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Fluorescent probes of D-(+)-gluconic acid δ-lactone based on binary hosts of chiral calix[5]arene

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Abstract—Chiral calix[5]arenes, (*R*)- and (*S*)-**1** and (*R*)- and (*S*)-**2**, were synthesized. The complexation properties of binary hosts [(*R*)-**1**·Cu^{2+}] and [(*S*)-**1**·Cu^{2+}] towards carbohydrates were explored. The fluorescent titration experiments show that they can selectively recognize D-(+)-gluconic acid δ-lactone **4** with the association constant $K'_R = 4.45\ (\pm 0.20) \times 10^4\ M^{-1}$ and $K'_S = 1.81\ (\pm 0.20) \times 10^4\ M^{-1}$ between various carbohydrates in a MeCN–H_2O (4:1 v/v) solution of HEPES buffer (0.3 mM, pH 7.4), respectively.

1. Introduction

Recently, considerable attention has been focused on multicomponent hosts due to their metal coordination interactions with guests such as anions, amino acids and carbohydrates, which can be significantly stronger than hydrogen bonding and other van der Waals interactions.[1–3] However there are only a few reports on chiral binary hosts and their application.

Carbohydrates play many important functions including structure formation, energy storage and metabolism in organisms. Chiral recognition of carbohydrates is one of the most sophisticated processes of enzymes in organisms. Although many efforts have been dedicated to mimicking the processes of these enzymes, they are mostly localized in weak interactions in non-aqueous systems or forming covalent bond based on boronic acid.[4,5] Herein, we report chiral fluorescent probes of D-(+)-gluconic acid δ-lactone **4** based on binary hosts containing Cu^{2+} and calix[5]arenes having a binaphthyl crown on the lower rim, which exhibit high selectivity for **4** over other carbohydrates in neutral aqueous solutions.

2. Results and discussion

2.1. Synthesis, structure and conformation of (*R*)- and (*S*)-1 and (*R*)- and (*S*)-2

Referring to the synthesis methods for chiral calix[4]-arenes having a binaphthyl crown on the lower rim,[6] (*R*)- or (*S*)-**1** was synthesized from (*R*)- or (*S*)-**3** with *p*-*tert*-butylcalix[5]arene, respectively (Scheme 1). The configurations of (*R*)- and (*S*)-**1** were assigned as in the pattern of 1,2-crown from their ^1H NMR spectra with one phenolic OH signal at 8.57 ppm for both (*R*)- and (*S*)-**1**, respectively.[7,8] (*R*)- and (*S*)-**1** exist as a cone conformation by the information of bridging methylene carbon signals at δ <33 ppm in their ^{13}C NMR spectra.[9] (*R*)- or (*S*)-**2** was synthesized from (*R*)- or (*S*)-**1**, respectively, with CH_3I in the presence of NaH in THF (Scheme 1).

2.2. Recognition of Cu^{2+}

In the fluorescence spectra of (*R*)- and (*S*)-**1**, maximum excitation and emission wavelengths were observed at 282 and 365 nm in MeCN–H_2O (4:1, v/v) solution with HEPES buffer (0.3 mM, pH 7.4), respectively. All of the fluorescent titration experiments were performed after mixing for 24 h. The emission spectra of (*R*)- and (*S*)-**1** in the presence of various concentrations of $Cu(ClO_4)_2$ are shown in Figure 1, from which it can be seen that the fluorescent intensity ($\lambda_{max} = 365$ nm) of (*R*)- or (*S*)-**1** decreased upon the addition of Cu^{2+} with no

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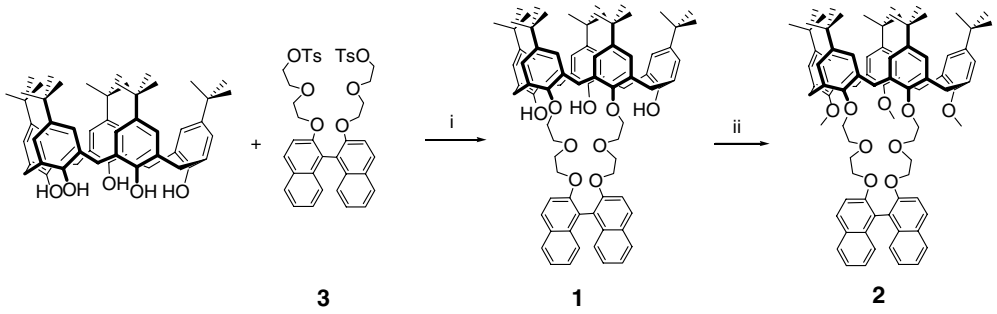

Scheme 1. Reagents and conditions: (i) K_2CO_3, toluene, 80 °C; (ii) CH_3I, NaH, THF, reflux.

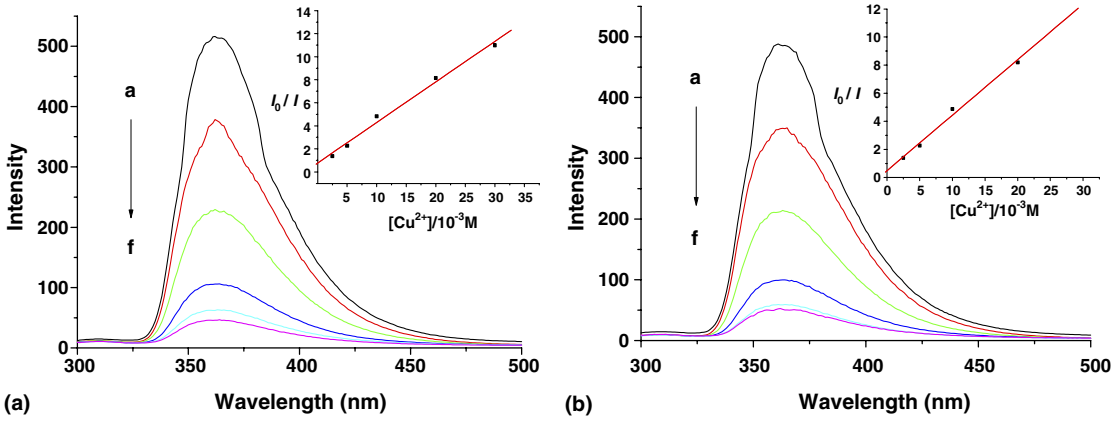

Figure 1. Fluorescent titrations of (*R*)-**1** (a) and (*S*)-**1** (b) with $Cu(ClO_4)_2$ in MeCN–H_2O (4:1, v/v) solution with HEPES buffer (0.3 mM, pH 7.4), $\lambda_{ex} = 282$ nm, $[(R)\text{-}\mathbf{1}] = [(S)\text{-}\mathbf{1}] = 1.0 \times 10^{-6}$ M, $[Cu(ClO_4)_2] = 1.0 \times 10^{-3}$ M. From a–f: 0.0, 2.5, 5.0, 10.0, 20.0, 30.0 equiv. Inset: the plot of I_0/I versus $[Cu^{2+}]$.

significant change of emission maxima. When the concentrations of Cu^{2+} increased up to 20 equiv, the fluorescent intensity of (*R*)- or (*S*)-**1** did not change upon continuous addition of Cu^{2+}. From the fluorescent titration experiments, the association constants were calculated as $K_R = 1.42\ (\pm 0.20) \times 10^6\ M^{-1}$ ($R = 0.995$) and $K_S = 1.22\ (\pm 0.20) \times 10^6\ M^{-1}$ ($R = 0.998$) in 1:1 stoichiometry with Stern-Volmer equation.

Similar measurements for other ions including Li^+, Na^+, K^+, Mg^{2+}, Ba^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+} and Zn^{2+} were performed with no obvious spectral change of (*R*)- or (*S*)-**1** appearing up to 30 equiv of these metal ions. These results imply that (*R*)- or (*S*)-**1** has high selective complexibility towards Cu^{2+} over other ions.

In the fluorescence spectra of (*R*)- and (*S*)-**2**, maximum excitation and emission wavelengths were observed at 280 and 365 nm in MeCN–H_2O (4:1, v/v) solution with HEPES buffer (0.3 mM, pH 7.4), respectively. However, similar fluorescent titration experiments prove that (*R*)- and (*S*)-**2** have no complexation ability towards any of these ions including Cu^{2+}.

2.3. Recognition of D-(+)-gluconic acid δ-lactone

The complex $[(R)\text{-}\mathbf{1}\cdot Cu^{2+}]$ or $[(S)\text{-}\mathbf{1}\cdot Cu^{2+}]$ formed from (*R*)- or (*S*)-**1** and 20 equiv Cu^{2+} in MeCN–H_2O (4:1, v/v) solution with HEPES buffer (0.3 mM, pH 7.4) was used as a binary host. In the fluorescent spectra of $[(R)\text{-}\mathbf{1}\cdot Cu^{2+}]$ and $[(S)\text{-}\mathbf{1}\cdot Cu^{2+}]$, maximum excitation and emission wavelengths are the same as those of (*R*)- or (*S*)-**1** at 282 and 365 nm, respectively.

The fluorescent titration experiments of $[(R)\text{-}\mathbf{1}\cdot Cu^{2+}]$ or $[(S)\text{-}\mathbf{1}\cdot Cu^{2+}]$ with some carbohydrates including D-(+)-xylose, D-(−)-ribose, 2-deoxy-D-ribose, D-(−)-arabinose, D-(+)-glucose, methyl α-D-glucopyranoside and D-(+)-gluconic acid δ-lactone **4** were carried out. The results indicated that these binary hosts exhibit high selectivity only to **4**. The emission spectra of $[(R)\text{-}\mathbf{1}\cdot Cu^{2+}]$ in the presence of various concentrations of **4** is shown in Figure 2a from which it can be seen that its fluorescent intensity ($\lambda = 365$ nm) increased upon the addition of **4** with no significant change in emission maxima. When the concentration of **4** increased up to 8 equiv, its fluorescent intensity increased to maximum. The association constant for $[(R)\text{-}\mathbf{1}\cdot Cu^{2+}]$-**4** in a 1:1 stoichiometry was calculated as $K'_R = 4.45\ (\pm 0.20) \times 10^4\ M^{-1}$ ($R = 0.991$) from Stern-Volmer equation in Figure 3. A similar case occurred for $[(S)\text{-}\mathbf{1}\cdot Cu^{2+}]$. When the concentration of **4** was up to 8 equiv, its fluorescent intensity increased to a maximum (Fig. 2b). The association constant for $[(S)\text{-}\mathbf{1}\cdot Cu^{2+}]$-**4** in 1:1 stoichiometry was calculated as $K'_S = 1.81\ (\pm 0.20) \times 10^4\ M^{-1}$ ($R = 0.995$) from the Stern-Volmer equation in Figure 3. The enantioselectivity K (K'_S/K'_R) is 2.4.

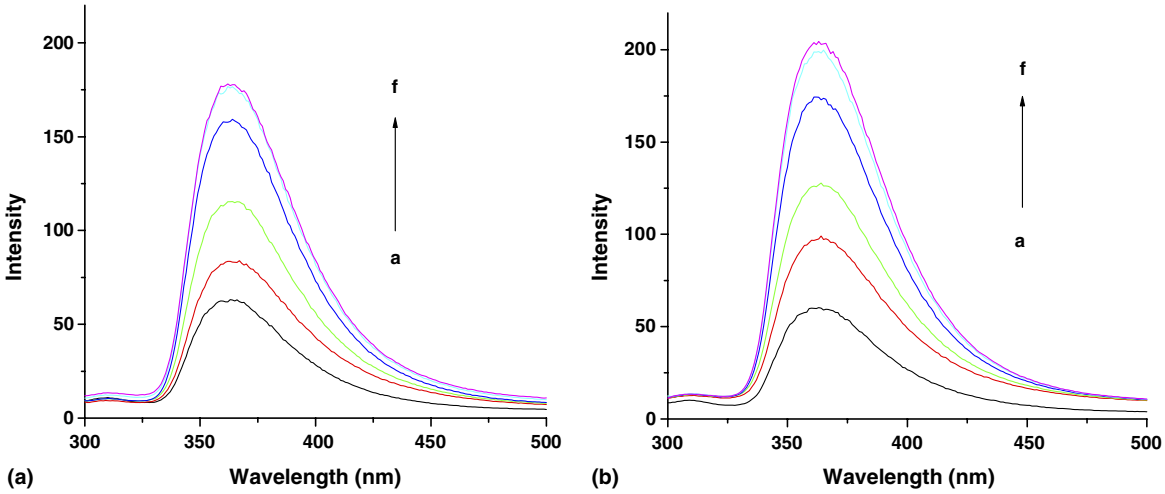

Figure 2. Fluorescent titrations of [(*R*)-**1**·Cu^{2+}] (a), [(*S*)-**1**·Cu^{2+}] (b) with **4** in MeCN–H_2O (4:1, v/v) solution with HEPES buffer (0.3 mM, pH 7.4), $\lambda_{ex} = 282$ nm, [(*R*)-**1**·Cu^{2+}] = [(*S*)-**1**·Cu^{2+}] = 1.0×10^{-6} M, [**4**] = 2.0×10^{-4} M. From a–f: 0.0, 2.0, 4.0, 6.0, 8.0, 10.0 equiv.

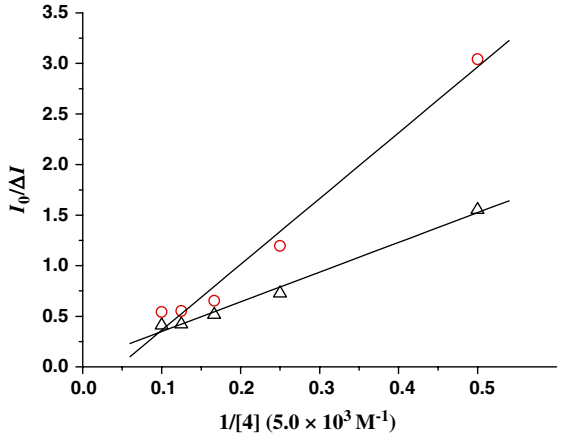

Figure 3. The plot of $I_0/\Delta I$ of [(*R*)-**1**·Cu^{2+}] (○) and [(*S*)-**1**·Cu^{2+}] (△) versus 1/[**4**].

Due to the methylated (*R*)- or (*S*)-**2** having no complexation ability towards Cu^{2+} and decreasing the fluorescent intensity upon the addition of Cu^{2+} to (*R*)- or (*S*)-**1**, the above-mentioned binary host, [(*R*)-**1**·Cu^{2+}] or [(*S*)-**1**·Cu^{2+}] may be a complex of Cu^{2+} with binaphthoxy and phenolic hydroxy oxygen of (*R*)- or (*S*)-**1**. It has been reported that a dinuclear or a mononuclear Cu^{2+} complex could recognize carbohydrates in alkaline but not in neutral solution,[3] so our results can be understandable. The high selectivity of the binary hosts to **4** may be due to the existence of carboxy group, the details are still under investigation.

3. Conclusion

Chiral calix[5]arenes, which have a binaphthyl crown on the lower rim, (*R*)-, (*S*)-**1** and (*R*)-, (*S*)-**2** were successfully synthesized. The complexes [(*R*)-**1**·Cu^{2+}] and [(*S*)-**1**·Cu^{2+}] were used as binary hosts to recognize carbohydrates. The fluorescent titration experiments show that the binary hosts can selectively recognize **4** between various carbohydrates.

4. Experimental

Column chromatography was conducted with 160–200 mesh silica gel. Melting points were measured with an X-4 digital indicating melting point apparatus. Optical rotations were recorded using an AA-10R polarimeter. IR spectra were obtained using JASCO FT/IR-480 plus spectrometer (KBr pellets). Mass spectra were recorded in MALDI-TOF MS using Bruker BIFLEX instrument. NMR spectra were recorded on Bruker AV 300 spectrometer. NMR chemical shifts are given in parts per million relative to tetramethylsilane.

4.1. General procedure for the preparation of 31,32-*p*-*tert*-butylcalix[5](*R*)-1,1′-bi-2-naphtho-crown-6 (*R*)-1 and 31,32-*p*-*tert*-butylcalix[5](*S*)-1,1′-bi-2-naphtho-crown-6 (*S*)-1

To a mixture of *p*-*tert*-butylcalix[5]arene (81 mg, 0.1 mmol) and K_2CO_3 (28 mg, 0.2 mmol) in toluene (100 mL) was added binaphthyl derivative (*R*)-**3** or (*S*)-**3** (77 mg, 0.1 mmol). The solution was heated at 80 °C for 3 days. After removal of the solvent in vacuo, the residue was acidified by 10% HCl and partitioned between water and CH_2Cl_2. (*R*)-**1** or (*S*)-**1** was obtained through column chromatography (petroleum ether/ethyl acetate, 20:1 v/v) as a white powder [(*R*)-**1**, 25 mg, yield 20%; (*S*)-**1**, 30 mg, yield 24%].

4.1.1. Compound (*R*)-1. Mp 164–166 °C; $[\alpha]_D^{25} = +106$ (*c* 0.9, CH_2Cl_2); IR (KBr) 3397, 2958, 1591, 1484; ^1H NMR ($CDCl_3$) δ 8.57 (s, 1H, OH), 7.85 (d, 1H, $J = 8.9$ Hz, binaphthylH), 7.75 (d, 1H, $J = 6.7$ Hz, binaphthylH), 7.74 (d, 1H, $J = 9.2$ Hz, binaphthylH), 7.70 (d, 1H, $J = 8.0$ Hz, binaphthylH), 7.57 (s, 1H, OH), 7.54 (d, 1H, $J = 9.1$ Hz, binaphthylH), 7.48 (d, 1H, $J = 8.9$ Hz, binaphthylH), 7.34 (s, 1H, OH), 7.31–7.09 (m, 12H, binaphthylH and ArH), 6.95 (s, 2H, ArH), 6.59 (s, 1H, ArH), 6.56 (s, 1H, ArH), 4.57–3.26 (m, 26H, $ArCH_2Ar$ and polyether chain), 1.29 (s, 9H, $C(CH_3)_3$), 1.26 (s, 9H, $C(CH_3)_3$), 1.22 (s, 9H, $C(CH_3)_3$), 1.07 (s, 9H, $C(CH_3)_3$), 0.70 ppm (s, 9H,

$C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 154.6, 154.0, 151.7, 151.6, 149.2, 148.3, 147.9, 146.4, 145.9, 143.0, 142.7, 142.4, 134.1, 134.0, 133.6, 133.5, 133.2, 132.7, 129.7, 129.6, 129.3, 129.2, 128.0, 127.9, 127.3, 127.1, 126.8, 126.7, 126.4, 126.3, 126.2, 126.1, 126.0, 125.9, 125.8, 125.6, 125.5, 125.4, 125.3, 125.2, 125.1, 125.0, 124.7, 124.3, 123.6, 123.5, 121.0, 120.0, 116.7, 115.3 (ArC), 72.8, 71.8, 71.0, 70.4, 70.3, 70.0, 69.7, 69.0 (polyether chain), 34.1, 34.0, 33.9, 33.8, 33.7 ($C(CH_3)_3$), 31.6, 31.5, 31.4, 31.3, 30.9 ($C(CH_3)_3$), 31.8, 30.8, 30.7 ppm ($ArCH_2Ar$); MALDI-TOF MS (*m*/*z*): 1260 ($[M+Na]^+$), 1276 ($[M+K]^+$). Anal. Calcd for $C_{83}H_{96}O_9$: C, 80.55; H, 7.82. Found: C, 80.15; H, 7.86.

4.1.2. Compound (*S*)-1. Mp 166–167 °C; $[\alpha]_D^{25} = -110$ (*c* 0.9, CH_2Cl_2); IR (KBr) 3389, 2959, 1591, 1483; ^1H NMR ($CDCl_3$) δ 8.57 (s, 1H, OH), 7.85 (d, 1H, $J = 9.0$ Hz, binaphthylH), 7.75 (d, 1H, $J = 7.2$ Hz, binaphthylH), 7.74 (d, 1H, $J = 9.0$ Hz, binaphthylH), 7.70 (d, 1H, $J = 8.0$ Hz, binaphthylH), 7.57 (s, 1H, OH), 7.54 (d, 1H, $J = 9.0$ Hz, binaphthylH), 7.48 (d, 1H, $J = 9.0$ Hz, binaphthylH), 7.34 (s, 1H, OH), 7.31–7.09 (m, 12H, binaphthylH and ArH), 6.96 (s, 2H, ArH), 6.59 (s, 1H, ArH), 6.56 (s, 1H, ArH), 4.57–3.26 (m, 26H, $ArCH_2Ar$ and polyether chain), 1.30 (s, 9H, $C(CH_3)_3$), 1.27 (s, 9H, $C(CH_3)_3$), 1.22 (s, 9H, $C(CH_3)_3$), 1.07 (s, 9H, $C(CH_3)_3$), 0.70 ppm (s, 9H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 154.6, 154.0, 151.7, 151.6, 149.2, 148.2, 147.8, 146.4, 145.9, 143.0, 142.7, 142.4, 134.1, 134.0, 133.6, 133.5, 133.2, 132.6, 129.6, 129.5, 129.3, 129.2, 128.0, 127.8, 127.3, 127.1, 126.7, 126.6, 126.4, 126.3, 126.2, 126.1, 126.0, 125.9, 125.8, 125.6, 125.5, 125.4, 125.3, 125.2, 125.1, 125.0, 124.6, 124.3, 123.6, 123.4, 121.0, 119.9, 116.6, 115.3 (ArC), 72.8, 71.8, 70.9, 70.4, 70.3, 70.0, 69.7, 69.0 (polyether chain), 34.0, 33.9, 33.8, 33.7 33.6 ($C(CH_3)_3$), 31.6, 31.5, 31.4, 31.3, 30.9 ($C(CH_3)_3$), 31.8, 30.8, 30.7 ppm ($ArCH_2$-Ar); MALDI-TOF MS *m*/*z* MALDI-TOF MS (*m*/*z*): 1260 ($[M+Na]^+$), 1276 ($[M+K]^+$). Anal. Calcd for $C_{83}H_{96}O_9$: C, 80.55; H, 7.82. Found: C, 80.59; H, 8.01.

4.2. General procedure for the preparation of 33,34,35-trimethoxy-31,32-*p*-*tert*-butyl-calix[5](*R*)-1,1′-bi-2-naphtho-crown-6 (*R*)-2 and 33,34,35-trimethoxy-31,32-*p*-*tert*-butylcalix[5](*S*)-1,1′-bi-2-naphtho-crown-6 (*S*)-2

To a mixture of (*R*)-**1** or (*S*)-**1** (124 mg, 0.1 mmol) and NaH (14 mg, 0.6 mmol) in MeCN (20 mL) was added CH_3I (37 μL, 0.6 mmol). The solution was refluxed for 8 h. After removal of the solvent in vacuo, the residue was acidified by 10% HCl and partitioned between water and CH_2Cl_2. (*R*)-**2** or (*S*)-**2** was obtained through column chromatography (petroleum ether/ethyl acetate, 15:1 v/v) as a white powder (*R*)-**2**, 124 mg, yield 97%; (*S*)-**2**, 125 mg, yield 98%.

4.2.1. Compound (*R*)-2. Mp 140–142 °C; $[\alpha]_D^{25} = +44$ (*c* 2.7, CH_2Cl_2); IR (KBr) 3427, 2958, 1592, 1480; ^1H NMR ($CDCl_3$) δ 7.91 (d, 1H, $J = 9.0$ Hz, binaphthylH), 7.84 (d, 1H, $J = 8.0$ Hz, binaphthylH), 7.77 (d, 2H, $J = 8.6$ Hz, binaphthylH), 7.50 (d, 1H, $J = 9.0$ Hz, binaphthylH), 7.41 (d, 1H, $J = 9.0$ Hz, binaphthylH), 7.32–6.95 (m, 16H, binaphthylH and ArH), 4.55 (d, 1H, $J = 14.1$ Hz, $ArCH_2Ar$), 4.26–4.02 (m, 6H, $ArCH_2Ar$ and polyether chain), 3.83–3.20 (m, 19H, $ArCH_2Ar$ and polyether chain), 2.98 (s, 3H, CH_3), 2.94 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 1.22 (s, 18H, $C(CH_3)_3$), 1.18 (s, 9H, $C(CH_3)_3$), 1.17 (s, 9H, $C(CH_3)_3$), 1.14 ppm (s, 9H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 155.0, 154.7, 154.6, 154.5, 154.2, 152.8, 152.5, 145.2, 145.1, 145.0, 144.8, 134.3, 134.2, 134.1, 134.0, 133.9, 133.8, 133.7, 133.6, 133.5, 133.0, 129.6, 129.3, 129.2, 129.1, 127.9, 127.8, 126.3, 126.2, 126.1, 126.0, 125.9, 125.8, 125.7, 125.6, 125.5, 125.4, 123.6, 123.5, 121.0, 120.2, 117.8, 115.0 (ArC), 72.2, 71.9, 70.6, 70.1, 70.0, 69.9, 69.6, 69.4 (polyether chain), 60.3, 60.2, 59.6 (CH_3), 34.2, 34.1, 34.0 ($C(CH_3)_3$), 31.5, 31.4 ($C(CH_3)_3$), 33.4, 31.9, 29.7 ppm ($ArCH_2Ar$); MALDI-TOF MS (*m*/*z*): 1302 ($[M+Na]^+$), 1318 ($[M+K]^+$). Anal. Calcd for $C_{86}H_{102}O_9$: C, 80.71; H, 8.03. Found: C, 80.54; H, 8.14.

4.2.2. Compound (*S*)-2. Mp 140–142 °C; $[\alpha]_D^{25} = -45$ (*c* 2.7, CH_2Cl_2); IR (KBr) 3416, 2961, 1593, 1480; ^1H NMR ($CDCl_3$) δ 7.91 (d, 1H, $J = 9.0$ Hz, binaphthylH), 7.83 (d, 1H, $J = 8.1$ Hz, binaphthylH), 7.76 (d, 2H, $J = 8.7$ Hz, binaphthylH), 7.50 (d, 1H, $J = 9.0$ Hz, binaphthylH), 7.40 (d, 1H, $J = 9.0$ Hz, binaphthylH), 7.32–6.95 (m, 16H, binaphthylH and ArH), 4.55 (d, 1H, $J = 14.1$ Hz, $ArCH_2Ar$), 4.26–4.01 (m, 6H, $ArCH_2Ar$ and polyether chain), 3.82–3.18 (m, 19H, $ArCH_2Ar$ and polyether chain), 2.98 (s, 3H, CH_3), 2.94 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 1.21 (s, 18H, $C(CH_3)_3$), 1.18 (s, 9H, $C(CH_3)_3$), 1.17 (s, 9H, $C(CH_3)_3$), 1.14 ppm (s, 9H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 155.0, 154.7, 154.6, 154.5, 154.2, 152.8, 152.5, 145.2, 145.1, 145.0, 144.8, 134.3, 134.2, 134.1, 134.0, 133.9, 133.7, 133.6, 133.5, 133.0, 129.6, 129.3, 129.2, 129.1, 127.9, 127.8, 126.3, 126.2, 126.1, 126.0, 125.9, 125.8, 125.7, 125.6, 125.5, 125.4, 123.6, 123.5, 121.1, 120.2, 117.8, 115.1 (ArC), 72.3, 71.9, 70.6, 70.2, 70.1, 70.0, 69.6, 69.4 (polyether chain), 60.3, 60.2, 59.7 (CH_3), 34.1, 34.0, 33.9 ($C(CH_3)_3$), 31.6, 31.5, 31.4 ($C(CH_3)_3$), 33.5, 32.0, 29.8 ppm ($ArCH_2Ar$); MALDI-TOF MS (*m*/*z*): 1302 ($[M+Na]^+$), 1318 ($[M+K]^+$). Anal. Calcd for $C_{86}H_{102}O_9$: C, 80.71; H, 8.03. Found: C, 80.41; H, 8.03.

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