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Molecular Recognition of Dihydroxybenzenes by Macrocyclic Polyamines in Langmuir Films and PVC Matrix

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Abstract

Lipophilic polyamines **1** and **2** form stable monolayers at the air–water interface. The shapes of the isotherms show a strong pH-dependence due to different stages of polyamine protonation. For all isomers of dihydroxybenzene the strong interaction with **1** and **2** can be observed at pH 4, 6, and 8. Polyamines **1** and **2** in the PVC liquid membrane act as the sensory element of the potentiometric sensor for selective determination of catechol in the presence of other isomers of dihydroxybenzenes.

Introduction

Macrocyclic polyamines still attract much attention because they can serve as hosts for metal cations [1–5], anions [6–11], and neutral molecules [12–14].

Kimura *et al.* have demonstrated that macrocyclic polyamines formed stable complexes with dihydroxybenzenes with a loss of proton in neutral aqueous solutions [8]. On this basis the potentiometric sensor for determination of dihydroxybenzenes was developed by Umezawa *et al.* [13–15]. It was found that liquid membranes incorporating lipophilic polyamines generate a selective anionic response in the presence of dihydroxy derivatives.

We have demonstrated that the polyamines shown in Figure 1 could also serve as a sensor element [16].

Presented polyamines **1** and **2** form a stable monolayer at the air-water interface [17, 18]. It was very interesting to study the monolayer behaviour in the presence of dihydroxybenzenes as guests in the subphase.

Experimental

The procedures of the synthesis of lipophilic hexaamines were published elsewhere [17]. The water for experiments was distilled and passed through a Milli-Q water purification system (resistance 18.2 Ω, pH 5.8). The hydrochloric acid and NaOH were from POCh of analytical grade. Isomers of dihydroxybenzenes, citric acid, and (*N*-[2-hydroxyethyl]piperazine-*N*′-[2-ethanesulfonic acid]) (HEPES buffer) were purchased from Sigma-Aldrich. The geometry optimisation was carried out using MM^+ HyperChem (HyperCube, Inc.)

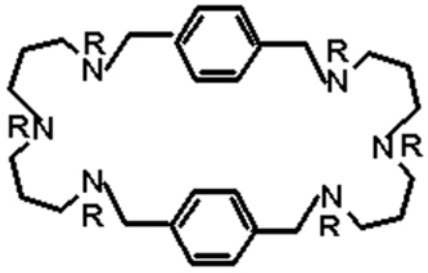

Figure 1. Structure of polyamines **1** and **2**.

Langmuir film preparation

Hexaamines were dissolved in pure chloroform at a concentration of 0.4 mg/mL and spread dropwise onto the subphase. Isotherms were registered after 15 min. The compression rate was 20 cm/min. The experiments were carried out on a computer controlled Nima trough equipped with two barriers, a Wilhelmy plate type microbalance and a surface potential vibrating probe KP-2. The presented isotherms of ΔV were qualitative only, because of some trouble with the stability of the potential. The trough was placed on a laminar flow hood. The temperature of the experiments was 20–22 °C. The concentration of dihydroxybenzenes in the subphase was 5×10^{-3} M. We observed oxidation of hydroquinone at pH 8. All measurements were repeated three times.

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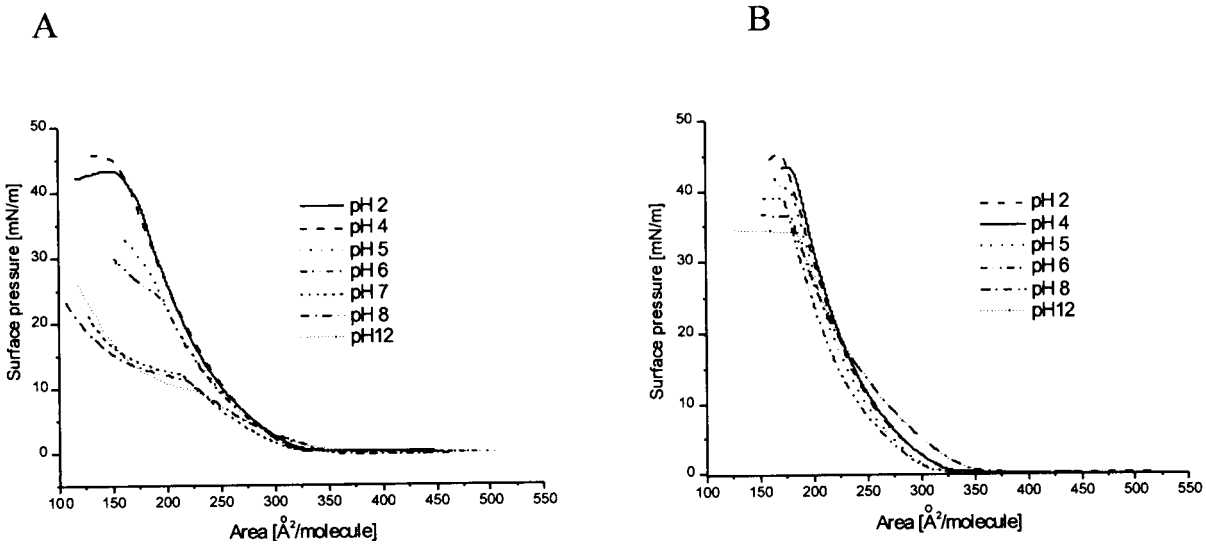

Figure 2. pH-dependence of $\pi - A$ isotherms of host **1** (A) and **2** (B) on the subphases containing 0.01 M HCl (pH 2), 0.01 M citric buffer (pH 4 and 6), 0.01 M HEPES buffer (pH 7 and 8) and 0.01 M NaOH pH 12.

Table 1. Characteristics of monolayers of hexaamines **1** and **2**

Hexaamine	Subphase	pH4		pH6		pH8	
		Area (Å^2)	π_c (mN/m)	Area (Å^2)	π_c (mN/m)	Area (Å^2)	π_c (mN/m)
1	Buffer	250	40	260	24	260	13
	Catechol	275	44	270	27	270	13
	Hydroquinone	225	41	285	22	275	12
	Resorcinol	285	41	280	26	300	14
2	Buffer	250	44	250	38	260	34
	Catechol	290	49	275	40	290	31
	Hydroquinone	270	46	260	38	300	31
	Resorcinol	300	45	265	38	310	31

Electrode preparation and potential measurements

The composition of PVC matrix liquid membranes were as follows: 1 wt% host, 66% DOP, 33% PVC. All components were dissolved in ca. 2 mL of freshly distilled THF and the resulting mixture was poured into a glassy ring to evaporate the solvent. A more detailed description of the method of membrane preparation and measurements was published in [16].

Results

Langmuir film investigation

The isotherms of surface pressure (π) for polyamines **1** and **2** depended very much on the substituents of the nitrogen atoms. The pH-dependence of π-A isotherms for **1** and **2** are demonstrated in Figure 2.

The isotherms for the alkyl chain derivative (**1**) significantly differ from those of **2**. We observed the kink on the isotherms registered on pure water and subphases with higher pH for the macrocycle **1**. For amphiphlic polyamines this kink may originate from the coexistence region [19], reorientation of molecules [20], or forming multilayers [21]. The collapse of the monolayer, in our case, appeared not just after the kink but rather after the plateau at a surface pressure of 15 mN/m and 13 mN/m for water and alkaline subphase, respectively. For pH 6 and lower, we observed collapse of the monolayer just after the kink [18].

Figures 3 and 4 demonstrate the isotherms for both polyamines on a buffer subphase without and with dihydroxybenzenes at a concentration of 5×10^{-3} M.

The monolayer characteristics are summarised in Table 1. The area presented in Table 1 corresponds to the limiting area per molecule obtained from extrapolation of the initial part of the isotherm and π_c is related to the collapse of the pressure of the monolayer.

Potential measurements

The investigated polyamines were incorporated in PVC matrix and the resulting membranes were mounted on a Tacussel Ag/AgCl electrode body. Figures 5 and 6 represent the potentiometric response of the membranes investigated to-

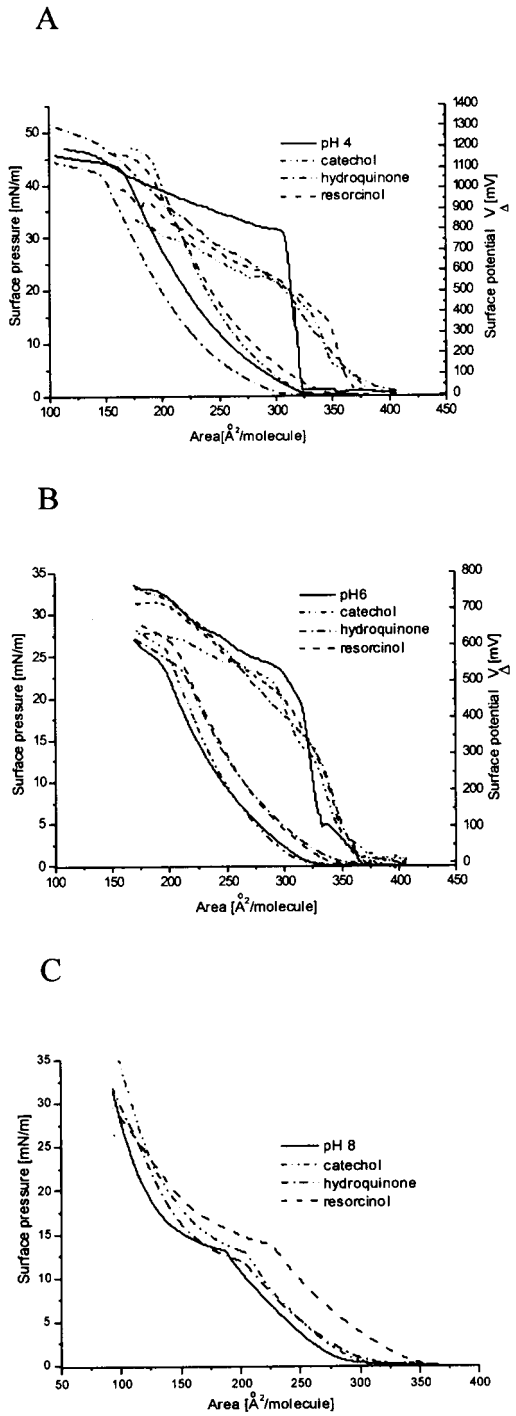

Figure 3. π-A and $\Delta V - A$ isotherms of polyamine **1** on buffers without and with 0.005 M dihydroxybenzenes: (A) pH 4, (B) pH 6, and (C) pH 8.

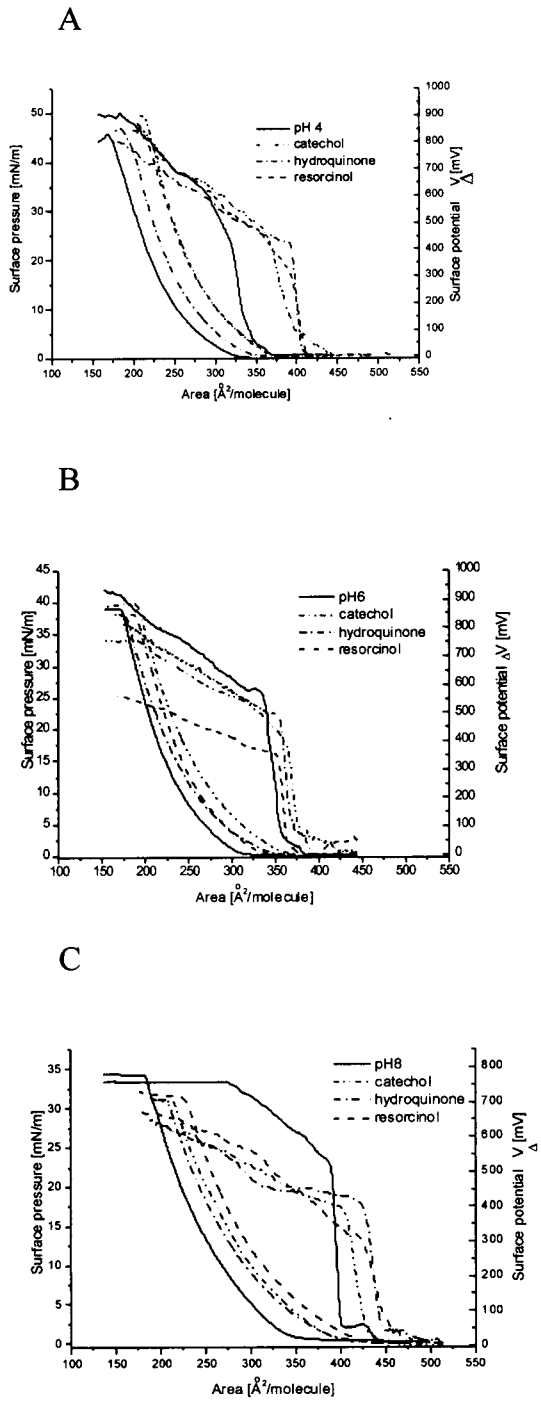

Figure 4. π-A and $\Delta V - A$ isotherms of polyamine **2** on buffers without and with 0.005 M dihydroxybenzenes: (A) pH 4, (B) pH 6, and (C) pH 8.

wards isomers of dihydroxybenzenes in three ranges of pH: 4.0, 6.0, and 8.0.

The selectivity coefficients of the electrodes with membranes incorporating polyamine **1** and **2** were also investigated [16]. The selectivity coefficients ($\log K_{\text{catechol,B}}$) were determined by the matched potential method [22], and their values are presented in Table 2. Table 2 shows additionally the dissociation constants (pK_a) and partition coefficients ($\log P_{\text{oct}}$) of the dihdroxybenzenes [23].

Discussion

Taking into account the limiting areas on pure subphase for the investigated polyamines we conclude that the macrocycle lay flat on the water–air interface. For alkyl derivative the **1** calculated (from geometry optimisation in MM+) the cross section area for the macrocycle was 129 ± 5 Å^2 .

When we compare these values with the limiting areas calculated from the isotherms (250–260 Å^2), it is clear that the branches in the alkyl derivative are not perpendicular to the subphase, but are stretched laterally. For the amide we

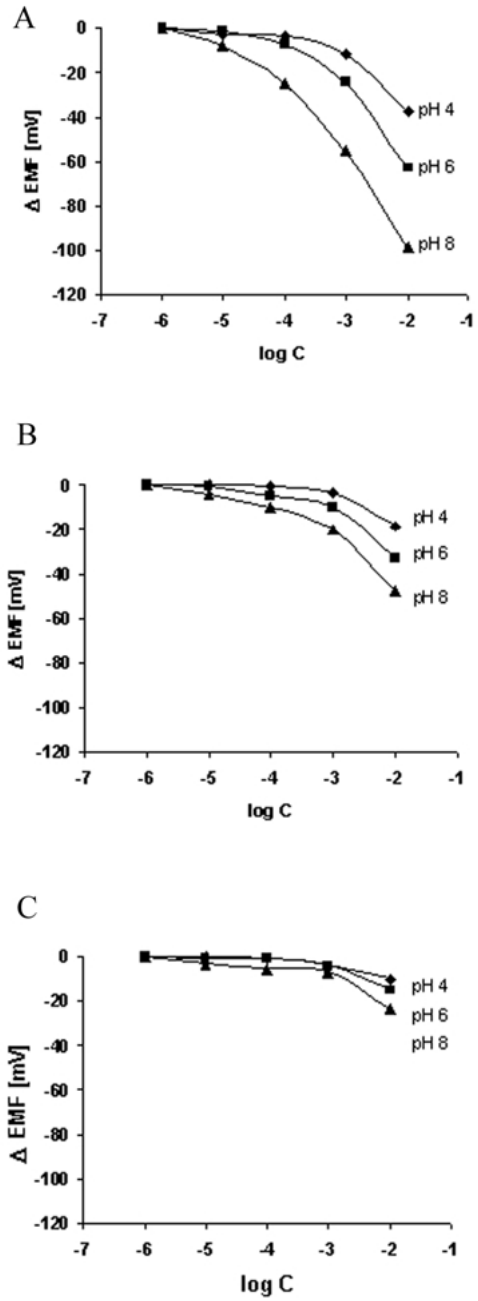

Figure 5. Potential vs. concentration curves obtained by an electrode containing host **1** for catechol (A), resorcinol (B), and hydroquinone (C). Mean values from three measurements.

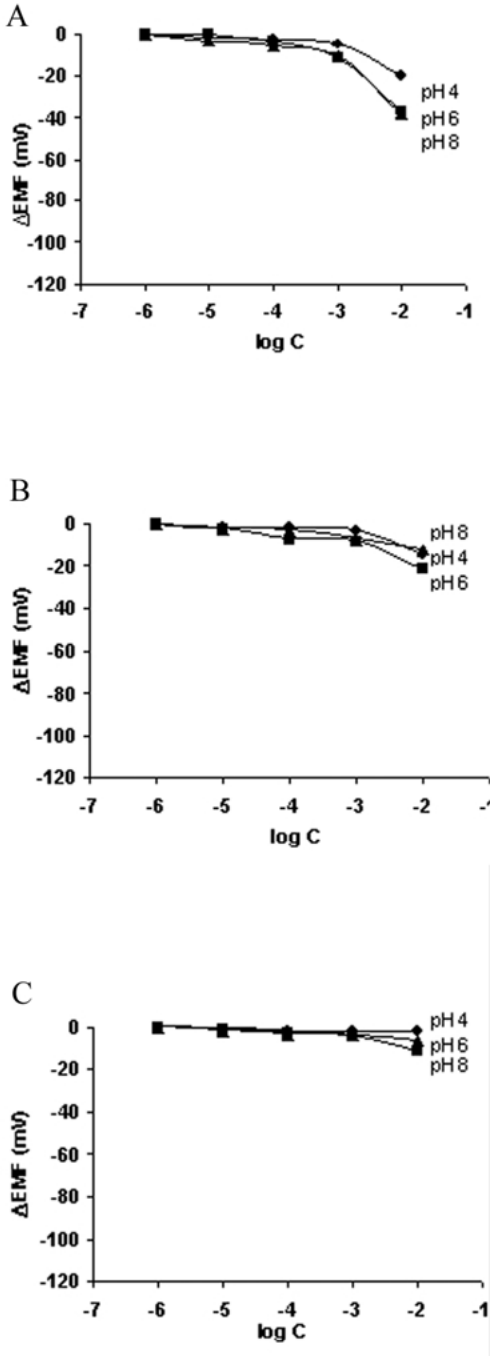

Figure 6. Potential vs. concentration curves obtained by an electrode containing host **2** for catechol (A), resorcinol (B), and hydroquinone (C). Mean values from three measurements.

anticipated that oxygen atoms from the carboxamide groups lay on the water surface. The calculated, as above, cross-section area for the carboxamide derivative was 250 ± 5 Å^2 (oxygen atoms attached to the amide group lie in the same plane as the macrocycle). So the alkyl branches in this case were almost perpendicular to the subphase. The same was observed for lipophilic macrocyclic amides [21]. Figure 7 illustrates the upper and lateral view for both polyamines.

The pH-dependence of the isotherms for both polyamines indicated that protonation of the macrocycle at the air–water interface occurred in two stages (first at range pH $<$ 12 to pH 8 and the second at pH 6 $-$ pH 4). The same observation was in the case of potential vs. pH measurements for PVC membranes containing alkyl and carboxamidealkyl hexaamine [16]. The NMR spectra indicated that in the first step two nonbenzylic nitrogen atoms were protonated [18].

Figures 3 and 4 demonstrate that polyamines **1** and **2** form monolayers on subphases containing dihydroxybenzenes. The limiting areas and, in most cases, the collapse pressure differ significantly from those obtained for buffers without hosts. In all cases the values of limiting areas were higher than in the latter case. This suggests that dihydroxybenzenes penetrate the cavity of host amines. In fact, cyclophane-type host molecules are capable of binding

Table 2. Potentiometric selectivity coefficients of the membrane electrodes with polyamines **1** and **2**, dissociation constants, and partition coefficients for dihydroxybenzenes

	(log $K_{\text{catechol,B}}$)							
	Polyamine **1**			Polyamine **2**				
Guest	pH4	pH6	pH8	pH4	pH6	pH8	pK_a	log P_{oct}
Catechol	0	0	0	0	0	0	9.36	0.95
Hydroquinone	-0.78 ± 0.01	-0.83 ± 0.21	-0.86 ± 0.08	-0.30 ± 0.08	-0.66 ± 0.03	-0.23 ± 0.09	9.44	0.79
Resorcinol	-1.59 ± 0.02	-2.01 ± 0.01	-1.63 ± 0.01	-1.19 ± 0.04	–	-0.73 ± 0.1	9.91	0.55

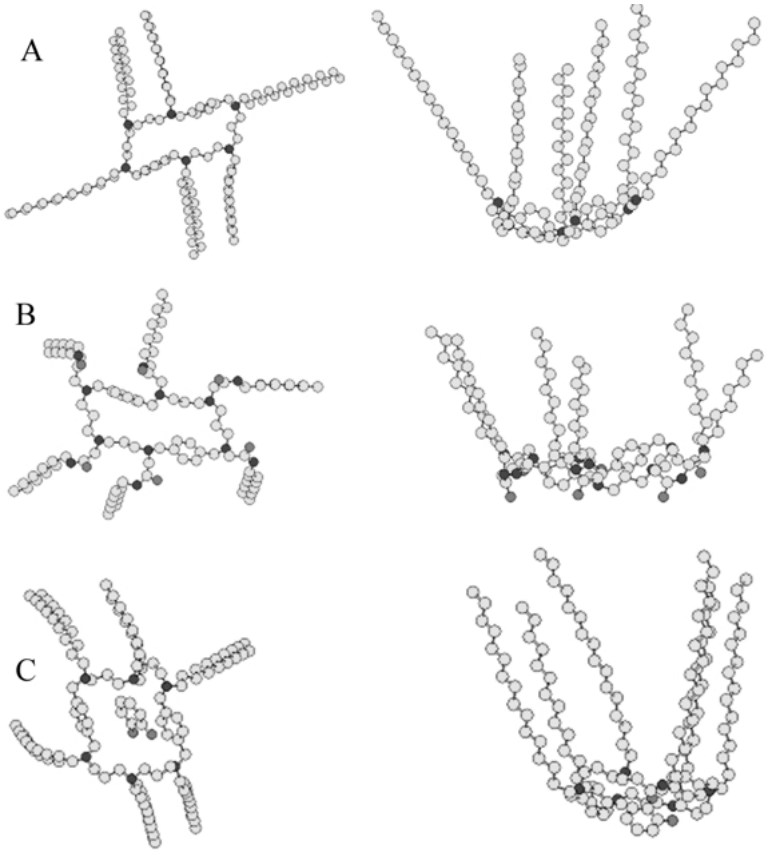

Figure 7. Top and lateral views of molecular structures of polyamines **1** (A) and **2** (B) obtained by MM^+ geometry optimisation. (C) Simulation for complex of host **1** with catechol.

aromatic substrates due to weak face-to-face, or edge-to-face aromatic interactions, and many examples have been provided in a monograph on cyclophanes [25]. Our macrocyclic polyamines can be considered as cyclophane-type molecules possessing two aromatic rings interacting with aromatic substrates, and additional binding of dihydroxybenzenes is conceivable through hydrogen bonding between hydroxyl groups and positively charged (protonated) nitrogen atoms of the macrocycle. The isotherms of the potential surface exhibited that the potential decreased in all cases when the guest was in the subphase. Interaction between polyamines and hydroxybenzenes may involve hydrogen bonds, but also π-π-stacking aromatic interactions.

Figures 5 and 6 show the potentiometric response of PVC membranes containing the host macrocycle **1** and **2** towards isomers of dihydroxybenzenes in three ranges of pH. The highest response for both membranes was observed for catechol. The sensitivity of the membranes increased with the increase of pH. The electrode with the membrane incorporating host **1** is characterised by a slightly better selectivity for catechol in the presence of the two other isomers.

The selectivity difference was probably caused by the proton stabilisation by the carboxamide groups in polyamine **2**. The selectivity of sensors investigated was governed by the acidity and lipophilicity of the target dihydroxybenzenes. Generally, the higher the acidity and lipophilicity of the guest, the larger the potentiometric response observed.

Taking into account the results for monolayers and in the PVC matrix, one could conclude that in the molecular recognition the surrounding environment plays a crucial role. The isomers of dihydroxybenzene which can be easily sensed possess a higher lipophilicity, and easily penetrate the PVC matrix.

Conclusion

Both polyamines could recognise the dihydroxybenzenes in the monolayer and in the PVC matrix. Electrodes with membranes containing host **1** and **2** could specify recognise catechol, so the hexaamines could act as sensory element.

Acknowledgements

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