temperature. An immediate color change from yellow to orange occurred, and IR analysis indicated complete conversion into a mixture of **7** (major) and **6** (minor). The solution was stirred in the dark for an additional 5 h, during which IR analysis indicated complete conversion into **9**. The volume was reduced to 2 mL, and diethyl ether added to precipitate the product as a yellow powder. Reprecipitation from acetone with diethyl ether afforded pure **9**-BF_4. Yield 83% (90 mg); IR (CH_2Cl_2): $\tilde{\nu}_{CO} = 2054$(s), 1991 cm^{-1}(s); ^1H NMR (CD_2Cl_2): $\delta = 7.0-7.6$ (m, 30H, Ph), 6.92 (m, 1H), 6.36 (d, $J_{H,H} =$ 6 Hz, 1H), 6.30 (m, 1H), 6.04 (t, $J_{H,H} = 6$ Hz, 1H), 5.52 (t, $J_{H,H} = 6$ Hz, 1H), 4.49 (d, $J_{H,H} = 7$ Hz, 1H); ^{31}P NMR (CD_2Cl_2): $\delta = 31.9$ ($J_{P,Pt} = 1910$, $J_{P,P} =$ 17 Hz), 17.1 ($J_{P,Pt} = 4440$, $J_{P,P} = 17$ Hz); elemental analysis: calcd: C 53.08, H 3.41; found: C 53.50, H 3.46. Crystals of **9**-$BF_4 \cdot Et_2O \cdot \frac{1}{4}CH_2Cl_2$ suitable for X-ray diffraction analysis were grown by room-temperature vapor diffusion of Et_2O into a solution containing an equimolar mixture of **5**-BF_4 and $[Pt(PPh_3)_2(C_2H_4)]$ in CH_2Cl_2. The crystals lose the diethyl ether molecules of crystallization rapidly at room temperature when exposed to air. Hence, the crystal selected for diffraction studies was cut and stored under Et_2O until used. Coating with fluoro-lube and maintaining a temperature of $-30\,^{\circ}C$ prevented loss of Et_2O of crystallization during X-ray data collection.

Received: February 2, 1999 [Z12983IE]
German version: *Angew. Chem.* **1999**, *111*, 2343–2346

Keywords: hydrodeoxygenations · insertions · manganese · metallacycles · platinum

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An Effective Fluorescent Sensor for Choline-Containing Phospholipids**

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The design and synthesis of abiotic receptors based on uncommon binding units are of particular interest in molecular recognition research since they allow for the manifestation of nonconventional binding forces such as those originating from the CH···O hydrogen bond.[1] While this interaction dictates the hydrogen bonding pattern and crystal

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[**] This research was supported by the Dirección General de Enseñanza Superior (grant nos. PB95-341 and PB96-143) and the Spanish Ministry of Education (predoctoral fellowship to R.P.).

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packing in many organic solids,[2] including biological macromolecules,[3] examples of CH···O bonding in solution are scarce.[4] Both theoretical calculations[5] and a variety of experimental evidence[2a, 4c, 6] suggest that the enthalpy of a typical CH···O contact is roughly 0.3–1 kcal mol^{-1}, depending on the polarity of the C–H bond. Thus, this attractive interaction could be harnessed for molecular recognition studies provided that multiple CH···O contacts can be included in the design of the host–guest complex. For example, eight intermolecular CH···O contacts could translate into an enthalpic contribution of 2.4–8 kcal mol^{-1} towards the free energy of association.

Recently, we described[7] a series of tripodal receptors that recognize tetraalkylammonium compounds in chloroform. In these receptors an ammonium ion guest is retained by a number of CH···O contacts.[8] The acceptors are carbonyl oxygen atoms from three secondary squaramides oriented towards the center of a tripodal structure resembling a molecular grapple (Figure 1). Now, we report on a class of fluorosensors based on these units that can signal the presence of choline phospholipids.[9]

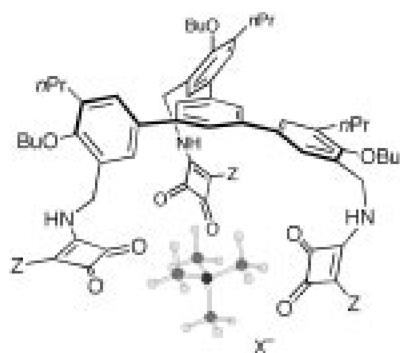


Figure 1. Representation of an idealized tripodal squaramide complex (left) and its mechanical equivalent (right). A tetramethylammonium ion is shown as the guest. Z = RNH$^-$, where R = alkyl or arylamino; X = BH_4^-, Cl^-, Br^-, I^-.

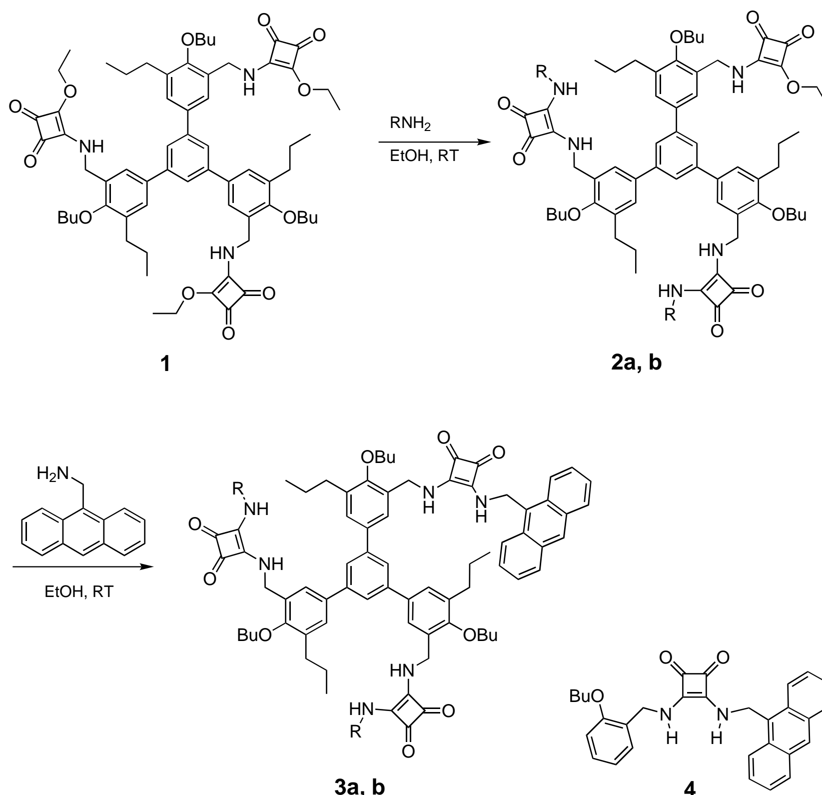
Choline phospholipids are important targets for molecular recognition, especially since important biological processes have been linked to the composition of cell wall phospholipids.[10] In our approach, we have developed a synthetic squaramidic probe that detects choline phospholipids, namely, dipalmitoyl phosphatidylcholine (DPPC) and sphingomyelin (SP).[11]

We previously established that simple tetraalkylammonium salts NR_4X (X = Cl, Br, I, BH_4^-) formed 1:1 complexes with our tripodal squaramidic receptors in chloroform (Figure 1). Taking advantage of these findings, we have synthesized two similar structures having the same squaramide-lined binding pocket while an anthryl ring was introduced as an active fluorescent component. This arrangement behaves as a tripodal molecular grapple that is structurally well disposed for signaling choline phospholipids because complexation induces conformational changes which effectively modulate the fluorescence intensity of the receptors.

The synthesis of **3a** and **3b** is outlined in Scheme 1. Condensation of triester **1** with *n*-octylamine and 4-(*N*,*N*-dimethylamino)aniline in ethanol gave the mixed squaramides **2a** and **2b**, respectively. Further condensation of **2a** and **2b** with 9-(aminomethyl)anthracene in ethanol provided **3a** and **3b**[12] in respective yields of 18 and 26% (from **1**) after purification. Squaramide **4** was also prepared as a model compound.

Compounds **3a** and **3b** are soluble in $CDCl_3$ at concentrations of up to 10^{-3} M, but their ^1H NMR spectra were unassignable due to broad resonances, suggesting the existence of several slow-exchanging conformers as well as some intramolecular hydrogen bonding between the squaramide moieties.[13] When ammonium salts such as benzyltrimethylammonium bromide (BTABr), DPPC and SP were added, key resonances in hosts **3a** and **3b** sharpened and shifted characteristically, indicating the formation of complexes. The trend of complexation-induced NMR shifts for DPPC and SP was the same as for the simple BTABr guest, implying that the ammonium moiety of DPPC and SP is indeed bound within the core of tripodal **3a**.

Despite the complexation-induced shifts, fluorescence spectrophotometry was chosen for a more accurate determination of the association constants. The steady-state fluorescence spectra of a **3a**,**b** and **4** in $CHCl_3$ (λ_{exc} = 369 nm) shown in Figure 2a, exhibit a structured set of bands assigned to the anthryl component; maximum intensities are located at 400, 421, and 441 ± 2 nm. Significant differences in the intensities



Scheme 1. Synthesis of **3a** (R = *n*-octyl) and **3b** (R = 4-(*N*,*N*-dimethylamino)phenyl). RT = room temperature.

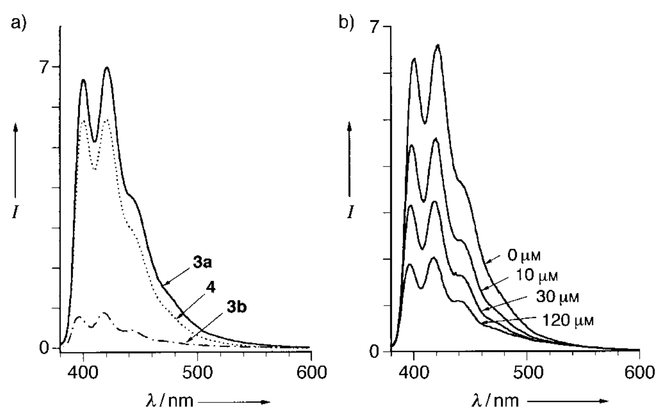


Figure 2. a) Fluorescence spectra of **3a**, **3b**, and **4** (λ_{exc} = 390 nm) recorded at constant concentration (5×10^{-6} M). b) From top to bottom, fluorescence spectra of **3a** (5×10^{-6} M) before and after addition of DPPC until the concentration reached the values given.

were also detected. Thus, while the emission spectrum of **3a** resembles closely that of model compound **4**, the intensity of **3b** is roughly eight times lower than that of **3a**, suggesting the existence of a self-quenching mechanism in **3b**. This intramolecular quenching can be rationalized in terms of a narrow energy gap between the strong *p*-dimethylaminoaniline electron donor and the anthryl acceptor.[10b, 14] We observed similar fluorescence quenching when an excess of 4-(*N,N*-dimethylamino)aniline was added to a solution of **4** in $CHCl_3$.

Decreases in the fluorescence emission of **3a** were observed immediately upon addition of dipalmitoyl phosphatidylcholine (DPPC) to a solution of **3a** in $CHCl_3$ (Figure 2b). Assuming that the effect of dynamic quenching or other mechanisms is small,[15] the observed DPPC-dependent quenching must reflect a significant complexation-induced conformational change.

Titration studies[16] performed with DPPC, SP, and BTABr in $CHCl_3$ confirm that the observed intensity change is a consequence of complexation. The stoichiometry of binding was assumed to be 1:1 since changes in the fluorescence intensity upon addition of the ammonium salts fit very nicely to the simple 1:1 binding model and signal saturation was evident upon addition of one equivalent of the guest. When possible, the association constants were also confirmed by UV absorption data.[17] For instance, titration of **3a** afforded association constants of 70000 ± 8100 and $55000 \pm 2900\,\text{M}^{-1}$ with DPPC and SP, respectively, values that closely resemble those obtained by fluorescence emission.

As indicated in Table 1, DPPC and SP bind to **3a** or **3b** with higher association constants than with BTABr or any other ammonium salt tested. Because of its high intensity of emission and pronounced fluorescence quenching upon complexation with ammonium salts, compound **3a** is well-suited to signal the presence of choline-containing phospholipids such as DPPC and SP. The intensity of the fluorescence emission of **3b** also decreases with the concentration of the ammonium salt. Moreover, a structureless emission band at 540 nm was observed upon complexation, which was assigned to the excimer. Unfortunately, this band is too weak for signaling the ammonium salts.

Table 1. Association constants K_a[a] and changes in fluorescence intensity ΔI of receptors **3a** and **3b** for selected tetraalkylammonium cell wall components and BTABr.

NR_4^+	Compd	K_a [M^{-1}]	ΔI [%]
BTABr	**3a**	10000 ± 1000	−66
BTABr	**3b**	35000 ± 4000	−47
DPPC	**3a**	81000 ± 5700	−86
DPPC	**3b**	158000 ± 28000	−51
SP	**3a**	53000 ± 5900	−60
SP	**3b**	111000 ± 19000	−26

[a] In $CHCl_3$ at 22 °C. Error calculated at a confidence level of 95 %.

Receptor **3a** also shows selectivity against other components usually found in the composition of cell membranes. Figure 3 compares the fluorescence intensity of **3a** upon addition of other phospholipids including phosphatidyl serine (PS), phosphatidyl ethanolamine (PE), and phosphatidyl

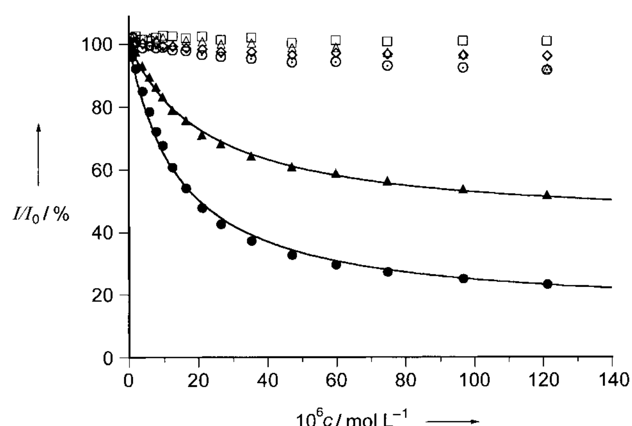


Figure 3. Experimental data (dots) and calculated fluorescence titration curves of **3a** with selected phospholipids: DPPC (●), SP (▲), PS (△), PE (◇), PI (⊙), and cholesterol (□). Experimental conditions as in Figure 2. Changes in intensity are recorded at 421 nm, the maximum of the emission spectrum.

inositol (PI). The effect of cholesterol was also tested as this substance is ubiquitous in cell membranes. Monitoring the fluorescence change of compound **3a** was used for sensing micromolar concentrations of PC and SP in artificial mixtures of cell membrane lipids. The method is also appropriate for measuring choline phospholipids from chloroform extracts obtained directly from cellular components.[18]

Having $C{=}O \cdots NR_4^+$ interactions at the center of the DPPC/**3a** complex (rather than $NH \cdots {}^-OP(O)OR_2$) is perhaps not so surprising since the charge of the NR_4^+ group is distributed over the four attached carbon atoms,[19] and up to twelve $CH \cdots O$ interactions can be envisaged in the DPPC/**3a** complex. We also note the minimal binding of PS, PE, and PI to **3a** (Figure 3). As for the binding selectivity towards DPPC, one can only speculate based on the current results. Secondary interactions between the phosphate oxygen atoms and the squaramido NH groups of **3a** could be possible if DPPC were to fold in between two of the three squaramide arms (while the R_4N^+ group remains anchored). In addition, the binding of **3a** to BTABr should restrict the translational freedom of the bromide ion about the BTA cation, leading to an entropic cost not present during DPPC complexation.[20] These factors

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could explain why the binding free energy for DPPC is 1.2 kcal mol^{-1} higher than that for BTABr.

We have designed a fluorosensor, in which unique squaric acid diamides serve as the binding substructure, for signaling the presence of selected choline phospholipids. We are currently testing the properties of similar squaramidic systems for signaling the presence of other relevant biomolecules.

Received: December 29, 1998
Revised version: March 25, 1999 [Z12837IE]
German version: *Angew. Chem.* **1999**, *111*, 2346–2349

Keywords: fluorescent sensors · molecular recognition · phospholipids · squaric acid · supramolecular chemistry

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[12] **3a**: M.p. 160°C; ^{1}H NMR (300 MHz, [D_6]DMSO, 24°C, TMS): δ = 8.76 (s, 1H, anthryl H10), 8.53 (d, ^3J (H,H) = 8.5 Hz, 2H, anthryl ArH), 8.23 (d, ^3J (H,H) = 7.9 Hz, 2H, anthryl ArH), 7.75–7.65 (m, 13H, spacer + anthryl ArH), 7.65–7.16 (br, 6H, NH), 5.88 (d, ^3J (H,H) = 5.3 Hz, 2H, NCH_2 anthryl), 4.90 (m, 6H, NCH_2 spacer), 3.92 (t, ^3J (H,H) = 6.10 Hz, 4H, OCH_2 butyl), 3.87 (t, ^3J (H,H) = 5.88 Hz, 2H, OCH_2 butyl), 3.54 (m, 4H, NCH_2 octyl), 2.72 (m, 6H, $ArCH_2$ propyl), 1.87–1.51 (m, 22H, CH_2 chain), 1.25 (m, 20H, CH_2 chain), 1.05 (m, 18H, CH_3), 0.87 (m, 6H, CH_3); FAB-MS (*m*-nitrobenzyl alcohol): *m*/*z* (%): 1435 (100) [M^+], 1436 (95) [M+H^+], 1437 (55) [M+2H^+]; elemental analysis calcd for $C_{91}H_{114}N_6O_9$: C 76.12, H 8.00, N 5.85; found: C 76.14, H 8.07, N 5.70. **3b**: M.p. 220°C; ^{1}H NMR (300 MHz, [D_6]DMSO, 24°C, TMS): δ = 9.53 (s, 2H, NH), 8.74 (s, 1H, anthryl H10), 8.53 (d, ^3J (H,H) = 8.6 Hz, 2H, anthryl ArH), 8.21 (d, ^3J (H,H) = 7.7 Hz, 2H, anthryl ArH), 7.85–7.50 (m, 17H, spacer + anthryl ArH + NH), 7.32 (d, ^3J (H,H) = 8.8 Hz, 4H, ArH), 6.77 (d, ^3J (H,H) = 9.0 Hz, 4H, ArH), 5.86 (d, ^3J (H,H) = 5.4 Hz, 2H, NCH_2 anthryl), 4.97 (d, ^3J (H,H) = 5.1 Hz, 4H, NCH_2 spacer), 4.84 (d, ^3J (H,H) = 5.3 Hz, 2H, NCH_2 spacer), 3.94 (t, ^3J (H,H) = 6.10 Hz, 4H, OCH_2 butyl), 3.83 (t, ^3J (H,H) = 6.7 Hz, 2H, OCH_2 butyl), 2.90 (s, 12H, $N(CH_3)_2$), 2.75 (t, ^3J (H,H) = 7.2 Hz, 4H, $ArCH_2$ propyl), 2.61 (t, ^3J (H,H) = 7.1 Hz, 2H, $ArCH_2$ propyl), 1.88–1.50 (m, 18H, CH_2 chain), 1.02 (m, 18H, CH_3); FAB-MS (NOBA): *m*/*z* (%): 1449 (95) [M^+], 1450 (100) [M+H^+], 1451 (50) [M+2H^+]; elemental analysis calcd for $C_{91}H_{100}N_8O_9$: C 75.39, H 6.95, N 7.73; found: C 75.10, H 6.93, N 7.71.

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[16] Fluorescence titration data were analyzed with the curve-fitting program Peakfit 3.0. of Jandel Scientific.

[17] UV titrations were performed by recording simultaneously changes in the absorption of **3a** (2×10^{-5} M) at five wavelengths (294, 296, 298, 300, 302 ± 2 nm) upon addition of BTABr, DPPC, and SP (ca. 2×10^{-4} M). UV data were analyzed by HOSTEST 5.0, see: C. S. Wilcox in *Frontiers in Supramolecular Chemistry and Photochemistry* (Eds.: H.-J. Schneider, H. Dürr), VCH, Weinheim, **1990**, p. 123.

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