in the range between a typical single (B–N: 1.58 Å) and a double (B=N: 1.41 Å) bond.[19]

The new metallasilaborates presented obey Wade's rules.[20]

Experimental Section

5: $[NEt_4][MeSiB_{10}H_{12}]$ (197.7 mg, 0.67 mmol) was dissolved in CH_2Br_2 (10 mL), cooled to the freezing point of the solvent, and added to a similarly cold solution of $Nb(NMe_2)_5$ (265.9 mg, 1.26 equiv) in dibromomethane (10 mL). The solution was allowed to warm to room temperature and stirred for four days. The resulting dark brown solution was filtered and then layered with hexane to give green-black crystals at $-30\,^{\circ}C$ that contained one equivalent of CH_2Br_2. Recrystallization from dichloromethane gave crystals containing one equivalent of CH_2Cl_2. Crystals for X-ray structure analysis were obtained by an analogous procedure using $[NBu_4]^+$ as counterion. Yield: 0.392 g (73 %). $^1H\{^{11}B\}$ NMR (CD_2Cl_2, 500 MHz, TMS): $\delta = 0.98$ (s, 3H, SiMe), 2.15 (s, 1H, H12), 2.21 (s, 1H, H9), 2.63 (s, 2H, H8/10), 2.67 (s, 6H, μ-NMe_2), 2.79 (s, 2H, H4/5), 3.00 (s, 6H, μ-NMe_2), 3.47 (s, 2H, H3/6), 4.97 (s, 2H, CH_2Br_2); ^{11}B NMR (CD_2Cl_2, 160 MHz, $Et_2O \cdot BF_3$): $\delta = 32.1$ (s, B7/11), 13.8 (d, $^1J = 134$ Hz, B 3/6), -2.2 (d, $^1J =$ 134 Hz, B9/4/5), -9.0 (d, $^1J = 134$ Hz, B8/10), -11.7 (d, $^1J = 134$ Hz, B12); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): $\delta = -4.6$ (s, MeSi), 51.5 (s, μ-NMe_2), 56.9 (s, μ-NMe_2); ^{29}Si NMR (CD_2Cl_2, 100 MHz, TMS): $\delta = 36.22$; C, H, N analysis (%): calcd: C 21.09, H 5.94, N 5.27; found: C 20.92; H 6.15, N 5.77.

6: Same procedure as for **5** with $[NEt_4][MeSiB_{10}H_{12}]$ (273.0 mg, 0.93 mmol) and $Ta(NMe_2)_5$ (397.2 mg, 0.98 mmol, 1.06 equiv). Yield: 0.564 g (69 %). $^1H\{^{11}B\}$ NMR (CD_2Cl_2, 500 MHz, TMS): $\delta = 0.98$ (s, 3H, SiMe), 2.37 (s, 1H, H12), 2.73 (s, 1H, H9), 2.80 (s, 6H, μ-NMe_2), 2.85 (s, 2H, H8/10), 3.11 (s, 6H, μ-NMe_2), 3.07 (s, 2H, H4/5), 3.31 (s, 2H, H3/6); ^{11}B NMR (CD_2Cl_2, 160 MHz, $Et_2O \cdot BF_3$): $\delta = 28.5$ (s, B7/11), 8.3 (d, $^1J = 134$ Hz, B 3/6), -5.1 (d, $^1J = 134$ Hz, B4/5), -6.1 (d, $^1J = 134$ Hz, B9), -10.8 (d, $^1J = 134$ Hz, B8/10), -13.4 (d, $^1J = 134$ Hz, B12); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz): $\delta = -5.0$ (s, MeSi), 51.6 (s, μ-NMe_2), 57.0 (s, μ-NMe_2); ^{29}Si-NMR (CD_2Cl_2, 100 MHz, TMS): $\delta = 30.25$; C, H analysis (%): calcd: C 19.04, H 5.13; found: C 19.27, H 5.33.

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[1] L. Wesemann, Y. Ramjoie, B. Ganter, B. Wrackmeyer, *Angew. Chem.* **1997**, *109*, 902–904; *Angew. Chem. Int. Ed. Engl.* **1997**, *8*, 888–890.

[2] M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr., P. A. Wegner, *J. Am. Chem. Soc.* **1968**, *90*, 879–896.

[3] D. J. Hyatt, J. L. Little, J. T. Moran, F. R. Scholer, L. J. Todd, *J. Am. Chem. Soc.* **1967**, *89*, 3342.

[4] W. H. Knoth, *J. Am. Chem. Soc.* **1967**, *89*, 3342–3344.

[5] L. Wesemann, Y. Ramjoie, M. Trinkaus, B. Ganter, *Inorg. Chem.* **1997**, *36*, 5192–5197.

[6] L. Wesemann, Y. Ramjoie, M. Trinkaus, T. Spaniol, *Eur. J. Inorg. Chem.* **1998**, 1263–1268.

[7] D. E. Bowen, R. F. Jordan, R. D. Rogers, *Organometallics* **1995**, *14*, 3630–3635.

[8] G. Chandra, M. F. Lappert, *J. Chem. Soc. A* **1968**, 1940–1945.

[9] M. U. Pilotti, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1990**, 2625–2632.

[10] F.-E. Baumann, J. A. K. Howard, O. Johnson, F. G. A. Stone, *J. Chem. Soc. Dalton Trans.* **1987**, 2917–2925.

[11] L. Barton, D. K. Srivastava in *Comprehensive Organometallic Chemistry II, Vol. 1* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, Oxford, **1995**, pp. 342–348.

[12] X-ray structure analysis of **5'**: $C_{21}H_{59}B_{10}Br_3N_3NbSi$; $M_r = 822.54$; triclinic space group $I\bar{1}$ (no. 2) non-standard setting; $a = 25.209(9)$, $b = 10.556(4)$, $c = 27.675(9)$ Å, $\alpha = 88.65(9)$, $\beta = 93.91(6)$, $\gamma = 91.00(9)^{\circ}$, $V = 7344(5)$, $Z = 8$, $\rho_{calcd} = 1.488\ g\,cm^{-3}$; $\mu_{lin.} = 3.64\ mm^{-1}$; Stoe IPDS diffractometer; $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å); graphite monochromator; data collection at 200(2) K on a single crystal $0.7 \times 0.5 \times 0.2\ mm^3$, $1.5^{\circ} \leq \theta \leq 22.7^{\circ}$, $0 \leq \phi \leq 200^{\circ}$; 15285 reflections measured, 8777 independent, 5071 observed with $I > 2\sigma(I)$; corrections for Lorentz and polarization factors; numerical absorption correction,[13] max./min. transmission 0.48/0.15; structure solution with direct methods and difference Fourier synthesis;[14] F^2 refinement, isotropic displacement parameters, hydrogen atoms in calculated positions (C–H 0.98, B–H 1.12 Å), split positions for Nb and Br atoms; convergence was obtained for 271 variables with $wR2 = 0.064$, $R1(\text{observed}) = 0.046$, GOF = 1.003; max./min. residual electron density $+0.76/-0.66\ e\,Å^{-3}$. The crystal structure is very close to monoclinic symmetry (pseudo symmetry $I2/a$), but neither the metric nor the reflection conditions for the higher symmetry are met. Although both independent anions might be connected by a twofold axis, the $[Bu_4N]^+$ ions differ in conformation. 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-115869. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-36-033; e-mail: deposit@chemcrys.cam.ac.uk).

[13] N. W. Alcock, P. J. Marks, K.-G. Adams, *Modified Version of ABSPSI, Program for Numerical Absorption Correction of Single Crystal Data*, Universität Karlsruhe, Germany, **1995**.

[14] G. M. Sheldrick, *SHELX-97, Program for Crystal Structure Determination*, Universität Göttingen, Germany, **1997**.

[15] K. E. Stockman, K. L. Houseknecht, E. A. Boring, M. Sabat, M. G. Finn, R. N. Grimes, *Organometallics* **1995**, *14*, 3014–3029.

[16] J. Arnold, T. D. Tilley, A. L. Rheingold, S. J. Geib, *Organometallics* **1987**, *6*, 473–479.

[17] G. I. Nikonov, L. G. Kuzmina, D. A. Lemenovskii, V. V. Kotov, *J. Am. Chem. Soc.* **1995**, *117*, 10133–10134.

[18] R. W. Chesnut, P. E. Fanwick, I. P. Rothwell, *Inorg. Chem.* **1988**, *27*, 752–754.

[19] P. Paetzold, *Adv. Inorg. Chem.* **1987**, *31*, 123–170.

[20] K. Wade, *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1–66.

Supramolecular Sensors for the Detection of Alcohols**

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In memory of Antonino Fava

The quest for selectivity is one of the key issues in developing new, efficient chemical sensors.[1] The use of supramolecular structures has proved to be one of the best approaches to

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generating new materials with molecular specificity for chemical sensing.[2] Here we report the preparation and chemical-sensor properties of a new class of cavitands, specifically designed to detect alcohol vapors by using mass-sensitive transducers. The quartz-crystal microbalance (QCM) piezoelectric sensor system is based on interactions of thin organic layers coated on the surface of a quartz crystal with analytes. The resulting mass increment of the organic layer lowers the fundamental resonance frequency f of the oscillating crystal.[3]

We previously showed that the use of cavitands as chemically sensitive layers leads to selective QCM sensors only if specific interactions, such as $\mathrm{CH}\cdots\pi$ interactions, are present between the preorganized cavity of the receptor and the analyte.[4] These interactions perturb the selectivity pattern expected on the basis of purely dispersive interactions between the analyte and the cavitand layer by adding their contribution to the sensor response. The $\mathrm{CH}\cdots\pi$ interactions alone provide significant specificity only in the presence of analytes with rather acidic methyl groups such as acetonitrile, nitromethane, and ethyl acetate.

To achieve high selectivity for a single class of analytes we designed new cavitand receptors **1**, **3**, and **5** that are capable of two synergistic interactions with the chosen analyte, namely, hydrogen bonding with the P=O group and $\mathrm{CH}\cdots\pi$ interactions with the π-basic cavity. The R, X, and Ar groups were chosen on the basis of the following considerations: a) The presence of long alkyl chains produces more highly dispersed, porous layers that allow easier access of the analytes to the bulk of the layer; b) the different X groups at the upper rim influence the π-basic character of the cavity; and c) the posphonate/phosphate moieties modulate the strength of hydrogen bonding. All mixed-bridged cavitands were prepared by a three- or four-step procedure, depending on the X substituent.[5] The presence of a stereogenic phosphorus(v) center as a bridging group gives rise to two diastereomers in which the P=O group is oriented inward ($\mathrm{PO_{in}}$) or outward ($\mathrm{PO_{out}}$) with respect to the cavity. The configuration of all diastereomers was assigned by established spectroscopic methods,[6] and confirmed in the case of **3** by X-ray structure analysis. The well-defined spatial orientation of the bridging P=O group with respect to the cavity strongly influences the complexation properties of these cavitands: A two-point interaction with suitable guests is possible only for the $\mathrm{PO_{in}}$ isomers **1**, **3**, and **5**, while in the $\mathrm{PO_{out}}$ isomers **2** and **4** the Ar group partially (**4**, Ar = OPh) or completely (**2**, Ar = Ph) occludes the cavity. Methylene-bridged cavitands **6** and **7** were synthesized by an established literature protocol.[7]

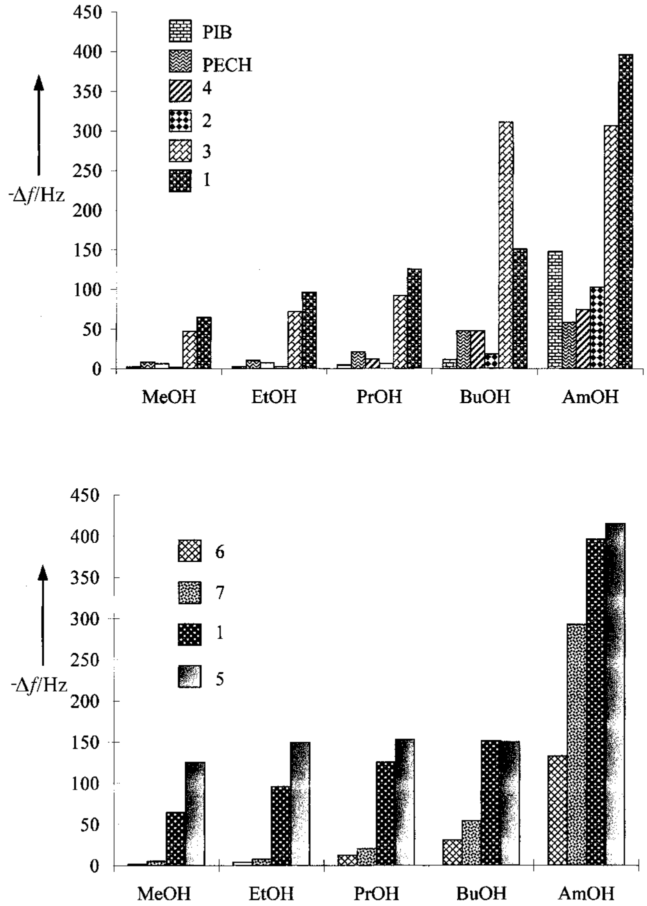
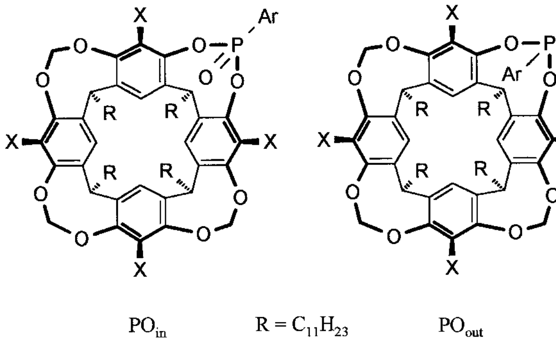


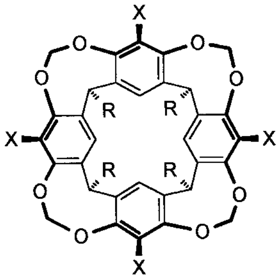
Figure 1. Selectivity patterns of cavitands **1**–**4**, PIB, and PECH (top) and of cavitands **1**, **5**, **6**, and **7** (bottom) towards linear $\mathrm{C_1-C_5}$ alcohols. Responses to 3000 ppm of each alcohol in nitrogen at 293 K. Each bar represents the mean value of four responses.

Layers of cavitands **1**–**7** and reference polymers polyisobutylene (PIB) and polyepichlorohydrin (PECH)[8] were deposited on both sides of gold-coated AT-cut quartz disks operating at 10 MHz (see Experimental Section). The coated disks were exposed at 20 °C to a constant flow of nitrogen with the desired content of analyte vapor (usually 3000 ppm). All sensor responses were highly reproducible and linear in the range 1000–4000 ppm. The responses of sensors coated with cavitands **1**–**7**, PIB, and PECH to linear $\mathrm{C_1-C_5}$ alcohols are summarized in Figure 1. The responses of the $\mathrm{PO_{in}}$ isomers **1**, **3** and **5** are always much higher than those of the $\mathrm{PO_{out}}$ isomers **2** and **4**. This dramatic enhancement arises from the presence of a preorganized cavity that can complex alcohols through a synergistic two-point interaction. Without such a specific interaction, the identical chemical constitution of the cavitands should give rise to similar selectivity patterns toward analytes, as is shown by the responses of the $\mathrm{PO_{out}}$ isomers, which are comparable to those of the reference polymers PIB and PECH.[9] The importance of cooperativity between $\mathrm{CH}\cdots\pi$ and hydrogen bonding interactions is demonstrated by comparison of the behaviors of **1** and **5** with those of **6** and **7**, in which only $\mathrm{CH}\cdots\pi$ interactions are operative (Figure 1, bottom). Both interactions can be fine-tuned by changing the X and Ar groups in the cavitand framework. Replacing the four Br substituents at the upper rim with $\mathrm{CH_3}$ groups enhances the π-basic character of the cavity and thus intensifies the $\mathrm{CH}\cdots\pi$ interactions (Figure 1, bottom). The better hydrogen bond acceptor capability of phosphonates relative to phosphates[10] is reflected in the higher responses of **1** versus **3** and **2** versus **4**, with the exception of *n*-butanol (Figure 1, top). A general enhancement of the responses of all receptors is associated with increasing number of carbon atoms in the alkyl chain. This behavior is due to the greater number of purely dispersive interactions, which are directly related to chain length,[11] and not to any strengthening of the



1 X = Br Ar = Ph
3 X = Br Ar = OPh
5 X = CH_3 Ar = Ph

2 X = Br Ar = Ph
4 X = Br Ar = OPh



R = $C_{11}H_{23}$

6 X = Br
7 X = CH_3

specific CH···π and hydrogen-bonding interactions, which should be comparable for all alcohols of the series. Nevertheless the selectivity of the PO$_{in}$ isomers toward linear alcohols is only diluted, but not cancelled, by the presence of these unspecific dispersive interactions.

Experiments with other classes of analytes indicated the preference of the PO$_{in}$ derivatives for alcohols over other compounds capable of CH···π interactions with the cavity, such as acetone, ethyl acetate, and chloroform (Figure 2).

The molecular structure of the complex **3**·EtOH confirms the two-point interaction between the PO$_{in}$ cavitands and alcohols (Figure 3). Two ethanol complexes are present in the asymmetric unit.[12] No guest molecules were found to reside among the alkyl chains at the lower rim of the cavitand. In each complex, the guest is anchored to the host by a hydrogen bond to the P=O moiety of the phosphate group (PO···O$_{guest}$ 2.78(1) and 2.91(2) Å), while the carbon chain is statistically distributed over two different orientations: one with the CH_2 group inside and the CH_3 group outside the cavity, and the other with the CH_2 outside and CH_3 inside (see Supporting Information). The main differences between the two complex units regard the strength of the host–guest interactive forces, which explains the presence of two independent molecules in the asymmetric unit. In one complex the guest is held only by the P=O···H–O$_{guest}$ hydrogen bond (PO···O$_{guest}$ 2.78(1) Å).

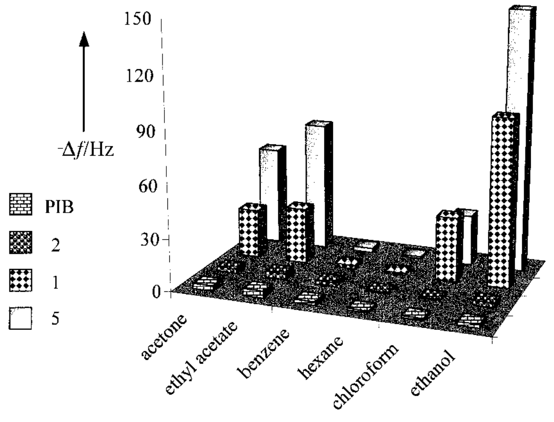


Figure 2. Selectivity patterns of cavitands **1**, **2**, **5**, and PIB to six organic vapors. Responses to 3000 ppm of each analyte in nitrogen at 293 K. Each bar represents the mean value of four responses.

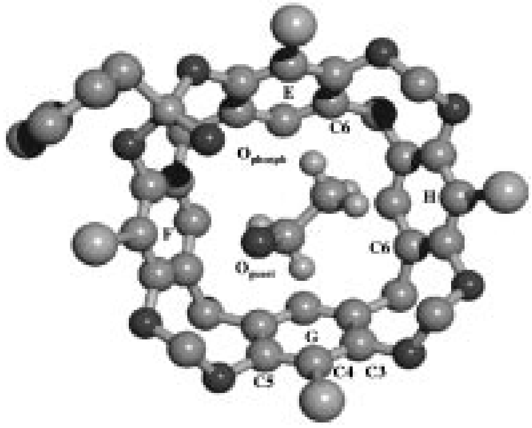


Figure 3. Molecular structure of **3**·EtOH (for clarity the undecyl groups on the lower rim are not shown).

In the other complex the P=O···H–O$_{guest}$ bond is weaker (PO···O$_{guest}$ 2.91(2) Å), but the guest ethanol molecule is involved in CH···π interactions between its CH_2 (or CH_3) group and the aromatic walls of the host. When the CH_2 group is inside the host cavity, the interactions involve one hydrogen atom of the CH_2 group and C3–C5 of ring G (H$_{guest}$···C$_{Ar}$ 2.880(9), 2.690(9), and 2.873(9) Å, respectively; orientation shown in Figure 3). Weaker CH···π interactions occur when the guest ethanol molecule is oriented with its CH_3 group inside the host cavity. In this case one hydrogen atom of the CH_3 group is anchored to C6 of ring H (H$_{guest}$···C$_{Ar}$ 2.822(9) Å), while another methyl hydrogen atom interacts with C6 of ring E (H$_{guest}$···C$_{Ar}$ 2.866(7) Å). The small mean atomic squared displacement of 0.08 Å^2 for the hydrogen atoms of the guest is consistent with attractive host–guest interactions, which restrict the atomic motion of the hydrogen atoms.

In conclusion, comparison of the responses of diastereomeric cavitands clearly shows that the simultaneous presence of two interactions, which is possible only for the PO$_{in}$ isomers, provides a remarkable increase in the response towards linear alcohols and that this strategy can be used to produce highly selective supramolecular mass sensors.

Experimental Section

General procedure for **1**–**5**: Phenylphosphonic acid dicloride or phenyl phosphoric acid dichloride (3.76 mmol) in dry THF (10 mL) was added dropwise over about 1 h to a solution of tetramethyl/tetrabromo triply bridged resorcinarene[5] (0.75 mmol) and triethylamine (7.51 mmol) in dry THF (100 mL). The resulting solution was stirred at room temperature for 1 d. After removal of triethylammonium chloride by filtration, the solvent was evaporated in vacuum to leave a yellow oil, which was purified by column chromatography. In all cases both PO_{in} and PO_{out} isomers were obtained. Analytically pure **1** and **2** were obtained as white solids in 39 and 17 % yield, respectively, after purification by chromatography (silica gel, CH_2Cl_2) followed by crystallization from ethanol. The same procedure afforded **3** and **4** as white solids in 43 and 19 % yield. Pure **5** was obtained as a white solid in 18 % yield after purification by chromatography (silica gel, Et_2O) followed by crystallization from acetonitrile. All compounds gave C and H elemental analyses within 0.4 % of theory, $[MH^+]$ signals of 100 % intensity in their CI-MS spectra, and ^1H NMR spectra consistent with their structure (see Supporting Information).

Apparatus and measurements: The flow chamber of the measuring system (Gaslab 20.1; IFAK, Magdeburg) contains four coated quartz crystals, a 10-MHz reference quartz crystal, and a thermocouple. The temperature of the chamber was kept at 20 ± 0.1 °C. The cavitand and polymeric layers were deposited on gold electrode areas on both sides of the quartz transducers by spraying solutions (0.1 % in $CHCl_3$) with an airbrush followed by evaporation of the solvent. The amount of material coated was controlled by measuring a frequency shift of $\Delta f = 20 \pm 0.05$ kHz on deposition of the layers. A stream of nitrogen ($500 \pm 5\,\mathrm{mL\,min^{-1}}$) containing one of the analytes was generated by dynamic gas mixing with two mass flow controllers. Organic vapors were generated by bubbling a stream of nitrogen carrier gas through the volatile liquids to produce a continuous steam saturated with vapor, the concentration of which depends on the vapor pressure of the liquid, which was calculated from Antoine's law.[13] This stream was diluted with nitrogen by the second mass flow controller to obtain an analyte concentration variable between 800 and 4000 ppm. All measurements were repeated four times, with variations in response of less than 5 %. A correction factor A was applied to all experimental data to take account of the different molecular weights (MW) of the analytes [Eq. (1)]. All correction factors were calculated with respect to methanol, the analyte with the lowest molecular weight.

$$f_{\mathrm{norm}} = f_{\mathrm{exp}} A \quad \text{where} \quad A = \mathrm{MW}_{\mathrm{methanol}}/\mathrm{MW}_{\mathrm{analyte}} \tag{1}$$

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[1] For a recent survey, see: *Acc. Chem. Res.* **1998**, *31*(5).

[2] a) F. C. J. M. Van Veggel in *Comprehensive Supramolecular Chemistry, Vol. 10* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, D. N. Reinhoudt), Pergamon, Oxford, **1996**, pp. 171–185; b) F. L. Dickert, A. Haunschild, *Adv. Mater.* **1993**, *5*, 887–895; c) K. D. Schierbaum, W. Göpel, *Synth. Met.* **1993**, *61*, 37–45; d) F. L. Dickert, U. P. A. Bäumler, G. K. Zwissler, *Synth. Met.* **1993**, *61*, 47–52; e) K. D. Schierbaum, T. Weiss, E. U. Thoden van Velzen, J. F. J. Engbersen, D. N. Reinhoudt, W. Göpel, *Science* **1994**, *265*, 1413–1415.

[3] J. Janata, *Principles of Chemical Sensors*, Plenum, New York, **1989**, pp. 55–80; see also R. Schumacher, *Angew. Chem.* **1990**, *102*, 347–361; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 329–343.

[4] a) J. Hartmann, J. Hauptmann, S. Levi, E. Dalcanale, *Sens. Actuators B* **1996**, *35–36*, 154–157; b) A. Arduini, A. Casnati, E. Dalcanale, A. Pochini, F. Ugozzoli, R. Ungaro in *Supramolecular Science: Where It Is and Where It Is Going* (Eds.: R. Ungaro, E. Dalcanale), Kluwer, Dordrecht, **1999**, pp. 67–94, (*NATO ASI Ser. c*, **1999**, *527*).

[5] E. Dalcanale, P. Jacopozzi, F. Ugozzoli, G. Mann, *Supramol. Chem.* **1998**, *9*, 305–316.

[6] a) T. Lippmann, H. Wilde, E. Dalcanale, L. Mavilla, G. Mann, U. Heyer, S. Spera, *J. Org. Chem.* **1995**, *60*, 235–242; b) P. Jacopozzi, E. Dalcanale, S. Spera, L. A. J. Chrisstoffels, D. N. Reinhoudt, T. Lippmann, G. Mann, *J. Chem. Soc. Perkin Trans. 2* **1998**, 671–677.

[7] D. J. Cram, S. Karbach, H.-E. Kim, C. B. Knobler, E. F. Maverick, J. L. Ericson, R. C. Helgeson, *J. Am. Chem. Soc.* **1988**, *110*, 2229–2237.

[8] R. A. McGill, M. H. Abraham, J. W. Grate, *CHEMTECH* **1994**, 27–37.

[9] J. W. Grate, S. J. Patrash, M. H. Abraham, C. My Du, *Anal. Chem.* **1996**, *68*, 913–917.

[10] a) M. D. Joesten, L. J. Schaad, *Hydrogen Bonding*, Marcel Dekker, New York, **1974**; b) T. Gramstad, *Acta Chem. Scand.* **1961**, *15*, 1337–1346; c) E. M. Armett, E. J. Mitchell, *J. Am. Chem. Soc.* **1971**, *93*, 4052–4053.

[11] Responses originating exclusively from dispersive interactions correlate with the boiling points of the analytes and to the partition coefficients K_p: S. J. Patrash, E. T. Zellers, *Anal. Chem.* **1993**, *65*, 2055–2066; E. Dalcanale, J. Greenblatt in *Sensors and Microsystems* (Eds.: C. Di Natale, A. D'Amico), World Scientific, Singapore, **1996**, pp. 30–34.

[12] Single-crystal diffraction measurements on an Enraf Nonius CAD4 diffractometer with $\mathrm{Cu}_{K\alpha}$ radiation ($\lambda = 1.54178$ Å); data collection and refinement for $C_{81}H_{111}O_{10}Br_4P \cdot CH_3CH_2OH$ at 295 K: transparent crystal, crystal dimensions $0.20 \times 0.40 \times 0.5$ mm, triclinic, space group $P\bar{1}$ (no. 2), $a = 24.425(5)$, $b = 23.603(5)$, $c = 15.364(5)$ Å, $\alpha = 105.41(2)$, $\beta = 92.14(2)$, $\gamma = 97.31(2)^\circ$, $V = 8446(4)$ Å^3, $Z = 4$, $M_r = 1641.42$, $\rho_{\mathrm{calcd}} = 1.290\,\mathrm{g\,cm^{-3}}$, $\mu = 2.9344\,\mathrm{mm^{-1}}$, $2\theta_{\max} = 140^\circ$; of 29701 ($\pm h$, $\pm k$, $+l$) reflections collected, 28561 were unique ($R_{\mathrm{int}} = 0.035$) and 11466 observed ($F_o > 4\sigma(F_o)$). The structure was solved by direct methods with SIR92 (A. Altomare, M. C. Burla, M. Camalli, G. Casciarano, C. Giacovazzo, A. Guagliardini, P. Polidori, *J. Appl. Crystallogr.* **1974**, *27*, 435–436) and refined on F^2 with SHELX96 software (G. M. Sheldrick, Göttingen, Germany). Data were corrected for Lorentz and polarization effects. No absorption correction was performed. The aliphatic chains were affected by severe static disorder, and some geometrical constraints were imposed. The guest molecules were also disordered over two or three different orientations with identical occupancy factors. All non-hydrogen atoms were refined anisotropically with the exception of the disordered aliphatic chains and guest molecules. Hydrogen atoms were taken in their calculated positions riding on the corresponding C atoms (1368 parameters). Final $R1 = 0.093$ and $wR2 = 0.2576$ with GOF = 1.219; max./min. residual electron density $0.97/-0.88\,\mathrm{e\,Å^{-3}}$. Geometrical calculations were obtained with PARST97 (M. Nardelli). 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-111939. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[13] *Handbook of Chemistry and Physics*, 54th ed., CRC Press, Cleveland, **1973–1974**, pp. D162–D181.