficult as pH decreases. The pH values, above which $\mathbf{7_2}$, $\mathbf{7_3}$, and $\mathbf{7_4}$ exhibited high *E* % values, are 7.0, 5.5, and 5.5, respectively. Therefore, the extractability of the oligo(benzoic acid)s follows the order $\mathbf{7_4} \approx \mathbf{7_3} > \mathbf{7_2}$, indicating that the presence of more than three carboxy units is important for the efficient extraction of lanthanoid ions. A similar observation has been made in the extraction of soft to intermediate metal ions with oligophenols [27]. It should be noted that Ho^{3+} was quantitatively extracted with $\mathbf{7_3}$ and

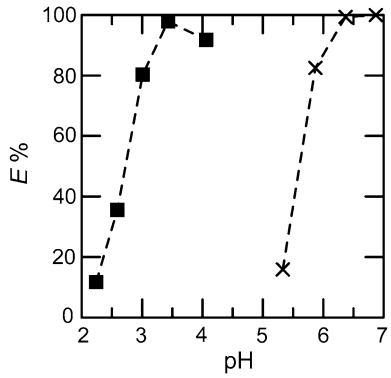


Fig. 6 The pH dependence of *E* % for Tb^{3+} with **5** (*times symbol*) and $\mathbf{7_4}$ (*filled square*). $CHCl_3$ was used as an organic phase

$\mathbf{7_4}$ at pH 7.0 even by reducing the extraction time (30 min). The comparison of the extraction performance among sulfur-bridged tetrakisphenol $\mathbf{6_4}$, sulfonyl-bridged tetrakis(benzoic acid) $\mathbf{7_4}$, and its sulfur-bridged analog $\mathbf{10_4}$ indicates that the replacement of the hydroxy groups is more effective than the oxidation of the bridging sulfur moieties for the improvement of the extractability toward lanthanoid ions. The extractability of $\mathbf{7_4}$ toward Tb^{3+} was also compared with that of sulfonylcalixarene **5** (Fig. 6), which is reported to exhibit high affinity toward hard metal ions [16]. It was found that Tb^{3+} was quantitatively extracted with $\mathbf{7_4}$ even at pH 3.5, when $CHCl_3$ was used as an organic phase; the performance is apparently superior to that of sulfonylcalixarene **5**.

Our next attention was directed toward the extraction selectivity of lanthanoid ions with the oligo(benzoic acid)s. Table 1 summarizes the half-extraction pH ($pH_{1/2}$) for the extraction of Pr^{3+}, Gd^{3+}, and Yb^{3+} with dimer $\mathbf{7_2}$ and tetramer $\mathbf{7_4}$, as compared to the results with sulfonylcalixarene **5** (The *E* % values somewhat depend on buffering agents. The $pH_{1/2}$ values could not be precisely determined for $\mathbf{7_3}$ because they fall around the pH range (pH $\approx$ 5.5) where the buffer has to be changed). A distinct difference in $pH_{1/2}$ was observed among the three ions when dimer $\mathbf{7_2}$ was employed. The extraction selectivity increased in the order $Pr^{3+} < Gd^{3+} < Yb^{3+}$, which correlates with the descending order of ion radius. It is easily conceivable that dimer $\mathbf{7_2}$, upon ligation to a metal ion with the two carboxy groups, adopts a rigid conformation suited for the discrimination of ion radii. However, the difference of the $pH_{1/2}$ values was not sufficient to separate the three ions; actually, the *E* % values of Yb^{3+}, Gd^{3+}, and Pr^{3+} were 88, 75, and 30 %, respectively, at pH 6.6.

Table 1 The $pH_{1/2}$ values for the extraction of lanthanoid ions

Ligands	$pH_{1/2}$		
	Pr^{3+}	Gd^{3+}	Yb^{3+}
5	5.77	5.78	5.59
$\mathbf{7_2}$	6.85	6.25	6.03
$\mathbf{7_4}$	2.70	2.71	2.75

$CHCl_3$ was used as an organic phase

X-ray structural analysis of a Tb^{3+} cluster of compound $\mathbf{7_4}$

In order to gain insight into the origin of the high extractability of oligo(benzoic acid) $\mathbf{7_4}$, as well as $\mathbf{7_3}$, toward lanthanoid ions, we prepared a Tb complex, which was found to be a metal cluster later (vide infra), and analyzed it by X-ray crystallography. Compound $\mathbf{7_4}$ (H_4L) was allowed to react with 1 molar equiv of $Tb(NO_3)_3{\cdot}6H_2O$ in the presence of an excess of Et_3N in refluxing toluene–methanol (4:1). After aqueous workup, the mixture was crystallized from CH_2Cl_2–hexane to give cluster **11** formulated as $[Tb_4L_4(H_2O)_6](Et_3NH)_4$. Single crystals suitable for X-ray analysis were obtained by vapor diffusion of diethyl ether to a CH_2Cl_2 solution of cluster **11** (Fig. 7). The cluster adopts a C_i-symmetric cyclic structure composed of four ate complexes $[TbL_{3/4}L_{1/4}]^-$ with four Et_3NH^+ as counter

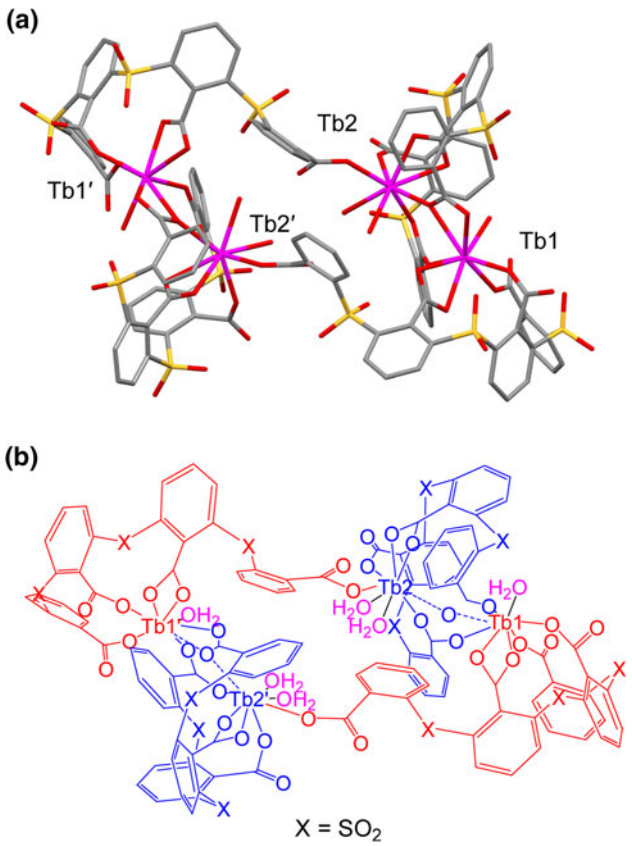


Fig. 7 Crystal structure of **11** (**a**) and its schematic view (**b**). Hydrogen atoms, ^{t}Bu groups, and included solvents are omitted for clarity

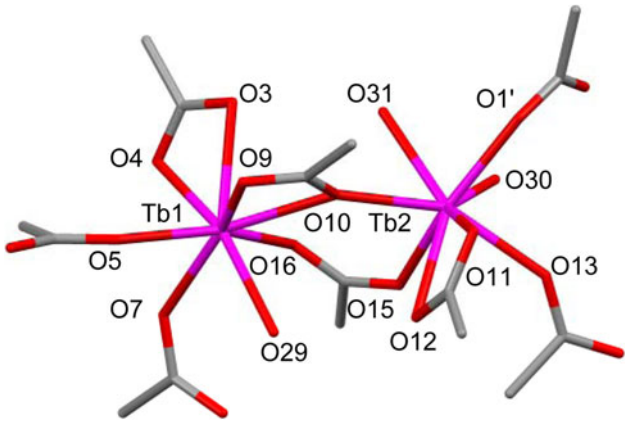


Fig. 8 Coordination spheres of Tb1 and Tb2 in X-ray structure of **11**. Selected atomic distances (Å): Tb1–O3 2.498(6), Tb1–O4 2.376(6), Tb1–O5 2.256(5), Tb1–O7 2.338(6), Tb1–O9 2.486(6), Tb1–O10 2.524(5), Tb1–O16 2.317(6), Tb1–O29 2.356(6), Tb2–O1′ 2.280(5), Tb2–O10 2.385(5), Tb2–O11 2.394(6), Tb2–O12 2.547(6), Tb2–O13 2.340(6), Tb2–O15 2.303(5), Tb2–O30 2.454(6), and Tb2–O31 2.405(5)

cations. There are two independent complexes (Tb1 and Tb2), with which the other two (Tb1′ and Tb2′) are related by an inversion center; the distances between two Tb^{3+} ions are 4.376 Å (Tb1–Tb2), 13.389 Å (Tb1–Tb1′), 7.378 Å (Tb2–Tb2′), and 9.919 Å (Tb1–Tb2′), respectively. Figure 8 shows the coordination environment around the metal centers. Each Tb^{3+} ion is octacoordinated as follows: An L_4^- anion binds to Tb1 with three consecutive carboxylato groups in monodentate (O7), monodentate (O5), and bidentate (O3 and O4) manners, respectively. The remaining terminal carboxylato group binds to Tb2′ in monodentate (O1) manner; this means that the carboxylato group related to this function by the inversion center binds to Tb2 in the same manner. On the other hand, another L_4^- anion binds to Tb1 with the two terminal carboxylato groups in monodentate (O16) and bidentate (O9 and O10) manners, respectively. It also binds to Tb2 with the four carboxylato groups in monodentate (O15), monodentate (O13), bidentate (O11 and O12), and monodentate (O10) manners, respectively. The remainders of the coordination spheres of Tb1 and Tb2 are filled with one and two water molecule(s), respectively. The X-ray structure revealed that $\mathbf{7_4}$ can flexibly ligate to a lanthanoid ion with plural carboxylato groups. It is easily conceivable that this nature contributed to the high extractability. However, at the same time, the structural flexibility seems to have decreased the metal selectivity. It is important to note that no sulfonyl oxygens coordinate to metal ions. This clearly indicates that the higher extractability of $\mathbf{7_4}$ than that of sulfur-bridged analog $\mathbf{10_4}$ is not indebted to the hard nature of the sulfonyl oxygen but originates from the electron-withdrawing effect of the sulfonyl function, which increases the acidity of two adjacent carboxy groups.

Conclusion

Sulfonyl-bridged oligo(benzoic acid)s $\mathbf{7}_n$ were prepared from the corresponding sulfur-bridged oligophenols and analyzed by X-ray crystallography. Solvent extraction experiments of lanthanoid ions with $\mathbf{7}_n$ revealed the relationship between the number of monomer unit and extractability, as well as selectivity. The origin of the high extractability of $\mathbf{7_4}$ was explained based on the X-ray structure of a Tb cluster.

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