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Synthesis, NMR conformational studies and host–guest behaviour of new (+)-tartaric acid derivatives

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Abstract—A series of dimeric α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanol TADDOLs has been prepared and host–guest interactions of these structures have been characterized using a series of ^{1}H NMR studies. Enantioselective recognition of the chiral alcohols glycidol and menthol was observed for phenyl and 2-naphthyl derivatives. The influence of steric bulk on the dynamic fluxional behaviour of the TADDOL structures was demonstrated by dynamic NMR.

1. Introduction

Resolution is of critical importance for the preparation of enantiomerically pure structures for use in organic synthesis, and for the study of chiral compounds with biological activity. Significant research effort has been focused upon the development of systems and techniques capable of the selective recognition of one of the enantiomers.[1] The often remarkable molecular complementarity displayed by macromolecular recognition systems provides opportunities for application in the resolution of racemates. TADDOLs, molecules containing the α,α,α′,α′-tetraaryl-1,3-dioxolane-4,5-dimethanol structure (Fig. 1), were first reported by Narasaka in 1986,[2] and have been shown to be useful as host molecules for the resolution of non-voluminous racemates.[3] These versatile chiral auxiliaries have also been used in a range of other application areas, for example, for chemical catalysis.[4–12]

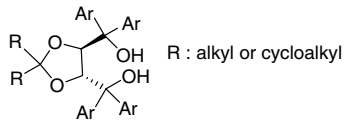

Figure 1.

Recently, a new generation of TADDOLs derived from cyclohexanediones and (+)-tartaric acid has been described, which can accommodate relatively voluminous guests.[13] But only a limited number of studies of this new class of host compounds have been reported.[14,15]

Herein, a series of TADDOLs **3a**–**d** (Scheme 1) derived from the bis-ketal of diethyl (+)-tartrate and 1,4-cyclohexanedione have been synthesized and the dynamic behaviour of these TADDOLs has been studied by ^{1}H NMR. Recognition of the synthetically useful small chiral alcohols (−)-menthol **4a**, (+)-menthol **4b**, (−)-glycidol **5a** and (+)-glycidol **5b** (Fig. 2) by the various TADDOLs has been examined. Resolution of these particular chiral alcohols, which are used in various asymmetric syntheses,[16–23] has been the focus of a number of recent studies.[24–28]

2. Results and discussion

2.1. Synthesis of the new TADDOLs derived from 1,4-cyclohexanedione and diethyl (+)-tartrate

The synthesis of a series of octa-aryl substituted TADDOLs was achieved using the methodology developed by

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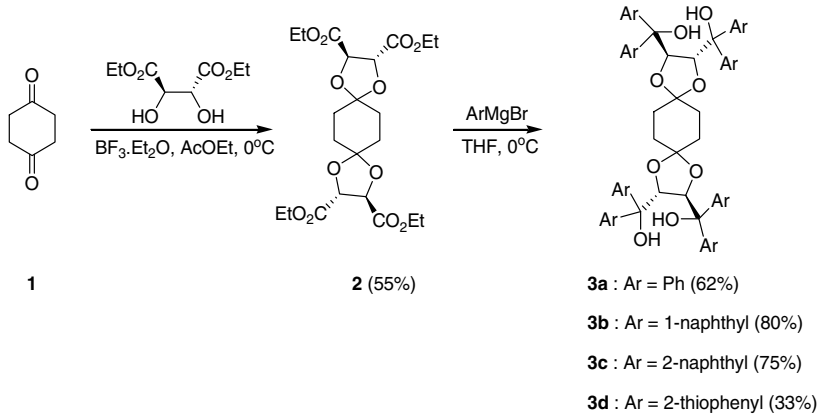

Scheme 1. Synthesis of the TADDOLs **3a**–**d**.

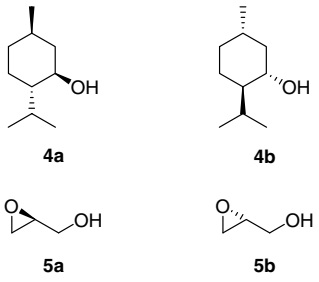

Figure 2.

Tanaka et al.[13] The reaction between the 1,4-cyclohexanedione **1** and diethyl (2*R*,3*R*)-(+)-tartrate in the presence of $BF_3{\cdot}Et_2O$ gave the tetraester **2** in moderate yield. Subsequent reaction of the intermediate **2** with various aryl Grignard reagents furnished the TADDOLs **3a**–**d** (Scheme 1).

2.2. Dynamic behaviour of the TADDOLs in solution

The room temperature ^{1}H NMR spectra of the 1-naphthyl TADDOL, **3b**, demonstrated broad peaks corresponding to the resonances of the aromatic and methine protons. Spectra recorded at elevated temperature resulted in a sharpening of these peaks. This indicated the presence of dynamic processes, which take place within the NMR time frame, and suggested a closer examination of the temperature dependence of the spectrum of **3b**, and those of the other TADDOL derivatives used in this study.

The TADDOLs all demonstrated temperature dependent dynamic behaviour from which coalescence temperature (T_C) could be determined for the methine protons, Table 1. Exchange rate constants (k_C) were calculated for **3b** and **3d** using the Eyring equation, and Gibbs free energies of activation ($\Delta G^{\neq}$) using k_C and T_C.[29] The spectra of the other TADDOLs were not sufficiently resolved at the lowest temperature studied (207 K) to permit the calculation of these factors.

In the case of the TADDOL **3d**, the ^{1}H NMR spectrum recorded in acetone-d_6 at low temperature (210 K) revealed an AB system comprised of two apparent doublets (^3J = 7.02 Hz) arising from the methine hydrogens. Increasing the temperature resulted in coalescence of these peaks (T_C = 229 K). By increasing the temperature to 250 K, the resonance arising from the methine protons was resolved into a sharp singlet (Fig. 3).

Table 1. Measured coalescence temperatures (T_C), exchange rate constants (k_C) and Gibbs free energies of activation ($\Delta G^{\neq}$) for the TADDOLs **3a**–**d** in acetone-d_6

Entry	TADDOL	T_C (K)	k_C (s^{-1})[a]	$\Delta G^{\neq}$ (kJ mol^{-1})[b]
1	**3a**	220	nr[d]	nr[d]
2	**3b**	334[c]	97	69.6 ± 2
3	**3c**	217	nr[d]	nr[d]
4	**3d**	229	210	45.4 ± 2

[a] $k_C = 2.22/\sqrt{(\Delta V^2 + 6J_{AB}^2)}$ s^{-1}.
[b] $\Delta G^{\neq} = 19.14T_C(10.32 + \log(T_C/k_C))$ J mol^{-1}.
[c] Measured in DMSO-d_6.
[d] nr = not resolved.

In contrast to the relatively high coalescence temperature of **3b**, 334 K, the T_Cs of the TADDOLs **3a**–**c** were found between 217 and 229 K. This indicated that the dynamic behaviour of **3b** is markedly different from the other members of this series. Indeed, the free energy barrier ($\Delta G^{\neq}$) for the dynamic NMR process in **3b** is higher than for **3d**, which we attribute to the greater steric hindrance arising from the bulkier 1-naphthyl moieties, which inhibit rotation of the side chains on the C–C bond of the five-membered rings. Interestingly, similar spectral behaviour was observed for the methylene protons of the cyclohexane ring, (though resolution could not be achieved within the temperature range studied) which indicates restricted interconversion between the two chair conformations of the cyclohexane ring.

Collectively, these observations allow us to conclude that these TADDOLs exhibit dynamic fluxional behaviour in solution.

2.3. Host–guest behaviour of the new TADDOLs

Previous studies have demonstrated that some TADDOL derived systems can function as chiral hosts for

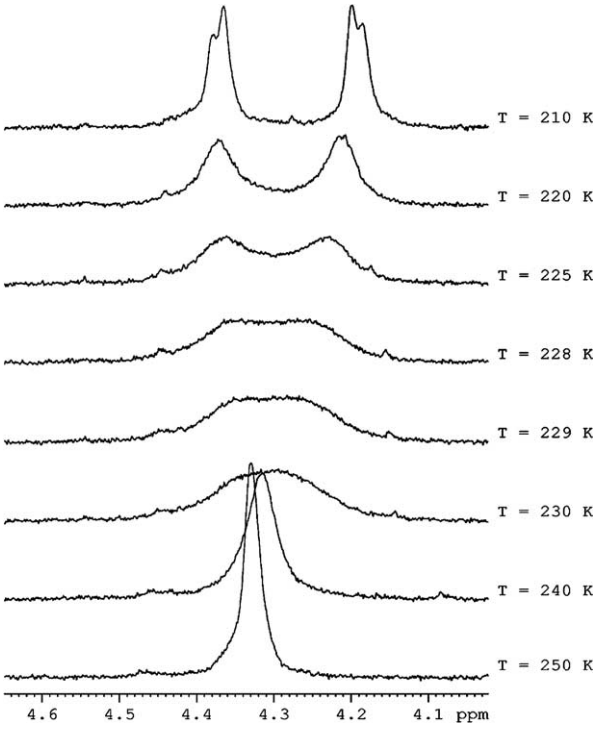

Figure 3. Variable-temperature ^{1}H NMR spectra of the methine protons **3d** in acetone-d_6.

the resolution of racemic mixture of alcohols.[5,13] ^{1}H NMR titration experiments were performed in order to determine the nature and strength of TADDOL–guest interactions with the small chiral alcohols (−)-menthol **4a**, (+)-menthol **4b**, (−)-glycidol **5a** and (+)-glycidol **5b** (Fig. 2). By analogy to the X-ray studies reported by Tanaka et al.,[13] it was anticipated that in non-polar media the guest alcohols would interact with the TADDOLs through hydrogen bonding interactions between the hydroxyls of the host and guest. Moreover, the nature of the pendant side chains and the inherent chirality of the TADDOLs themselves were expected to influence the ligand selectivities of the host structures.

In the case of the TADDOL, **3a**, developed by Tanaka et al.,[13] enantioselective recognition of both menthol and glycidol was observed (Table 2, entries 1–4). In all cases, the sequential addition of the ligand to the TADDOL led to a concentration dependent downfield shift of the TADDOL hydroxyl proton resonance. Non-linear regression analysis of the binding isotherms, Figure 4, afforded apparent dissociation constants (app. K_d) for the various interactions. The mechanism of interaction in $CDCl_3$ solution, that is, hydrogen bonding between ligand and receptor hydroxyl moieties, is comparable to that described by Tanaka et al.[13] As reflected in the differences in the app. K_d for the respective complexes, the observed enantioselectivity of the TADDOL for menthol was superior to that for the small structure glycidol.

In the case of the naphthyl group containing TADDOLs **3b** and **3c** the steric bulk of the pendant side chains is greater than in the case of **3a**. On account of the nature of the point of attachment of the naphthyl group to the

Table 2. Dissociation constants [K_d (μM)] for complex formation

Entry	Host (TADDOL)	Guest (chiral alcohol)	K_d (μM)[a]
1	**3a**	**4a**	550 ± 30
2	**3a**	**4b**	100 ± 30
3	**3a**	**5a**	190 ± 60
4	**3a**	**5b**	630 ± 20
5	**3b**	**4a**	nc[b]
6	**3b**	**4b**	nc[b]
7	**3b**	**5a**	nc[b]
8	**3b**	**5b**	nc[b]
9	**3c**	**4a**	60 ± 7
10	**3c**	**4b**	1040 ± 30
11	**3c**	**5a**	170 ± 30
12	**3c**	**5b**	170 ± 30
13	**3d**	**4a**	30 ± 0.9
14	**3d**	**4b**	10 ± 4
15	**3d**	**5a**	10 ± 1
16	**3d**	**5b**	10 ± 1

[a] Apparent dissociation constants were calculated with non-linear line fitting to a one-site model with the software package Prism (version 3.03, GraphPad Software, USA).

[b] nc = no complexation were observed under these experimental conditions.

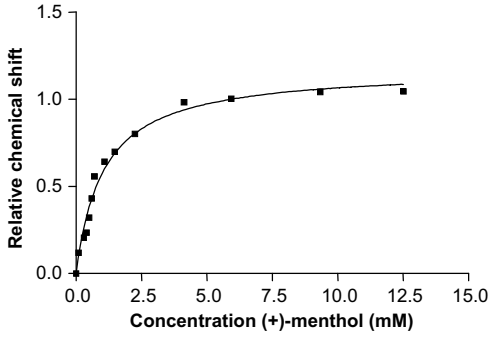

Figure 4. Binding isotherm from a TADDOL **3c**/(+)-menthol **4b** titration in $CDCl_3$.

TADDOL, the 1-naphthyl derivative, **3b**, was perceived to provide more steric crowding around the hydroxyls than the 2-naphthyl case, **3c**. This is reflected in the results of the dynamic NMR studies described previously.

Titration studies with the 2-naphthyl derivative, **3c** (Table 2, entries 9 and 10), showed both a reversal in selectivity for the enantiomers of menthol, as compared to the phenyl derivative, **3a**. However, in the case of glycidol no enantioselectivity was observed. Interestingly, the affinity of both (−)- and (+)-glycidol for **3c** lie between the affinities of the favoured and unfavoured enantiomers of menthol, (−) and (+), respectively. The performance of **3c** was found to be in stark contrast to that of **3b**, the 1-naphthyl derivative (Table 2, entries 5–8). In this case, no changes in the ^{1}H NMR spectra of the TADDOL were observed upon ligand addition (up to 30 mM). This lack of ligand–TADDOL interaction was attributed to the excessive steric crowding around the diol units afforded by the 1-naphthyl groups, thus eliminating the possibility for access of the ligands to the TADDOL hydroxyls. This observation concurs

with the inferences drawn from the dynamic NMR studies described above. The extent to which access is denied is reflected in the fact that titrations with the small chiral alcohol, glycidol ($C_3H_6O_2$), induced no change in the chemical shift of the TADDOL hydroxyl proton. Job-plot analysis of the interaction between **3c** and the enantiomers of menthol was performed in order to establish the stoichiometry of the host–guest system. A 1:1 complex was observed for both the TADDOL **3c**/(−)-menthol **4a** (Fig. 5) and for TADDOL **3c**/(+)-menthol **4b** systems. This result is in contrast to the 1:2 complex observed by Tanaka et al. in X-ray diffraction studies of the TADDOL **3a** and 2-methyl-1-butanol.[13] The reason for the difference in complex stoichiometry is not obvious from the experimental information available. Possible explanations may involve the bulkier nature of the pendant side chains of **3c** and the fact that the stoichiometries were obtained in different states (solid and solution).

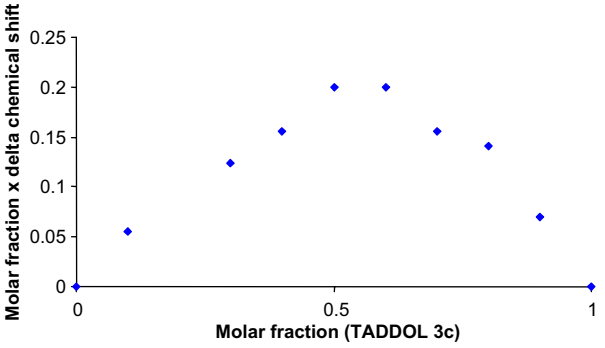

Figure 5. Job-plot curve observed for the system TADDOL **3c**/(−)-menthol **4a**.

Tanaka et al. have previously described the importance of the pendant side chains on the capacity of TADDOL systems to discriminate selectively between ligand structures.[13] The results presented here provide further support for this and highlight the delicate balance between structure and recognition characteristics available in these systems, for example, the reversal in enantioselectivity for menthol observed when comparing the phenyl **3a** and 2-naphthyl **3c** derivatives.

Studies using the thiophenyl TADDOL **3d** demonstrated high affinity for both glycidol and menthol, though no enantioselectivity was observed under these conditions (Table 2, entries 13–16). We suggest that the observed binding is non-specific in character, and most probably involves hydrogen bonding-like interactions between the ligands and the sulfur atoms of the thiophenyl.

3. Conclusion

A series of new TADDOLs has been prepared and host–guest interactions of these structures have been characterized using a series of ^{1}H NMR titration studies. The results highlight the significance TADDOL structure on ligand selectivity. The effect of steric bulk on the dynamic behaviour of the TADDOLs was demonstrated by NMR. The observed enantioselectivities suggest the use of TADDOLs as chiral selectors for chromatographic stationary phase development, in particular for the resolution of low molecular weight chiral alcohols, which are valuable tools for use in synthetic organic chemistry.

4. Experimental

4.1. General

Melting points were determined on a Büchi 510 instrument and were not corrected. Optical rotation was measured on a Perkin–Elmer 141 polarimeter. Flash chromatography and MPLC (medium pressure liquid chromatography) were performed on silica gel (Merck 60).[30] High resolution mass spectra were obtained by electronspray ionization (ESI) or fast atom bombardment (FAB). THF was dried over sodium/benzophenone. The ^{1}H NMR and the ^{13}C NMR spectra were recorded at 250/500 MHz and 63/125 MHz, respectively. $CDCl_3$, DMSO-d_6 and acetone-d_6 were used as solvents while the signals of the solvents served as internal standards. Chemical shifts (δ) are reported in ppm and J values given in hertz. ^{13}C NMR spectra were partially resolved by using DEPT experiment ($\theta = 135°$). The IR absorptions are cited in cm^{-1}.

4.2. (2*R*,3*R*,10*R*,11*R*)-Tetrakis(ethyl carboxylate)-1,4,9,12-tetraoxadispiro[4.2.4.2]tetradecane 2

To a solution of diethyl (2*R*,3*R*)-(+)-tartrate (27.7 mL, 162 mmol) in AcOEt (170 mL) was added the 1,4-cyclohexanedione **1** (10 g, 89.2 mmol). The reaction mixture was then cooled to 0 °C and $BF_3{\cdot}Et_2O$ (25.7 mL, 202.7 mmol) was added dropwise. After stirring for 2 h at this temperature, the reaction mixture was stirred at rt overnight. The pH of the reaction mixture was adjusted to 7/8 with NaOH (2 M). Then the phases were separated and the aqueous phase was extracted three times with EtOAc. The combined organic phases were dried over $MgSO_4$ and evaporated in vacuo. The crude product was recrystallized from EtOH to give **2** as a white powder (24 g, 55%). Mp = 95–96 °C; $[\alpha]_D^{20} = -25.6$ (c 1.01, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 4.80 (s, 4H, 4 × CH), 4.30–4.25 (dq, $^3J = 7.0$, $^3J = 2.3$, 8H, 4 × CH_2CH_3), 1.96 (s, 8H, 4 × CH_2), 1.33–1.30 (t, $^3J = 7.0$, 12H, 4 × CH_2CH_3); ^{13}C NMR (66 MHz, $CDCl_3$, 298 K): δ 169.7 (4 × CO), 113.2 (2 × OCO), 77.3 (4 × CH), 61.8 (4 × OCH_2CH_3), 32.7 (4 × CH_2), 14.0 (4 × OCH_2CH_3); HRMS calcd for $C_{22}H_{32}O_{12}Na$ $(M+Na)^+$ 511.1791. Found 511.1801. Calcd for $C_{22}H_{32}O_{12}$: C, 54.09; H, 6.60. Found: C, 54.45; H, 6.50.

4.3. (2*R*,3*R*,10*R*,11*R*)-Tetrakis(hydroxydiphenylmethyl)-1,4,9,12-tetraoxadispiro[4.2.4.2]tetradecane 3a

A solution of **2** (1 g, 2.32 mmol) in THF (4 mL) was added to a cold solution of PhMgBr in THF (40 mL), prepared in situ from Mg (0.9 g, 37.02 mmol) and

bromobenzene (5.45 g, 34.71 mmol). The mixture was stirred for 2 h at 0 °C and at rt overnight. Then a saturated solution of NH_4Cl was added with some water and the aqueous phase was extracted three times with EtOAc. The combined organic phases were dried over $MgSO_4$ and evaporated to dryness. Recrystallization of the crude solid from EtOH gave pure **3a** as a white powder (1.32 g, 62%). Mp = 267–270 °C; $[\alpha]_D^{20} = -29.6$ (*c* 0.98, $CHCl_3$). The spectroscopic data found were in accordance to the work published by Tanaka et al.[13]

4.4. (2*R*,3*R*,10*R*,11*R*)-Tetrakis[hydroxydi(1-naphthyl)-methyl]-1,4,9,12-tetraoxadispiro[4.2.4.2]tetradecane 3b

Same procedure as for compound **3a** with 1-bromonaphthalene (15.9 g, 76.81 mmol) instead of bromobenzene. The crude product was purified by MPLC using cyclohexane/EtOAc (1:4) as the eluent. Recrystallization from EtOH of the resulting crystals gave **3b** as a white powder (5.44 g, 80%). Mp = 235–240 °C; $[\alpha]_D^{20} = -47.5$ (*c* 1.01, $CHCl_3$). ^{1}H NMR (500 MHz, DMSO-d_6, 353 K): δ 8.00–6.70 (m, 56H, H arom), 5.50–4.90 (2 br s, 8H, $4\times$CH and $4\times$OH), 2.20–1.00 (m, 8H, $4\times CH_2$); ^{13}C NMR (125 MHz, DMSO-d_6, 353 K): δ 145.0, 134.0, 133.9, 133.4, 132.1, 131.9, 131.0, 128.2, 127.7, 127.6, 127.1, 126.1, 124.7, 124.4, 124.2, 124.0, 123.8, 123.7, 123.2 (all C arom or CH arom, and OCO), 80.1, 71.1 ($4\times$CH and $4\times C(C_6H_5)_2$), 31.4 ($4\times CH_2$); HRMS calcd for $C_{94}H_{72}O_8Na$ $(M+Na)^+$ 1351.5125. Found 1351.5104. Anal. Calcd for $C_{94}H_{72}O_8$: C, 84.91; H, 5.46. Found: C, 84.63; H, 5.67.

4.5. (2*R*,3*R*,10*R*,11*R*)-Tetrakis[hydroxydi(2-naphthyl)-methyl]-1,4,9,12-tetraoxadispiro[4.2.4.2]tetradecane 3c

Same procedure as for compound **3a** with 2-bromonaphthalene (15.9 g, 76.81 mmol) instead of bromobenzene. The crude yellow crystals were recrystallized from EtOH to give **3c** as a white powder (5.1 g, 75%). Mp = 190–196 °C; $[\alpha]_D^{20} = -42.6$ (*c* 1.22, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$, 298 K): δ 8.16 (s, 4H, H arom), 7.89–7.86 (m, 12H, H arom), 7.75–7.68 (m, 12H, H arom), 7.58–7.50 (m, 16H, H arom), 7.41–7.37 (m, 8H, H arom), 7.28–7.24 (dd, $^3J = 1.7$, $^3J = 8.7$, 4H, H arom), 4.86 (s, 4H, $4\times$CH), 4.55 (br s, 4H, $4\times$OH), 1.43–1.33 (m, 8H, $4\times CH_2$); ^{13}C NMR (66 MHz, $CDCl_3$, 298 K): δ 142.6, 140.2, 132.66, 132.60, 132.56, 128.6, 128.0, 127.5, 127.31, 127.28 (all C arom), 127.0, 126.6, 126.1, 126.0, 125.7 (all CH arom), 109.4 ($2\times$OCO), 80.9 ($4\times$CH), 78.6, 77.2 (both $C(C_6H_5)_2$), 33.7 ($4\times CH_2$); HRMS calcd for $C_{94}H_{72}O_8Na$ $(M+Na)^+$ 1351.5125. Found 1351.5129. Anal. Calcd for $C_{94}H_{72}O_8$: C, 84.91; H, 5.46. Found: C, 84.65; H, 5.62.

4.6. (2*R*,3*R*,10*R*,11*R*)-Tetrakis[hydroxydi(2-thienyl)-methyl]-1,4,9,12-tetraoxadispiro[4.2.4.2]tetradecane 3d

Same procedure as for compound **3a** with 2-bromothiophene (2.83 g, 17.35 mmol) instead of bromobenzene. The crude product was purified by MPLC using a continuous gradient from cyclohexane to EtOAc. Recrystallization of the crude crystals from a mixture cyclohexane/EtOAc gave **3d** as a grey powder (0.38 g, 33%). Mp = 261–264 °C; $[\alpha]_D^{20} = +40.4$ (*c* 1.04, $CHCl_3$). IR (KBr): 3284. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K): δ 7.31–7.28 (dd, $^3J = 5.1$, $^3J = 1.1$, 4H, H arom), 7.26–7.24 (dd, $^3J = 5.1$, $^3J = 1.1$, 4H, H arom), 7.20–7.18 (dd, $^3J = 3.6$, $^3J = 1.2$, 4H, H arom), 7.09–7.07 (dd, $^3J = 3.6$, $^3J = 1.2$, 4H, H arom), 7.02–6.99 (dd, $^3J = 5.1$, $^3J = 3.6$, 4H, H arom), 6.95–6.91 (dd, $^3J = 5.1$, $^3J = 3.6$, 4H, H arom), 4.70 (br s, 4H, $4\times$OH), 4.41 (s, 4H, $4\times$CH), 1.59–1.48 (m, 8H, $4\times CH_2$); ^{13}C NMR (66 MHz, $CDCl_3$, 298 K): 149.7, 145.5 (both C arom), 126.6 (CH arom), 126.55 (CH arom), 126.52 (C arom), 125.8 (CH arom), 125.7 (CH arom), 125.5 (CH arom), 109.8 ($2\times$OCO), 82.5 ($4\times$CH), 75.7 ($4\times C(C_6H_5)_2$), 33.4 ($4\times CH_2$); HRMS calcd for $C_{46}H_{40}O_8S_8Na$ $(M+Na)^+$ 999.0387. Found 999.0363. Anal. Calcd for $C_{46}H_{40}O_8S_8$: C, 56.53; H, 4.13; S, 26.25. Found: C, 56.80; H, 4.50; S, 25.80.

4.7. Dynamic NMR

^{1}H NMR spectra were recorded at 500 MHz. The solvents used were acetone-d_6 (99.8%) and DMSO-d_6 (99.8%).

4.8. NMR titrations

A solution of the TADDOL (5 mM) in $CDCl_3$ was titrated with consecutive addition of a solution, in the same solvent, containing the host (37.5, 50 or 100 mM) and the TADDOL (5 mM). ^{1}H NMR spectra were recorded at 250 MHz at 298 K. $CDCl_3$ (99.9%) was used a solvent. Apparent dissociation constants were calculated with non-linear line fitting to a one-site model with the software package Prism (version 3.03, GraphPad Software, USA). Each regression is based on not less than seven data points and is presented with the standard error. The goodness of fit (R^2) was 0.9182 or better in all cases.

4.9. Job plot

Samples were prepared in $CDCl_3$ (99.9%) containing different molar fractions of the TADDOL **3c** and a chiral alcohol **4a** or **4b** from 0 to 1.0, with a constant total concentration of 8.3 mM. ^{1}H NMR spectra were recorded at 250 MHz at 298 K.

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