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Synthesis of Partially Bridged Phosphonate and Thiophosphonate Resorcinarenes

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Dedicated to Prof. D.N. Reinhoudt on the occasion of his 65th birthday

The synthesis of partially bridged thiophosphonate and phosphonate resorcinarenes is reported in this paper. Resorcinarenes functionalised at the upper rim with two or three P═X (X = S,O) bridges oriented towards the molecular cavity are obtained from the treatment of the corresponding (iiii) tetrasubstituted cavitand with 1,2-dihydroxybenzene and base in DMF. This synthetic route selectively promoted the formation of one of the two disubstituted resorcinarenes, the AC isomer. The crystal structure of the AC-dithiophosphonated resorcinarene 4 has been determined.

Keywords: Thiophosphonated resorcinarenes; Phosphonated resorcinarenes; Partially bridged cavitands; 1,2-dihydroxybenzene

INTRODUCTION

Cavitands are particularly attractive as host molecules owing to the wide choice of suitable bridging groups. In fact, the appropriate structural preorganisation of the host in combination with the appropriate set of complementary binding sites leads to the formation of highly stable complexes with neutral and charged guests [1]. The most common bridging groups employed for cavitands are alkylenedioxy [2] and derivatives [3], dialkylsilicon [4,5], heterophenylene [6,7] and phosphoryl [8,9]. In particular, phosphoryl derivatives are able to form strong complexes with cationic guests, such as metal ions [10,11], alkali metal and ammonium cations [12] and are efficient hydrogen bond acceptors in the complexation of alcohols [13–15]. Owing to their high binding capabilities, P═O groups have been included in preorganised structures to increase the stability of the complexes thus formed. Dutasta and co-workers reported the synthesis and the study of the binding properties of tetrabridged phosphonated cavitands having all the inward configuration of the P═O groups [16]. To ensure strong binding, the P═O groups must be oriented towards the cavity (indicated as (iiii)).

Partially bridged thiophosphonate and phosphonate resorcinarenes (Fig. 1) are attractive molecules as intermediates in the preparation of preorganised and multidentate cavitand ligands.

In particular, we are interested in AC-disubstituted resorcinarenes **4** and **7** for their potential use as ligand precursors in the self-assembly of coordination cages capable of molecular recognition. A synthetic study of these partially bridged building blocks is presented herein as well as the X-ray crystallographic investigation of the AC-dithiophosphonated resorcinarene **4**.

RESULTS AND DISCUSSION

Synthesis of Resorcinarenes Bearing Two and Three P═X (X = S,O) Bridges at the Upper Rim

The starting cavitand **1** (Scheme 1) was prepared in good yields according to the protocol reported in the

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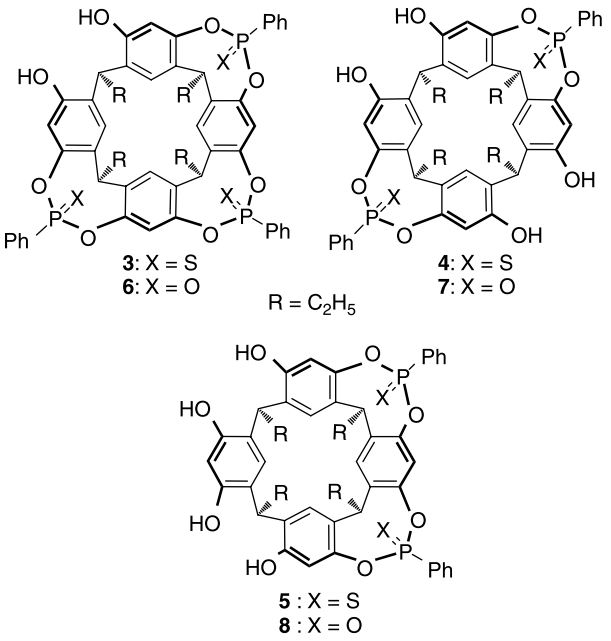
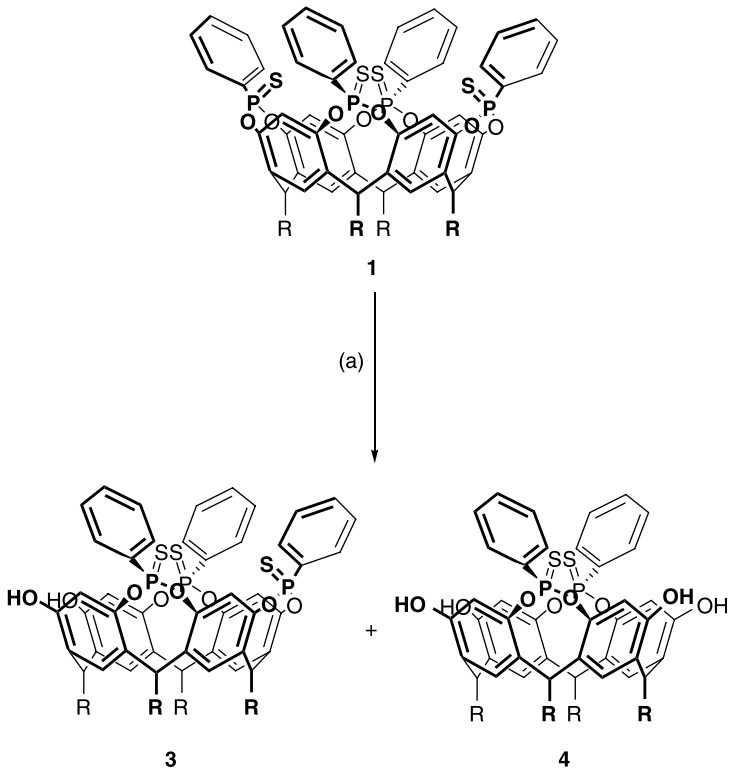


FIGURE 1 Partially bridged thiophosphonate and phosphonate resorcinarenes: tri- and disubstituted molecules.

literature [10] starting from the ethyl-footed resorcinarene. Briefly, 4.05 equivalents of dichlorophenylphosphine were added to the resorcinarene solution under basic conditions to give a tetraphosphonito cavitand. The intermediate was treated with sulphur to obtain the desired tetraphosphonate cavitand **1**. This synthetic procedure allows the formation of the (iiii) stereoisomer with the four P═S groups oriented towards the molecular cavity as the major product. In order to synthesise partially bridged thiophosphonate resorcinarenes, we performed the same protocol reducing the amount of bridging agent. When 2.8 equivalents of dichlorophenylphosphine were used, cavitand **1** was obtained as the major product in low yield (14%), while the tribridged compound **3** was also formed (6%) and only traces of the distal AC- and vicinal AB-dibridged resorcinarenes were found (**4** and **5**). Other attempts to obtain one of the partially bridged resorcinarene in higher yields by varying the stoichiometric amount of phosphine derivative were unsuccessful. Therefore, this approach proved to be inadequate for the preparation of suitable amounts of partially bridged resorcinarenes.

A novel approach for the selective excision of one and two quinoxaline units from the tetraquinoxaline cavitand has been developed by Gutierrez-Tunstad and co-workers [17]. After the treatment of tetraquinoxaline cavitand with 1,2-dihydroxybenzene under basic conditions, they reported a overall yield of approximately 56% for triquinoxaline resorcinarene and approximately 48% for AC-diquinoxaline resorcinarene. The AB-diquinoxaline isomer was obtained in a maximum yield of 11%. Following this



SCHEME 1 Preparation of the (iii) tri- and the (ii) AC-dithiophosphorylated resorcinarenes. (a) 1,2-Dihydroxybenzene, K_2CO_3, dry DMF, 80°C, 5 h.

approach, we investigated the behaviour of (iiii) tetrathiophosphonate cavitand in the presence of 1,2-dihydroxybenzene under basic conditions.

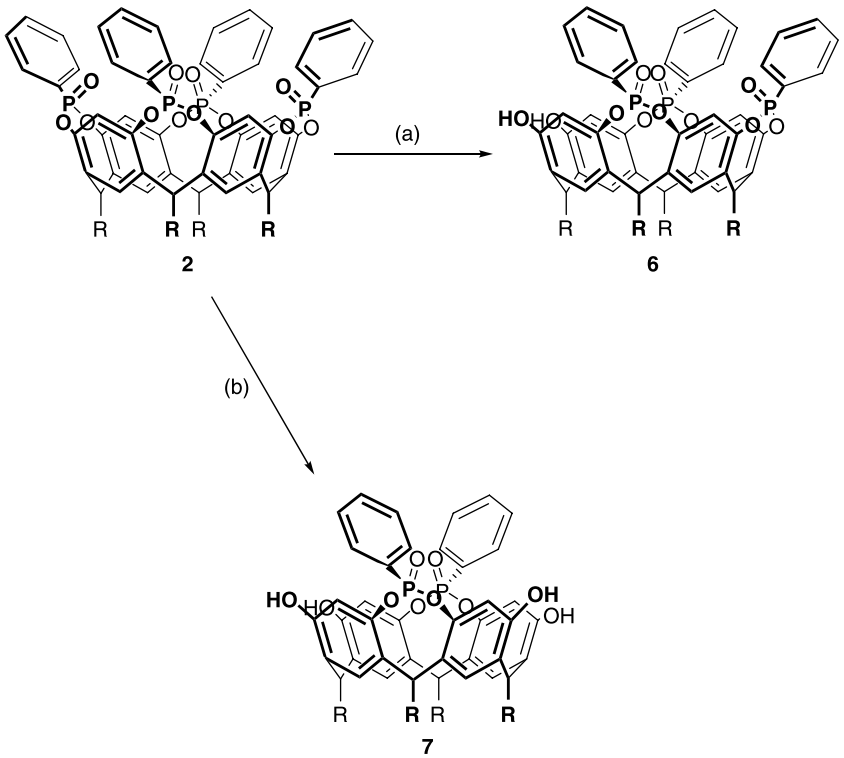
In order to prepare the (iii) trisubstituted resorcinarene **3**, the (iiii) tetrathiophosphonate cavitand **1** was reacted with 1 equivalent of 1,2-dihydroxybenzene in the presence of K_2CO_3 as base (Scheme 1).

Under these conditions, we obtained (iii) trithiophosphonated resorcinarene **3** as the major product in a yield of 52%. When 2 equivalents of 1,2-dihydroxybenzene were added to the reaction, a mixture of the (iii) trithiophosphonated resorcinarene **3** (21%), the (ii) AC-dithiophosphonated isomer **4** (28%) and only traces of the (ii) AB-dithiophosphonated isomer **5** were isolated. Higher yields of the desired product **4** were not achieved when the amounts of 1,2-dihydroxybenzene was increased. Moreover, during the reaction, the stereochemistry of the residual P═S groups did not change. Therefore, this synthetic route allows a good control of the product distribution between the dibridged resorcinarenes without altering the P═S stereochemistry.

The stability of phosphonate derivatives was also investigated under basic conditions in the presence of 1,2-dihydroxybenzene. Tetraphosphonate cavitand **2** is readily available following Dutasta's synthetic procedure [16]. In analogy to (iiii) tetrathiophosphonate cavitand **1**, the treatment of compound **2** with 1,2-dihydroxybenzene and K_2CO_3 in DMF led to the abstraction of a variable number of P═O bridges depending on the number of equivalents of nucleophile used (Scheme 2).

When 1 equivalent of 1,2-dihydroxybenzene was added to a mixture of cavitand **2** and K_2CO_3 in DMF, the (iii) triphosphonate resorcinarene **6** was obtained in good yields (65%). Under these conditions, a small amount of the (ii) AC-diphosphonate isomer **7** was isolated, but neither the corresponding (ii) AB isomer nor the starting compound were observed. Similarly, when 2 equivalents of 1,2-dihydroxybenzene were used, we obtained the (ii) AC-diphosphonate isomer **7** as the major product (62% yields) without the presence of the (ii) AB-diphosphonate isomer **8**.

In comparison with (iiii) tetrathiophosphonate cavitand **1**, the selective excision of one or two phosphonate groups from (iiii) tetraphosphonate cavitand **2** is more sensitive to the amount of nucleophile used. In particular, the reaction of 2 equivalents of 1,2-dihydroxybenzene with (iiii) tetrathiophosphonate cavitand **1** leads to the formation of similar amount of (ii) and (iii) resorcinarenes, whereas that with (iiii) tetraphosphonate cavitand **2** produces exclusively the AC isomer. Also in this case, the nucleophilic attack of 1,2-dihydroxybenzene to the P═O bridges does not change the stereochemistry of the remaining bridges. This last aspect is crucial to retain the recognition properties in the partially bridged resorcinarenes bearing P═O groups.



SCHEME 2 Abstraction of one or two phosphoryl bridges from the tetraphosphonate cavitand **2**. (a) 1 eq. 1,2-dihydroxybenzene, K_2CO_3, dry DMF, 80°C, 5 h. (b) 2 eq. 1,2-dihydroxybenzene, K_2CO_3, dry DMF, 80°C, 5 h.

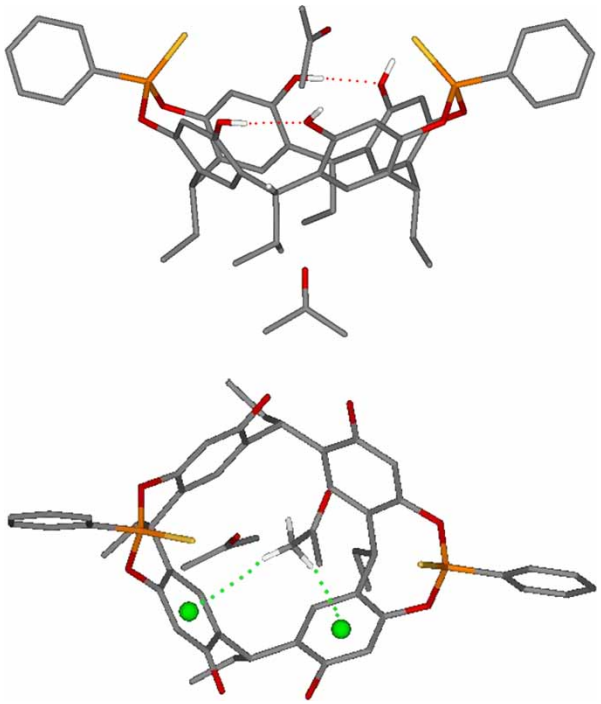


FIGURE 2 Molecular structure of resorcinarene A showing the intramolecular hydrogen bonds as yellow dotted lines (above) and the CH–π interactions as green dotted lines (below; only the hydrogens involved in the interactions are shown). Colour code: carbon, grey; hydrogen, white; oxygen, red; phosphorus, orange; sulphur, yellow; centroid, green.

X-ray Crystallographic Investigation

The stereochemistry of the (ii) AC-disubstituted isomer has been confirmed also by the X-ray crystal structure of resorcinarene **4** (Figs. 2 and 3; [18])[1]. Crystals of **4** were obtained by slow evaporation of a solution of **4** in acetone. Compound **4** crystallises in the space group $P21/n$ as two independent resorcinarenes A and B. The structure of each resorcinarene shows indeed the presence of two P═S groups pointing inside the cavity and of four C_2H_5 chains at the lower rim. The cavity is stabilised by a network of intramolecular O—H···O hydrogen bonds among the OH groups on the phenyl rings at the upper rim, with the O···O distances spanning from 2.691(3) to 2.784(3) Å and the O—H···O angles spanning from 167.2(2)° to 175.2(2)°. Each resorcinarene crystallises with two acetone molecules, one dispersed in the lattice and another with a CH_3 group inside the cavity, giving rise to two weak CH···π interactions (resorcinarene A:C—H···centroid distances of 3.061(2) and 3.294(3) Å, with C—H···centroid angles of 147.6(4)° and 147.6(3)°, respectively; resorcinarene B: C—H···centroid distances of 3.001(2) and 3.105(3) Å, with C—H···centroid angles of 157.5(2)° and 143.1(4)°, respectively; Fig. 2).

In the lattice, the resorcinarenes A and B face each other to give a supramolecular dimer stabilised by a network of hydrogen bonds involving the acetone molecules inside the cavity and the OH groups at the upper rim [O3D–O3S 2.675(3) Å, O3D–H3D O3S 168.8(2)°; O3E–O1S 2.695(3) Å, O3E–H3E O1S 166.1(2)°] (Fig. 3).

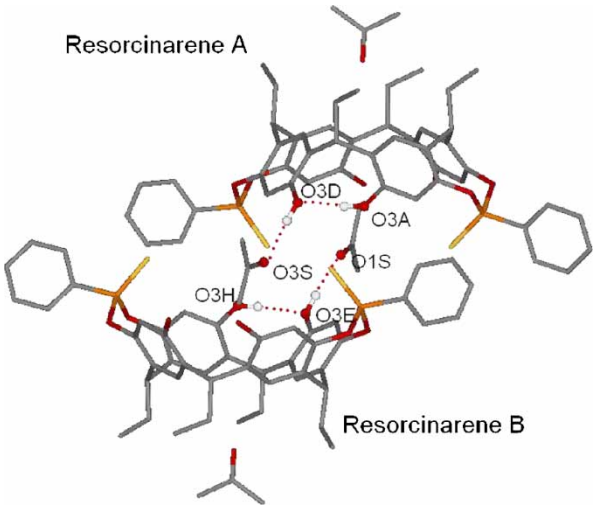


FIGURE 3 The dimer formed by resorcinarenes A and B through a network of hydrogen bonds involving the acetone guests. Colour code: carbon, grey; hydrogen, white; oxygen, red; phosphorus, orange; sulphur, yellow.

CONCLUSIONS

An effective protocol for the preparation of partially bridged thiophosphonate and phosphonate resorcinarenes is reported. Different amounts of 1,2-dihydroxybenzene were used to perform the abstraction of one or two P═X (X = S, O) bridges from the corresponding tetrabridged cavitands in good yields. This synthetic route allowed a good control of the product distribution, producing mainly the (ii) AC-dibridged isomer and the (iii) trisubstituted resorcinarene. Moreover, during the excision of the P═X groups, the configuration of the remaining P═X (X = S, O) bridges on the molecules is retained. These compounds are useful precursors for the preparation of differently functionalised cavitands having specific molecular recognition properties [19].

EXPERIMENTAL

Materials and Methods

All commercial reagents were ACS grade. All solvents were dried over 3 Å and 4 Å molecular sieves. ^{1}H NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer at 300 K, and all chemical shifts were reported in parts per million (ppm) in relation to the proton resonances resulting from incomplete deuteration of the NMR solvents. ^{31}P NMR spectra

were recorded on a Bruker 162 MHz spectrometer and all chemical shifts were reported in ppm relative to external 85% H_3PO_4 at 0.00 ppm. Electrospray ionisation mass spectrometry (ESI-MS) experiments were performed on a Waters ZMD spectrometer equipped with an electrospray interface. Column chromatography was performed by using silica gel 60 (Merck 70–230 mesh) as a stationary phase. Cavitands **1** [10] and **2** [16] were prepared according to the protocols reported in the literature.

Synthesis of the (iii) Trithiophosphonated Resorcinarene 3 and the (ii) AC-Dithiophosphonated Resorcinarene 4

A mixture of cavitand **1** (0.500 g, 0.43 mmol), K_2CO_3 (0.599 g, 4.34 mmol) and freshly recrystallised 1,2-dihydroxybenzene (0.095 g, 0.87 mmol) in 10 mL of dry DMF was stirred in a sealed tube at 80°C for 5 h. The reaction mixture was then cooled and poured into ice-cold brine. The solid formed was then filtered, washed with water and dried. The crude product was purified by column chromatography (SiO_2; CH_2Cl_2/ethyl acetate = 95/5) to give **3** in a 21% yield (0.095 g, 0.09 mmol), followed by **4** in a 28% yield (0.108 g, 0.12 mmol).

3

^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 8.17$ (m, 6H, P—Ar*H*), 7.55 (m, 9H, P—Ar*H*), 7.32 (s, 2H, ArH_{down}), 7.20 (s, 2H, ArH_{down}), 6.68 (d, 2H, ArH_{up}, $^4J_{HP} = 2.2$ Hz), 6.49 (s, 2H, ArH_{up}), 4.60 (m, 3H, ArC*H*), 4.29 (t, 1H, ArC*H*, $J = 7.9$ Hz), 2.40–2.23 (m, 8H, ArCH—CH_2), 1.09–0.91 (m, 12H, CH_2CH_3); ESI-MS: m/z 1037 $[M + Na]^+$; methanol.

4

^{1}H NMR (acetone-d_6, 300 MHz): $\delta = 8.22$ (dd, 4H, P—Ar*H*, $^3J_{PH} = 14.8$ Hz, $J_{HH} = 6.9$ Hz), 7.78 (s, 4H, ArH_{down}), 7.75 (m, 2H, P—Ar*H*), 7.67 (m, 4H, P—Ar*H*), 6.44 (s, 4H, ArH_{up}, $^4J_{HP} = 2.2$ Hz), 4.63 (t, 2H, ArC*H*, $J = 8.1$ Hz), 4.34 (t, 2H, ArC*H*, $J = 8.0$ Hz), 2.51 (m, 4H, ArCH—CH_2), 2.40 (m, 4H, ArCH—CH_2), 1.05 (t, 6H, CH_2CH_3, $J = 7.2$ Hz), 0.92 (t, 6H, CH_2CH_3, $J = 7.2$ Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 81.2$ (s, 2P); ESI-MS: m/z 877 $[M + H]^+$, 899 $[M + Na]^+$; acetone.

Crystal Structure Determination of Compound 4

The molecular structure of compound $C_{48}H_{46}O_8S_2P_2{\cdot}2C_3H_6O$ **4** was determined by single-crystal X-ray diffraction methods. Crystallographic and experimental details are summarised in Table I.

Intensity data were collected using a Mo Kα radiation on a Bruker AXS Smart 1000 single-crystal diffractometer equipped with a CCD area detector at 293(2) K. The structure was solved by direct methods with the SIR97 program [20] and refined on F_0^2 by full-matrix least-squares procedures with the SHELXL-97 program [21]. The data reduction for **4** was performed using the SAINT [22] and SADABS [23] programs. All the non-hydrogen atoms were refined with anisotropic atomic displacements. The hydrogen atoms were included in the refinement at idealised geometries (C—H 0.95 Å) and refined 'riding' on the corresponding parent atoms. The weighting scheme used in the last cycle of refinement was $w = 1/[\sigma^2 F_o^2 + (0.0695P)^2 + 4.56219P]$. Geometric calculations and molecular graphics were performed with the PARST97 program [24] and the DS ViewerPro 5.0 package. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-655076. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

TABLE I Crystallographic data and refinement details for resorcinarene **4**.

	Resorcinarene **4**
Formula	$C_{54}H_{58}O_{10}P_2S_2$
Formula weight	993.06
Crystal system	Monoclinic
Space group	*P21/n*
a (Å)	11.611(1)
b (Å)	50.654(5)
c (Å)	17.557(2)
β (°)	97.519(1)
V (Å^3)	10,237(2)
Z	8
D_c (g cm^{-3})	1.289
$F(000)$	4192
μ (mm^{-1})	0.224
$\theta_{min,max}$ (°)	2.83, 26.84
Reflections collected	83,251
Independent reflections	19,682 ($Rint = 0.0389$)
Obs. refl. [Fo$>4\sigma$(Fo)]	14,100
Data/restr./param.	19,682/0/1255
R indices [Fo$>4\sigma$(Fo)][a]	$R1 = 0.0558$, $wR2 = 0.1372$
R indices (all data)	$R1 = 0.0848$, $wR2 = 0.1481$
$\Delta\rho_{min,max}$/eÅ^{-3}	−0.311, 0.232
S[b]	1.025

[a] $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, $wR_2 = [\Sigma w(Fo^2 - Fc^2)^2/\Sigma w\,Fo^4]^{1/2}$. [b] Goodness-of-fit $S = [\Sigma w(Fo^2 - Fc^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p the number of parameters.

Synthesis of the (iii) Triphosphonated Resorcinarene 6

Sixty-six milligrams (0.6 mmol) of freshly recrystallised 1,2-dihydroxybenzene were dissolved in approximately 50 mL of DMF and 828 mg of K_2CO_3 (ca. 10 eq.) were added. After the addition of 650 mg (0.6 mmol) of cavitand **2**, the reaction mixture was

heated to 80°C and stirred for 5 h. The reaction mixture was then cooled to room temperature and DMF was completely evaporated in *vacuum*. The solid was dissolved in CH_2Cl_2 and three extractions with acidic water were performed. The final product was purified by silica gel chromatography with CH_2Cl_2–EtOH as eluent (90/10 v/v). The yield of the reaction was 65% (375 mg).

^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 9.56$ (bs, 2H, Ar—O**H**), 8.05 (m, 6H, P—Ar**H**), 7.59 (m, 9H, P—Ar**H**), 7.36 (s, 2H, Ar$\mathbf{H}_{down}$), 7.17 (s, 2H, Ar$\mathbf{H}_{down}$), 6.93 (s, 2H, Ar$\mathbf{H}_{up}$), 6.80 (s, 2H, Ar$\mathbf{H}_{up}$), 4.60 (m, 3H, ArC**H**), 4.37 (t, 1H, ArC**H**, $J = 7.9$ Hz), 2.38 (m, 6H, ArCH—C$\mathbf{H}_2$), 2.26 (m, 2H, ArCH—CH_2), 1.08 (t, 6H, $CH_2C\mathbf{H}_3$, $J = 7.2$ Hz), 1.00 (t, 3H, $CH_2C\mathbf{H}_3$, $J = 7.2$ Hz), 0.94 (t, 3H, $CH_2C\mathbf{H}_3$, $J = 7.2$ Hz); ESI-MS: m/z 989 $[M + Na]^+$; methanol.

Synthesis of the (ii) AC-diphosphonated Resorcinarene 7

K_2CO_3 (0.511 g, 3.69 mmol) and freshly recrystallised 1,2-dihydroxybenzene (0.081 g, 0.74 mmol) were added to a solution of cavitand **2** (0.402 g, 0.37 mmol) in 12 mL of dry DMF. The reaction mixture was stirred at 80°C for 5 h, cooled at room temperature and then poured into ice-cold brine. The solid formed was filtered, washed with water and dried. The desired product **7** (183 mg) was collected by filtration in a 62% yield after the treatment of the crude with diethyl ether.

^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.94$ (m, 4H, P—Ar**H**), 7.60 (m, 2H, P—Ar**H**), 7.48 (m, 4H, P—Ar**H**), 7.01 (s, 4H, Ar$\mathbf{H}_{down}$), 6.37 (s, 4H, Ar$\mathbf{H}_{up}$), 4.40 (t, 2H, ArC**H**, $J = 7.0$ Hz), 4.28 (t, 2H, ArC**H**, $J = 7.8$ Hz), 2.26 (m, 4H, ArCH—C$\mathbf{H}_2$), 2.17(m, 4H, ArCH—C$\mathbf{H}_2$), 0.96 (t, 6H, $CH_2C\mathbf{H}_3$, $J = 6.9$ Hz), 0.87 (t, 6H, $CH_2C\mathbf{H}_3$, $J = 6.9$ Hz); ESI-MS: m/z 868 $[M + Na]^+$, 884 $[M + K]^+$; methanol.

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