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Article

New Fluorogenic Dansyl-Containing Calix[4]arene in the *Partial Cone* Conformation for Highly Sensitive and Selective Recognition of Lead(II)

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A new efficient and highly selective fluorescent chemosensor for determination of Pb^{2+} has been obtained by covalent attachment of two pendent proton-ionizable dansylcarboxamide groups to the calix[4]arene preorganized in the *partial cone* conformation. This geometry of the calixarene moiety was chosen on the basis of the prior ^1H NMR study of conformations adopted by the flexible dansyl-containing prototype upon complexation with lead ion. In acidic MeCN-H_2O (1:1 v/v) solutions, the *partial cone* fluoroionophore allowed for detection of Pb^{2+} at the levels as low as 2.5 ppb, which is totally compatible with the regulations of the U.S. Environmental Protection Agency and the World Health Organization on the limiting content of this hazardous pollutant in drinking water.

Introduction

Heavy metal ions, such as Pb^{2+}, introduced into the environment at elevated levels as a result of human activities cause serious health-related problems to the society. In particular, lead(II) present in drinking water has severe negative effects on physical and mental development of children.[1] To minimize the risk, the content of this toxic pollutant in water must be controlled. Therefore, the search for new reagents allowing for selective and sensitive determination of Pb^{2+} in aqueous media is constantly receiving the attention of scientists. For this purpose, optical fluorescence-based sensors seem especially attractive because they provide a more efficient and less expensive alternative to standard practices such as, for example, atomic absorption and inductively coupled plasma spectroscopy. A typical optical chemosensor for the recognition of metal ions consists of a selective ligand with a covalently attached fluorophore which responds to the complexation-induced changes in the electron environment by spectral variation.[2] Fluoroionophores built on the calixarene scaffolds are a promising and quickly developing group of such reagents.[3] However, only few examples of fluorogenic calixarene-based receptors for sensing of hazardous heavy metal ions,[4,5] in particular Pb^{2+},[6,7] are available. Among the latter, a *cone* calix[4]arene with four pendent lower-rim dansyl groups is worth of special note for its sensitivity and selectivity for Pb^{2+} recognition.[6a,7]

Earlier, we reported a conformationally mobile calix[4]arene containing two dansylcarboxamide groups (**1**) as a highly selective optical sensor of Hg^{2+} in extraction from acidic (pH 2.5, HNO_3) aqueous solutions into chloroform.[4] Under the applied experimental conditions, **1** allowed for detection of mercury at micromolar concentrations in the presence of

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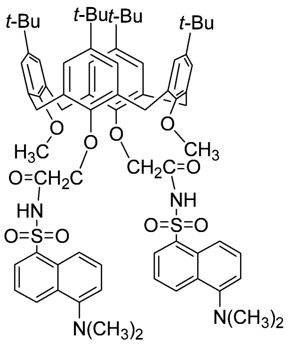
a large excess of different other metal cations. More recently, Leray et al.[7] showed that sensitivity of **1** for Hg^{2+} may be improved about 25-fold with selectivity remaining high when the recognition is carried out in $MeCN-H_2O$ (3:2, v/v) solution (pH 4.0, $HClO_4$). Although in the absence of mercury **1** was capable of complexation with lead ion, Pb^{2+} did not cause any notable interference with optical recognition of Hg^{2+} by **1** in the competitive experiments.[7] We hypothesized that preorganization of the calixarene moiety of **1** in the conformation appropriate for binding of Pb^{2+} and, at the same time, disfavored by Hg^{2+} may yield a fluorescent receptor with improved recognition ability toward lead ion. Herein, we present the results of our study on the design of a new highly efficient Pb^{2+}-selective optical chemosensor, fluorogenic calix[4]arene **2** immobilized in the *partial cone* (*paco*) conformation, containing two pendent proton-ionizable dansylcarboxamide groups.



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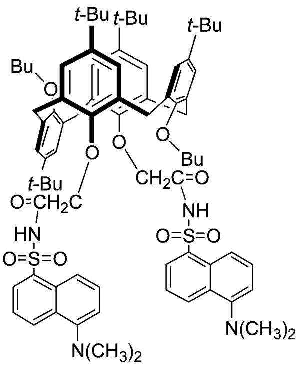

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Experimental Section

Materials. Flexible fluorogenic calixarene **1** was prepared as described earlier.[4] Lead(II) nitrate, lead(II) carbonate, lead(II) acetate, mercury(II) acetate, and mercury(II) oxide from Aldrich and Strem, all of the highest quality available, and HPLC-grade MeCN from Fisher were used as received; ACS-grade chloroform from Fisher was washed with deionized water and dried over Na_2CO_3.

Methods and Instrumentation. The corrected fluorescence spectra were obtained with a Shimadzu RF-5301PC spectrofluorometer. NMR spectra were recorded with a Bruker Avance spectrometer (400.13 MHz for ^1H, 100.62 MHz for ^{13}C) at temperature 298 K. Chemical shifts are expressed in ppm downfield from tetramethylsilane used as internal standard; J values are given in Hz. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass-spectra of the metal complexes were measured using dithranol or methyl ester of α-cyano-4-hydroxycinnamic acid[8] matrix on a Perkin-Elmer Biosystems Voyager-DE STR workstation equipped with a two-stage acceleration ion source. High resolution electrospray ionization (ESI) mass-spectra were obtained on an Agilent 6210 TOF LC/MS instrument.

Synthesis of 26,28-Dibutoxy-25,27-bis(*N*-dansyl-carbamoylmethoxy)-5,11,17,23-tetrakis(1,1-dimethylethyl)-calix[4]arenes (2) in the *Paco* Conformation. A solution of *paco*-diacid **3**[9] (1.00 g, 1.14 mmol) and oxalyl chloride (0.60 g, 4.57 mmol) in CH_2Cl_2 (20 mL) was stirred under N_2 at 25 °C for 15 h, and the solvent was removed in vacuo to provide the corresponding diacid chloride. A solution of the diacid chloride in tetrahydrofuran (THF, 20 mL) was added to a mixture of 5-(dimethylamino)naphthalene-1-sulfonamide (dansylamide, 0.63 g, 2.51 mmol) and NaH (0.14 g, 5.70 mmol) in THF (15 mL), and the mixture was stirred under N_2 at room temperature for 15 h. After that, H_2O (2 mL) was added (CAUTION!). THF was evaporated in vacuo, and CH_2Cl_2 (40 mL) and water (20 mL) was added to the residue. The organic layer was washed with 5% aqueous Na_2CO_3, then water, dried (Na_2SO_4), and evaporated in vacuo. The residue was purified by column chromatography on silica gel with CH_2Cl_2-MeOH (97/3) as eluent. The product was dissolved in CH_2Cl_2, and the solution was washed with 2 M aqueous HCl, then water, dried ($MgSO_4$), and evaporated in vacuo to give **2** as a yellow solid (1.12 g, 73% yield), mp 161–162 °C. ^1H NMR ($CDCl_3$): δ 0.31–0.40 (m, 2H), 0.45 (t, $J = 7.2$, 3H), 0.53–0.72 (m, 7H), 1.03–1.16 (m) + 1.10 (s) (11H), 1.20 (s, 9H), 1.24 (s, 18H), 2.13 (t, $J = 6.4$, 2H), 2.81–2.99 (m) + 2.90 (s) + 2.93 (d) (16H), 3.26 (d, $J = 13.0$, 2H), 3.80 (d, $J = 16.3$) + 3.85 (d, $J = 16.3$) (4H), 4.14 (d, $J = 13.0$, 2H), 4.30 (d, $J = 15.0$, 2H), 6.93 (br d, 2H), 6.97 (s, 2H), 7.07 (s, 2H), 7.17–7.23 (m, 4H), 7.54 (t, $J = 8.0$, 2H), 7.71 (t, $J = 8.1$, 2H), 8.42 (d, $J = 8.6$, 2H), 8.57 (d, $J = 7.8$, 4H), 10.42 (br s, 2H); ^{13}C NMR ($CDCl_3$): δ 13.83, 13.91, 18.31, 19.04, 29.83, 29.89, 31.35, 31.41, 31.44, 31.67, 34.00, 34.04, 39.14, 45.40, 70.37, 72.83, 74.87, 115.07, 118.55, 123.62, 124.63, 126.45, 126.57, 127.72, 128.74, 129.65, 129.73, 131.55, 132.54, 133.34, 133.47, 133.60, 134.16, 135.58, 145.20, 145.92, 146.23, 148.49, 151.38, 152.07, 154.89, 169.03. HRMS (ESI): found 1339.6778 $(M - H)^-$ (calcd for $C_{80}H_{99}N_4O_{10}S_2$ 1339.6803); found 1363.6722 $(M + Na)^+$ (calcd for $C_{80}H_{100}NaN_4O_{10}S_2$ 1363.6779), 1341.6904 $(M + H)^+$ (calcd for $C_{80}H_{101}N_4O_{10}S_2$ 1341.6959). Anal. Calcd for $C_{80}H_{100}N_4O_{10}S_2$: C 71.61, H 7.57, N 4.18. Found: C 71.32, H 7.61, N 4.11.

Lead(II) and Mercury(II) Complexes of 1. Metal complexes of the ionized calixarene used in the ^1H NMR studies were prepared in the two following ways. (a) Similarly to the earlier reported procedure,[10] the ligand in MeCN (or $CHCl_3$) was stirred with $PbCO_3$ or HgO, respectively, for 20 h. The solution was filtered, evaporated, and dried in vacuo. The residue was dissolved in CD_3CN ($CDCl_3$), and the ^1H NMR spectrum was measured. (b) An excess of lead(II) or mercury(II) acetate, respectively, was added to a solution of **1** in CD_3CN ($CDCl_3$), and the ^1H NMR spectrum was measured.

^1H NMR spectra of the complexes (signals for the dominant conformations): *Paco* **1**-Pb ($CDCl_3$): δ 0.04 (br s, 3H), 1.01(s, 18H), 1.15 (s, 9H), 1.33 (s, 9H), 2.79 (s, 12H), 3.02 (d, $J = 12.5$, 2H), 3.18 (d, $J = 12.9$, 2H), 3.40 (s, 3H), 3.53 (d, $J = 12.9$, 2H), 3.80 (d, $J = 12.5$, 2H), 4.59 (d, $J = 15.7$, 2H), 5.30 (d, $J = 15.7$, 2H), 6.85 (d, 2H), 6.94 (s, 2H), 7.03 (s, 2H), 7.12 d + 7.14 d (4H), 7.48 (t, $J = 8.0$, 2H), 7.67 (t, $J = 6.7$, 2H), 8.22 (d, $J = 6.8$, 2H), 8.36 (d, $J = 8.5$, 2H), 8.74 (d, $J = 8.5$, 2H). *1,3-Alternate* **1**-Hg (CD_3CN): δ 1.30 (br s, 36H), 2.86 (s, 12H), 3.46 (s, 6H), 3.83 (s, 8H), 4.34 (s, 4H), 7.25 (d, $J = 7.0$) + 7.30 (s) + 7.35 (s) (10H), 7.64 (br s, 4H), 8.22 (d, $J = 6.7$, 2H), 8.41 (d, $J = 8.6$, 2H), 8.53 (d, $J = 8.2$, 2H). *Cone* **1**-Hg (CD_3CN): δ 0.82 (s, 18H), 1.34 (s, 18H), 2.91 (s, 12H), 3.25 (d, $J = 13.1$, 4H), 3.82 (s, 6H), 4.37 (d, $J = 13.1$, 4H), 4.58 (s, 4H), 6.53 (s, 4H), 7.25 (s, 4H), 7.34 (d, $J = 7.1$, 2H), 7.69 (t, $J = 7.5$, 4H), 8.54 (d, $J = 6.4$, 2H), 8.65 (d, $J = 8.3$) + 8.69 (d, $J = 8.8$) (4H).

X-ray Crystallography. X-ray quality crystals of the complex $[Pb\mathbf{4}(CH_3CN)(H_2O)]_4$ were obtained by slow evaporation of the CD_3CN solution. A colorless crystal of dimensions 0.32 × 0.22 ×

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Table 1. Crystallographic Data for the Structure of Complex $[\text{Pb}\mathbf{4}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]_4$

	$[\text{Pb}\mathbf{4}(\text{CH}_3\text{CN})(\text{H}_2\text{O})]_4$
formula	$C_{256}\ H_{316}\ N_{12}\ O_{40}\ Pb_4\ S_4$
formula wt	5158.21
temperature, K	203(2) K
wavelength, Å	0.71073 Å
crystal color	white
crystal system	orthorhombic
space group	*P bc n*
a (Å)	22.2504(6)
b (Å)	30.5529(7)
c (Å)	41.1767(10)
α,°	90
β,°	90
γ,°	90
V, $Å^3$	27992.5(12)
Z	4
D(calcd), Mg m^{-3}	1.224
μ, mm^{-1}	2.492
F(000)	10592
crystal size, mm^3	0.32 × 0.22 × 0.06
θ range, °	4.56 to 24.71
h, *k*, *l* range	$-26 \leq h \leq 26$
	$-35 \leq k \leq 35$
	$-48 \leq l \leq 35$
reflection collected	113411
independent reflection	23504
R_{int}	0.1701
T (min., max.)	1.00000, 0.60245
refinement method	full-matrix least-squares on F^2
GOF on F^2	1.065
R1, wR2 $[I > 2\sigma(I)]$	0.0849, 0.1599
R1, wR2 (all data)	0.2038, 0.2191
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$, e·$Å^{-3}$	2.117, −1.556

0.06 mm^3 was mounted on glass fiber using a small amount of epoxy cement. Data were collected on an Oxford Diffraction Gemini R CCD diffractometer. The crystals were irradiated using Mo Kα radiation ($\lambda = 0.71073$) with 1° scans. An Oxford Diffraction Cryojet XL low temperature device was used to keep the crystals at constant temperature of 203(2) K during data collection. Crystallographic data for the complexes are presented in Table 1.

Data collection was performed, and the unit cell was initially refined using CrysAlis CCD, Version 1.171.31.8.[11] Data reduction was performed using CrysAlis Red, Version 1.171.31.8[12] and XPREP v6.12.[13] Corrections were applied for Lorentz polarization. Empirical absorption correction was applied using spherical harmonics, implemented in the SCALE3 ABSPACK scaling algorithm.[12] The structure was solved and refined with the aid of the programs in the SHELXTL-plus [v6.10] system of programs.[14] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

Crystallographic data for the structure reported in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 658643.

Results and Discussion

Design of the Optical Chemosensor for Pb^{2+}. Choosing the Appropriate Calix[4]arene Conformation. It was demonstrated in a number of earlier publications[9,10,15] that upon complexation with a metal ion in solution, a flexible calixarene tends to adopt the shape which is the most appropriate for accommodating the guest. A calix[4]arene moiety with two opposite arene units bearing small-sized *CH_3*O-substituents (like in **1**) and, because of this, capable of oxygen-through-the-annulus rotation can adopt three distinctive basic conformations: *cone*, *paco*, and *1,3-alternate*. These calixarene conformations may be identified by ^{1}H NMR spectroscopy, in particular, by the characteristic patterns of signals in the spectra for *t*-Bu and Ar-*CH_2*-Ar group protons.

Our previous studies of nonfluorogenic analogs of **1**, flexible di-ionizable calix[4]arene-*N*-(X-sulfonylcarboxamides), revealed that *paco* was the principal geometry of these ligands in their complexes with Pb^{2+} in $CDCl_3$.[10] To verify whether **1** has the same conformational preference, its ^{1}H NMR spectra in the presence of Pb^{2+} were investigated. In this study, the complex formation of **1** with Pb^{2+}, which proceeds via the dansylcarboxamide NH-proton displacement by the metal ion, was achieved in two different ways: by adding excess of lead(II) acetate to the solution of the ligand in CD_3CN and by reacting **1** with solid $PbCO_3$ in CD_3CN and $CDCl_3$ as described in the Experimental Section.

In the ^{1}H NMR spectrum of **1** in CD_3CN solution at ambient temperature, most of the signals are broad, which suggests fast interconversion between several ligand conformations. (Two fragments of this spectrum are shown in Figures 1a and 2a.) However, a pair of well-separated singlets of equal integral intensity, evident in this spectrum in the region for *t*-Bu group protons (Figure 1a), indicates that *cone* is the dominant conformation of **1** in CD_3CN in the absence of coordinating metal ions.[16] An analogous pattern of signals is observed in the ^{1}H NMR spectrum of **1** in $CDCl_3$ (shown in the Supporting Information Figure S-1). Addition of increasing amounts of Pb^{2+} (as lead acetate) to the solution of **1** CD_3CN produced overall dramatic changes in the appearance of the ^{1}H NMR spectrum of the ligand. With about a 4-fold excess of Pb^{2+} over **1**, the proton signals sharpened, and at first revealed a substantial presence of calixarene in the *1,3-alternate* conformation: a typical pair

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(11) *CrysAlis CCD*, Version 1.171.31.8 (release 12–01–2007 CrysAlis171. NET); Oxford Diffraction Ltd.: Abingdon, U.K., 2007.

(12) *CrysAlis RED*, Version 1.171.31.8 (release 12–01–2007 CrysAlis171. NET); Oxford Diffraction Ltd.: Abingdon, U.K., 2007.

(13) *XPREP*, v6.12; Bruker AXS Inc.: Madison, WI, 2001.

(14) *SHELXTL*, v6.10; Bruker AXS Inc.: Madison, WI, 2000.

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(16) (a) Adopting of the *cone* conformation by a flexible calix[4]arene may be assisted by inclusion of MeCN or $CHCl_3$ molecules in the hydrophobic cavity. For sample X-ray structures of the corresponding calixarene-solvent complexes, see McKervey, M. A.; Seward, E. M.; Ferguson, G.; Ruhl, B. L. *J. Org. Chem.* **1986**, *51*, 3581–3584. (b) de Namor, A. F. D.; Castellano, E. E.; Salazar, L. E. P.; Piro, O. E.; Jafou, O. *Phys. Chem. Chem. Phys.* **1999**, *1*, 285–293. (c) Smirnov, S.; Sidorov, V.; Pinkhassik, E.; HavlicÈek, J.; Stibor, I. *Supramol. Chem.* **1997**, *8*, 187–196. (d) Gutsche, D. C.; Dhawan, B.; No, K. H.; Muthukrishnan, R. *J. Am. Chem. Soc.* **1981**, *103*, 3782–3792. (e) Benevelli, F.; Bond, A.; Duer, M.; Klinowski, J. *Phys. Chem. Chem. Phys.* **2000**, 3977–3981.

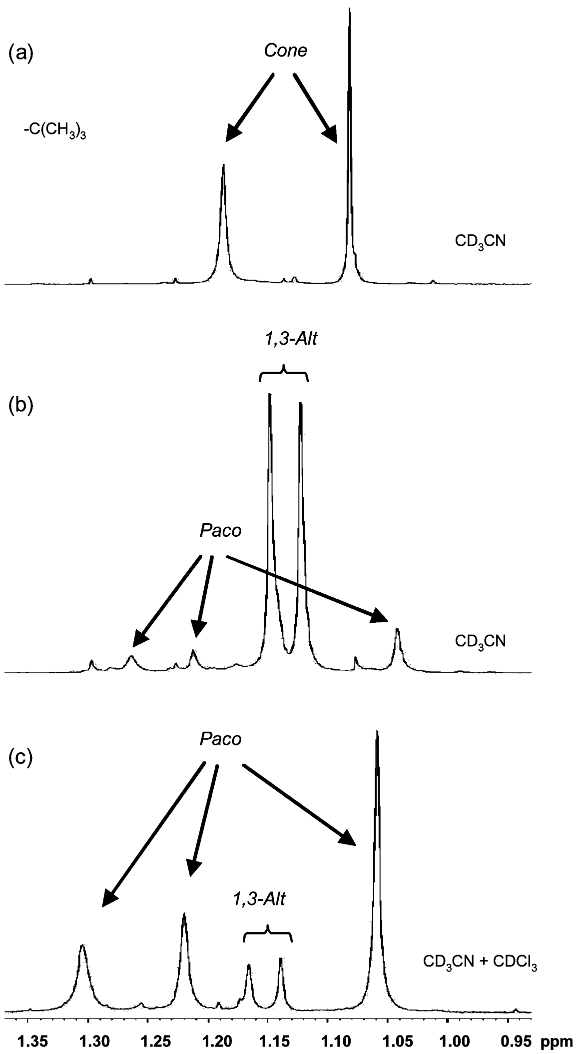


Figure 1. ^{1}H NMR spectra of **1** in CD_3CN in the absence of metal ions (a) and in the presence of excess of $Pb(CH_3COO)_2$: (b) the spectrum recorded immediately upon addition of Pb^{2+}; and (c) the spectrum of the same sample after formation of a precipitate, with a few drops of $CDCl_3$ added to increase the solubility of the complex.

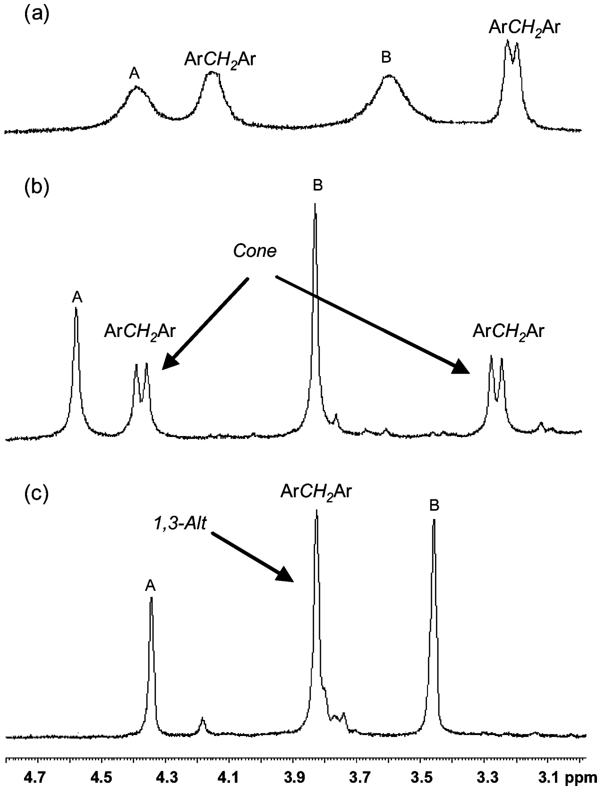


Figure 2. ^{1}H NMR spectra (CD_3CN) in the region of Ar-CH_2-Ar protons for **1** (a) and Hg^{2+}−**1** complexes obtained by the reaction of **1** with excess of $Hg(CH_3COO)_2$ (b) and HgO (c). (The signals for other groups of protons of **1**, OCH_2 and OCH_3, observed in the same region of the spectrum are indicated as A and B, respectively.)

of closely positioned, equally intense singlets for the *t*-Bu group protons may be seen in Figure 1b for this geometry. Along with the *1,3-alternate*, weaker signals for the *paco* conformation of **1**, with its unique set of three *t*-Bu proton singlets in the ratio of integral intensities of 2:1:1, are noticeable in this spectrum. Yet, the spectral picture for the sample continued changing in time, and the concomitant slow development of a white precipitate took place. To increase the complex solubility, a few drops of $CDCl_3$ were added to the above CD_3CN solution, and the ^{1}H NMR spectrum of the sample was measured again. In this spectrum of the Pb^{2+}−**1** complex (Figure 1c), dominance of the calixarene in the *paco* conformation in the presence of a smaller amount of the *1,3-alternate* species is obvious.

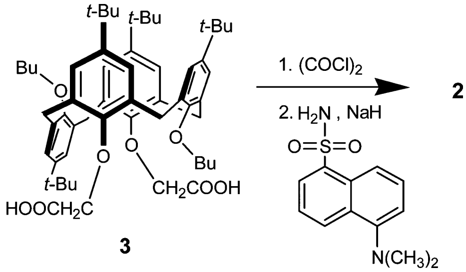
The ^{1}H NMR spectrum for the Pb^{2+}-complex obtained by the reaction of **1** with $PbCO_3$ in $CDCl_3$ was similar to that shown in Figure 1c, with the characteristic patterns of signals for the *paco* (the principal conformation) and the *1,3-alternate* calixarene (Supporting Information Figure S-2; unfortunately, in the spectrum for the analogous sample obtained in CD_3CN, all of the peaks were broadened significantly because of exchange processes, which made it inappropriate for structural elucidation).

Hence, under different experimental conditions, *paco* and *1,3-alternate* were found to be the preferred conformations of **1** in complexation with Pb^{2+}. Consequently, preorganization of such a dansyl-containing calixarene in either of these two geometries may be expected to promote the affinity of the ionophore for Pb^{2+}. At the same time, we were interested in obtaining a chemosensor which, along with enhanced Pb^{2+}-binding efficiency, would possess improved selectivity for lead over other relevant metal ions, in particular, over such a major competitor as Hg^{2+}. To prevent the interference of these two metal ions, it was important to ensure that the conformation chosen for the preparation of the new Pb^{2+}-sensing reagent is not favored by Hg^{2+} as well. Therefore, the geometric preferences of **1** in complexation with Hg^{2+} were studied by ^{1}H NMR similarly to the procedures described for Pb^{2+}, vide supra.

The ^{1}H NMR spectra in CD_3CN for **1** and its mercuric complexes in the region of Ar-CH_2-Ar group protons are illustrated in Figure 2. The corresponding spectra of the Hg^{2+}−**1** complexes in the region of *t*-Bu group protons are shown in the Supporting Information Figures S-3 and S-4. Reaction of **1** with excess of $Hg(CH_3COO)_2$ (Figure 2b) and solid HgO (Figure 2c) resulted in a significant sharpening of the NMR signals in the complexes relative to those in the free ligand (Figure 2a). Apparently, coordination of Hg^{2+} by the ligand slowed down the conformation exchange processes. However, unlike for the above discussed complexation of **1** with Pb^{2+}, which revealed consistency of the ligand conformational preferences under varying conditions for the complex preparation, reaction of **1** with weakly acidic $Hg(CH_3COO)_2$ and a base, HgO, yielded Hg^{2+}−complexes with contrasting dominant geometries.[17] In the former case, the *cone* was found to be the principal calixarene conformation. A typical pair of doublets for this geometry, at 3.25 and 4.38 ppm, for the calixarene Ar-CH_2-Ar protons is evident in Figure 2b.[18] In agreement, the *t*-Bu group protons in this complex produced two equal singlets at 0.82 and 1.34 ppm (Supporting Information Figure S-3). Meanwhile, for the solution of the Hg^{2+}−**1** complex prepared by the reaction of **1** with HgO, the pattern of signals in the ^1H NMR spectrum in CD_3CN clearly indicated *1,3-alternate* as the prevailing calixarene conformation. As shown in Figure 2b, Ar-CH_2-Ar protons in this complex produced a singlet at 3.83 ppm characteristic for a methylene group bridging two anti-oriented aryl units. Also, one broad singlet for the protons of four *t-Bu* groups of **1** in the spectrum of this mercuric complex (Supporting Information Figure S-4) is consistent with dominance of the *1,3-alternate* ligand geometry (unfortunately, NMR structural study of the Hg−**1** complexes in $CDCl_3$ was hampered by the significant broadening of the spectra, analogously to the behavior of nonfluorogenic analogs of **1** reported earlier[10]).

Therefore, the interaction of **1** with Hg^{2+} under different conditions was found to produce complexes in which the calixarene adopted predominantly the *1,3-alternate* or *cone* conformation. However, no indication of the ligand in the *paco* conformation was evidenced in the NMR spectra of these complexes. In agreement, our previous investigation[10] of solvent extraction of Hg^{2+} by the conformational isomers of the di-ionizable calix[4]arene-*N*-(X-sulfonylcarboxamides) (nonfluorogenic analogs of **1**) showed that the complexation efficiency of the preorganized ionophores varied as *1,3-alternate* > *cone* > *paco*. At the same time, the *paco* geometry of **1** was obviously preferred by Pb^{2+}. On the basis of the above considerations, the *paco* was identified as the most appropriate conformation for a new Pb^{2+}-selective calixarene containing two lower-rim pendent dansylcarboxamide groups (**2**).

Synthesis of the *Paco* Calixarene 2. **2** was obtained in two steps from the calix[4]arene diacid **3**[9] immobilized in the *paco* conformation as shown in the scheme below. Conversion of **3** into the corresponding acid chloride followed by reaction with dansylamide in the presence of NaH in THF afforded **2** in 75% yield. The compound has been characterized by elemental analysis, HRMS (ESI), ^1H NMR, and ^{13}C NMR, as described in the Experimental Section. For the original ^1H NMR spectrum of **2** in $CDCl_3$, see the Supporting Information Figure S-5.



Pb^{2+} Recognition Studies of 2. Dependence of the Fluorescence of 2 on the Solution pH. The acidic nature of the sulfonylamide NH-groups in **2** results in proton dissociation of this ligand in solution and, therefore, suggests that complex formation of **2** may proceed via proton displacement by a metal cation. Because of this, the effect of acid-dissociation of **2** on its fluorescence spectrum in MeCN−H_2O (1:1 v/v) mixture was evaluated prior to the metal complexation studies in the same solvent. Evolution of the emission spectrum of **2** at varied pH is shown in Figure 3a. The pattern of spectral changes observed for **2** is typical for the proton-ionizable fluorogenic ionophores containing *N*-dansylcarboxamide groups,[5b,c,19] including the flexible analog **1**. Thus, the emission band of undissociated **2**, which was observed at $\lambda_{em} = 544$ nm (with excitation at 330 nm) in acidic solutions (pH < 3.0, dil. HNO_3), exhibited a gradual hypsochromic shift, $\Delta\lambda_{em}$, of up to 48 nm accompanied by enhancement of the fluorescence intensity, *I*, as the solution pH increased from 2.0 to 10.0. The fluorescence pH profile of this ligand is presented in Figure 3b (filled circles) as a plot of $\Delta\lambda_{em}$ versus pH. For comparison, the analogous dependence obtained for **1** under otherwise identical conditions is shown in Figure 3b (empty circles). As is obvious from the shape of the curves in Figure 3b, the fluorescence pH profiles of **1** and **2** followed the same trend to simultaneous deprotonation of both of the pendent dansylcarboxamide groups.[20] At the same time, rigid **2** fixed in the *paco* conformation possessed a somewhat lower NH-acidity than its flexible analog. Such a difference might arise from possible involvement of the two pendent dansylamide groups of **2** in an intramolecular hydrogen bonding favored by their mutual spatial orientation.

For the further metal recognition studies of **2** in MeCN−H_2O (1:1 v/v), a working pH of 4.0 was chosen. As evident from the fluorescence pH profile of **2** (Figure 3b), at this pH, the ligand exists predominantly in undissociated form, H_2L. (By the same criterion, the pH of 3.5 was selected for complexation studies of **1** used for comparison of Pb^{2+} sensing by the *paco* and flexible fluorogenic calixarenes).

Optical Sensing of Pb^{2+} by 2. Addition of increasing amounts of Pb(II) nitrate to a solution of predominantly neutral **2** in MeCN−H_2O (1:1 v/v) at pH 4.0 (HNO_3) produced gradual changes in the emission spectrum of the

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(17) A detailed study of Hg^{2+}-**1** complexes is beyond the scope of the present work and will be published elsewhere.

(18) This observation is in agreement with the conclusion made in ref 7 for complexation of **1** with excess Hg^{2+} in CD_3CN-D_2O.

(19) Métivier, R.; Leray, I.; Valeur, B. *Photochem. Photobiol. Sci.* **2004**, *3*, 374–380.

(20) Similarly, a simultaneous deprotonation of pendent dansylamide groups was described earlier for the tripodal ligand. Prodi, L.; Bolletta, F.; Montalti, M.; Zaccheroni, N. *Eur. J. Inorg. Chem.* **1999**, *3*, 455–460.

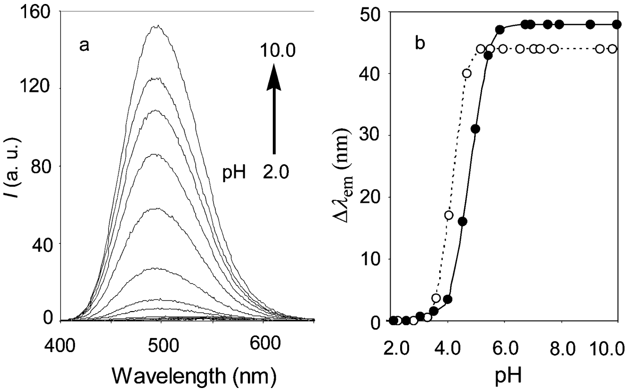

Figure 3. pH Dependence of fluorescence of **2** in MeCN−H_2O (1:1 v/v): (a) evolution of the emission spectrum of **2** with increasing pH (λ_{ex} 330 nm); (b) dependence of the hypsochromic shift of the emission band ($\Delta\lambda_{em}$) on the solution pH for **2** (●) and **1** (○).

ligand (Figure 4a) typical for dansylcarboxamide NH-proton displacement during metal ion complexation.[5b,7] The spectral response of **2** to variation in the formal concentration of Pb^{2+} (C_{Pb}) was monitored in both single-wavelength mode, by enhancement of the emission intensity at the wavelength of completely ionized ligand species, L^{2-} ($\lambda_{em} = 496$ nm), and dual-wavelength mode, by increase in the ratio of fluorescence intensities of ionized and neutral **2** (I_{496}/I_{544}). The graphs of these two dependencies have similar shapes (the plot of I_{496}/I_{544} vs C_{Pb} is presented in Figure 4b, while I/I_0 (496 nm) vs C_{Pb} is given in the Supporting Information Figure S-6). As shown in Figures 4c and 4d, both of the dependencies are well linearized in the coordinates of I_{496}/I_{544} (and I/I_0, respectively) versus log C_{Pb}, and either of them may be used as a calibration plot for the determination of microconcentrations of Pb^{2+}. With $C_2 = 1.25 \times 10^{-5}$ M under the indicated above conditions of solvent and pH, the detection limit of lead(II) defined as three times the signal-to-noise ratio was 1.2×10^{-8} M or 2.5 μg/L, which completely satisfies the maximum contaminant level for this metal in drinking water (MCL = 15 μg/L) regulated by the U.S. Environmental Protection Agency[1a] and 10 μg/L limit governed by the World Health Organization guidelines.[1b] To the best of our knowledge, such a level of sensitivity is the highest among the reported to date for fluorescent chemosensors of Pb^{2+}. This result is comparable only with that for the *cone*-shaped calix[4]arene tetra-dansylcarboxamide,[6a,7] which detection limit at 4.0 μg/L (MeCN−H_2O 3:2, v/v, pH 5.2, lutidine buffer) was considered unprecedented until now.

Preorganized versus Flexible Calixarene in Complexation of Pb^{2+}. Recognition of Pb^{2+} by **2** was compared with that by the flexible analog, **1,** in MeCN−H_2O (1:1 v/v) at pH 3.5(HNO_3) (see the section above for the choice of working pH). For the same ligand concentration, nonionized **1** exhibited noticeable fluorescence changes at significantly higher lead concentrations than neutral **2**. The plot of I_{502}/I_{546} versus C_{Pb} (where I_{502} and I_{546} are the emission intensities of the ionized and neutral **1**, respectively) is shown in Figure 4d. Hence, preorganization of the calixarene in the appropriate conformation obviously improved the efficiency of Pb^{2+} binding.

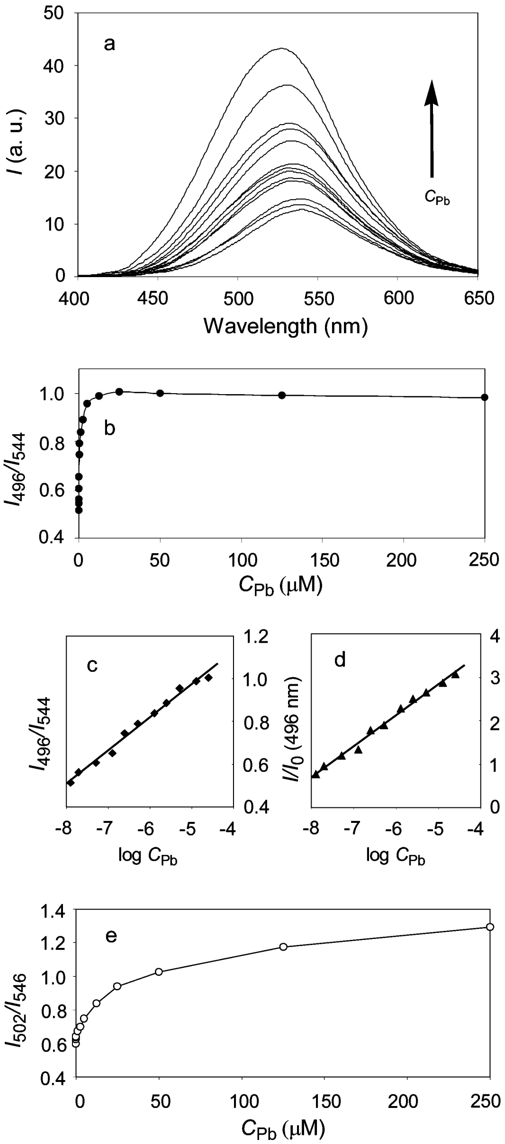

Figure 4. Optical sensing of Pb^{2+} by **2** in MeCN−H_2O (1:1 v/v) at pH 4.0 (HNO_3): (a) evolution of the fluorescence emission spectrum of **2** (λ_{ex} 330 nm) in the presence of increasing concentrations of Pb^{2+}; (b) ratiometric curve, I_{496}/I_{544} vs C_{Pb} ($C_2 = 2.5 \times 10^{-5}$ M); (c) calibration plot of I_{496}/I_{544} vs log C_{Pb} ($C_2 = 2.5 \times 10^{-5}$ M); (d) calibration plot of I/I_0 vs log C_{Pb} (λ_{em} 496 nm; $C_2 = 1.25 \times 10^{-5}$ M); (e) ratiometric curve, I_{502}/I_{546} vs C_{Pb} for the recognition of Pb^{2+} by **1** (shown for comparison purposes; pH 3.5, $C_1 = 2.5 \times 10^{-5}$ M, λ_{ex} 330 nm).

The following interesting common feature of lead(II) interaction with **1** and **2** is worth mentioning. Although both of the pendent dansylcarboxamide groups of these di-ionizable calixarenes were expected to participate in Pb^{2+} binding via the NH-proton displacement, the maximum magnitude of the blue shifts observed for the emission bands of **1** (31 nm) and **2** (26 nm) in the presence of a 1000-fold excess of the metal was significantly smaller than the λ_{em} (44 and 48 nm, respectively) produced by deprotonation of these ligands at elevated solution pH. In our opinion, such a relatively small complexation-induced shift of the emission band may result either from monoionization of **1** in its complex with Pb^{2+} (i.e., formation of $PbHL^{-}$ species) or from coordination of Pb^{2+} with L^{2-} in a fashion that moderates the increase in the electron density on the 5-methylaminonaphthalene rings caused by the deprotonation of the adjacent NH-groups. The latter might be observed, for instance, in the case of Pb^{2+} coordination with the carbamoyl oxygen rather than the nitrogen atom of the carboxamide group.[21] A possibility of such bonding of Pb^{2+} with calixarene-dansylcarboxamide will be illustrated vide infra.

From the comparison of the ratiometric curves for **2** and **1** (Figure 4b,d, correspondingly), one may expect different metal-to-ligand stoichiometry of Pb^{2+} complexation for the *paco* and flexible calixarenes. Analysis[22] of the fluorescence data for **1** revealed the dominance of a 1:1 complex with apparent formation constant of $\log K_f^{app} = 2.99$. Although the shape of the dependencies of I_{496}/I_{544} versus C_{Pb} (Figure 4b) and I/I_0 (496 nm) versus C_{Pb} (Supporting Information Figure S-6) for **2** suggests a possibility of binding of more than one ligand molecule per Pb^{2+} ion, fluorescence measurements for this calixarene did not allow for confident complex speciation in the region of low metal concentrations, whereas with the ratio of formal metal and ligand concentrations, $C_{Pb}/C_2 > 0.5$, a 1:1 complex with $\log K_f^{app} = 6.53$ was found to be the principal species.

MALDI-TOF mass-spectrometry with a dithranol matrix applied to the solutions of **2** in $MeCN-H_2O$ (1:1 v/v) in the presence of varied concentrations of Pb^{2+} at pH 4.0 confirmed formation of the 1:1 complex and showed no presence of complex species with other M/L-stoichiometry. Thus, the mass-spectra in the positive mode contained the peaks with *m/z* of 1547.82 and 1569.74 attributed to the species [(Pb**2**) + H^+] and [(Pb**2**) + Na^+], respectively. At the same time, an interesting phenomenon was observed for these mass-spectra. Even for the samples prepared with excess of Pb^{2+} over the ligand in solution (based on the fluorescence measurements, **2** was complexed almost entirely), the peak for the protonated free **2** (*m/z* 1363.82) was the most intense, and a smaller peak for the sodiated **2** (*m/z* 1385.81) was also evident, as well as the signals for [(Pb**2**) + H^+] and [(Pb**2**) + Na^+] (for a sample original MALDI-TOF mass-spectrum, see the Supporting Information Figure S-7). This may be an indication of the existence in the above samples of complexes with stoichiometry of **2**/$Pb^{2+} > 1$ that dissociate to 1:1 species under the applied ionization conditions.

Selectivity of Pb^{2+} Recognition by 2. As mentioned above, the flexible fluorogenic ligand **1** provided highly selective recognition of Hg^{2+} with no significant interference from Pb^{2+} and many other metal ions.[4,7] By preorganization of the calixarene in the appropriate conformation for complexation with Pb^{2+}, we aimed at obtaining a receptor with enhanced sensitivity and selectivity toward this cation. With respect for the propensities of the flexible prototype, competitiveness of lead complexation by the *paco* ligand in the presence of mercury was of particular interest in this study.

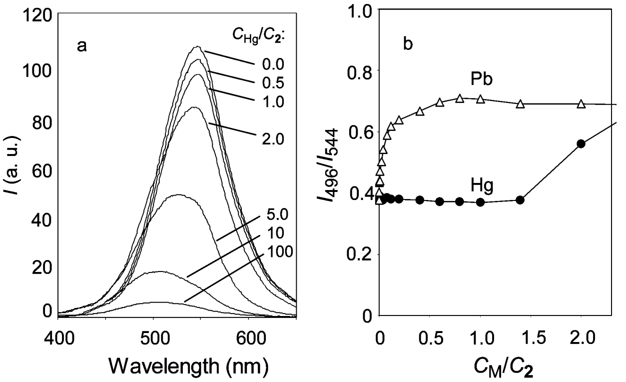

Figure 5. Recognition of Hg^{2+} by **2** in $MeCN-H_2O$ (1:1 v/v) at pH 4.0 (HNO_3): (a) changes in the fluorescence spectrum of **2** (λ_{ex} 330 nm) in the presence of varying concentrations of Hg^{2+}; and (b) ratiometric curves, I_{496}/I_{544} vs C_M/C_2, for the recognition of Hg^{2+} (●) and Pb^{2+} (△) by **2** ($C_2 = 1.25 \times 10^{-5}$ M).

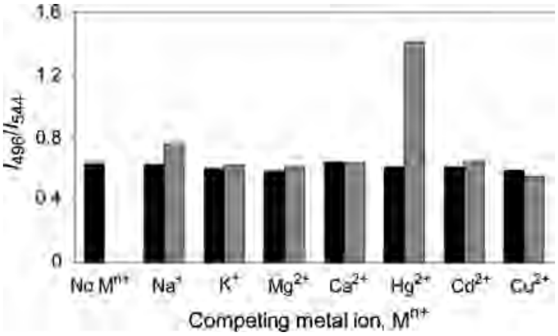

Figure 6. Selectivity of **2** for Pb^{2+} in competitive recognition studies for the binary mixtures of Pb^{2+} and competing metal ions, M^{n+}, with C_{Pb}/C_M 1:1 (black bars) and 1:100 (grey bars) ($MeCN-H_2O$ (1:1 v/v), pH 4.0; $C_2 = C_{Pb} = 1.25 \times 10^{-5}$ M; λ_{ex} 330 nm).

Therefore, changes of the fluorescence spectrum of **2** upon addition of varying amounts of mercury(II) nitrate in $MeCN-H_2O$ (1:1 v/v) at pH 4.0 (HNO_3) were studied. Similarly to the behavior of **1**, with increasing concentration of Hg^{2+}, **2** demonstrated the tendency to decrease in the fluorescence intensity as rationalized in terms of photoinduced electron transfer (PET) (Figure 5a). However, unlike **1**, the *paco* calixarene possessed relatively low sensitivity toward Hg^{2+} since no noticeable fluorescence quenching was observed for the solutions with the ratio of metal and ligand concentrations $C_{Hg}/C_2 < 0.5$. Contrary, **2** responded to ppb levels of Pb^{2+}, as described above. Also, in contrast with recognition of Pb^{2+} under otherwise identical conditions, only in the presence of excess of mercury over **2** was the blue shift of the emission band observed. Consequently, the ratio of fluorescence intensities I_{496}/I_{544} of **2** upon addition of relatively small amounts of Hg^{2+} remained unchanged, while that for Pb^{2+} increased (Figure 5b). On the basis of this difference, the high Pb^{2+}/Hg^{2+} selectivity of **2** may be envisioned in solutions with mercury content not exceeding the ligand concentration (e.g., 1.25×10^{-5} M in Figure 5b).

Competitive complexation experiments for **2** were carried out in solutions equimolar in **2** and Pb^{2+} ($C_2 = C_{Pb} = 1.25 \times 10^{-5}$ M), containing also Hg^{2+} or other relevant metal ions, M^{n+}, at the levels of $C_M/C_{Pb} = 1.0$ and 100 (shown as black and gray bars, respectively, in Figure 6). As evident from the graph in Figure 5c, in the former case, no significant

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[21] (a) For examples of crystal structures with $Pb^{2+}\cdots O{=}C$ coordination of amides, see No, K. H.; Kim, J. S.; Shon, O. J.; Yang, S. H.; Suh, I. H.; Kim, J. G.; Bartsch, R. A.; Kim, J. Y. *J. Org. Chem.* **2001**, *66*, 5976–5980. (b) Battistuzzi, G.; Borsari, M.; Menabue, L.; Saladini, M. *Inorg. Chem.* **1996**, *35*, 4239–4247.

[22] Valeur, B. *Molecular Fluorescence. Principles and Applications*; Wiley-VCH: Weinheim, 2002; pp 341–342.

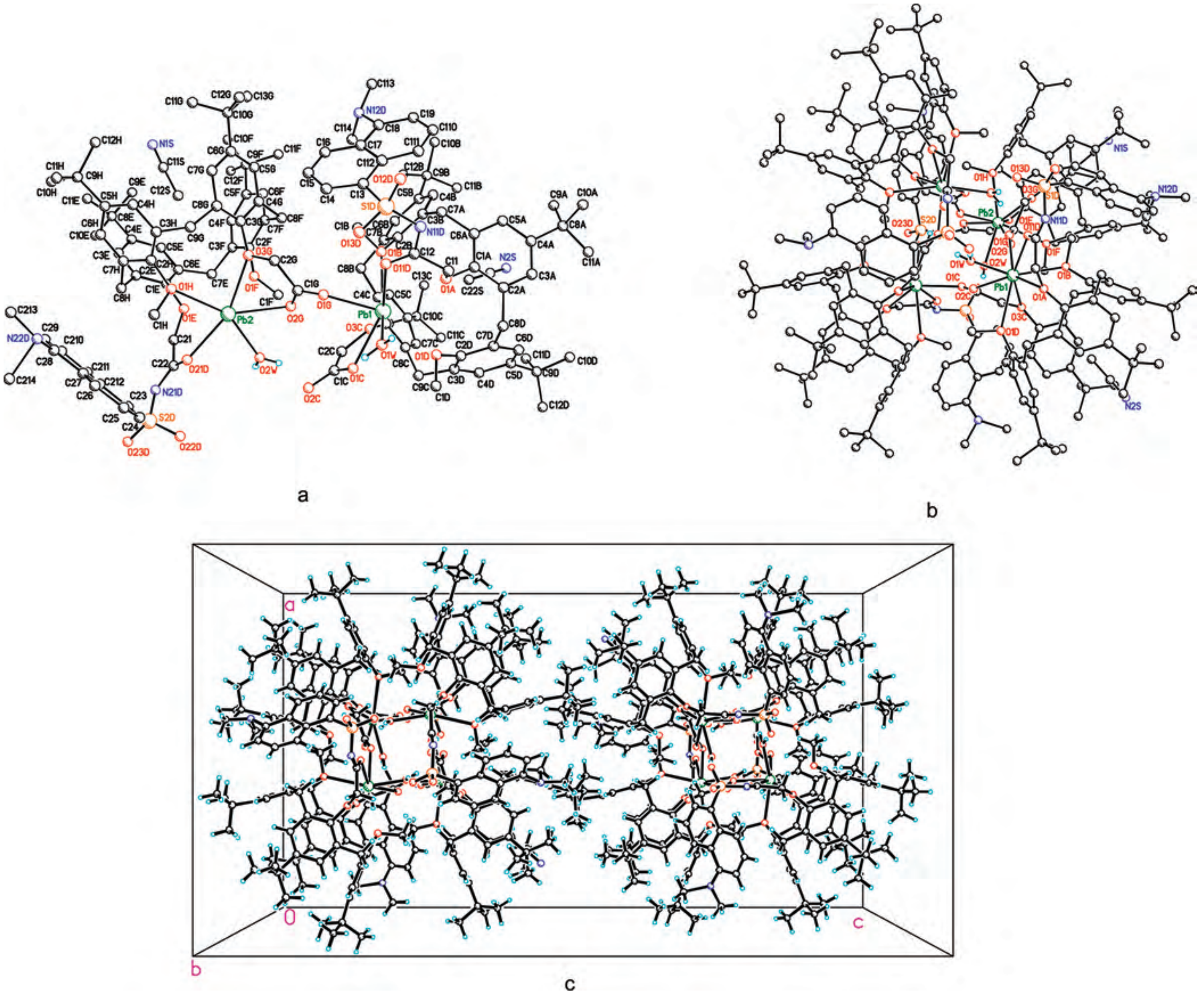


Figure 7. Crystal structure of [Pb**4**(CH_3CN)(H_2O)]$_4$: (a) the asymmetric unit, dimer [Pb**4**(CH_3CN)(H_2O)]$_2$; (b) the tetramer [P b**4**(CH_3CN)(H_2O)]$_4$; and (c) crystal packing.

interferences with Pb^{2+} recognition by **2** were observed. However, sensing of Pb^{2+} was affected considerably by the presence of a 100-fold excess of Hg^{2+} and, to a much lesser extent, Na^+. Some other metal ions under the same conditions caused only minor deviations in the I_{496}/I_{544}. Therefore, the preorganization of the dansyl-containing calixarene in the *paco* conformation improved both effectiveness and selectivity of optical recognition of Pb^{2+}.

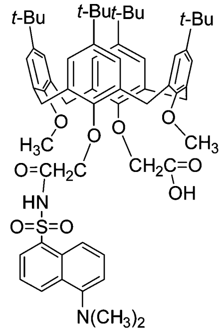
Accidental Discovery: Pb^{2+}-Complex of a Calix[4]arene Monodansylcarboxamide, 4. To the best of our knowledge, no crystallographic data for complexes of dansyl-containing calixarenes with lead(II) or mercury(II) have been available in the literature to date. Regretfully, our attempts to prepare X-ray appropriate single-crystals for the complexes of these metal ions with **2** and **1** have been unsuccessful so far. However, an accidental discovery described below provided insight into a possible coordination mode of Pb^{2+} with pendent ionized dansylcarboxamide groups of the fluorogenic calixarenes.

A sample obtained by an unusually long (more than 1 month) contact of **1** with $PbCO_3$ in MeCN, after it had been filtered, evaporated and redissolved in CD_3CN, showed an ^1H NMR spectrum dramatically different from the spectra discussed in the section Choosing the Appropriate Calix[4]-arene Conformation. In particular, appearance of this NMR spectrum in the region for the *t*-Bu proton signals (Supporting Information Figure S-8) clearly indicated dominance of the calixarene in the *cone* conformation. The MALDI-TOF mass-spectrum of the sample in MeCN was measured using methyl ester of α-cyanohydroxycinnamic acid as a matrix. The mass-spectrum in the positive mode (Supporting Information Figure S-9) contained the peaks for protonated, sodiated, and potassiated 1:1 complex of Pb^{2+} with $\mathbf{1}^{2-}$ (*m*/*z* 1463.10 for [Pb**1** + H]$^+$, 1485.20 for [Pb**1** + Na]$^+$, and 15010.78 for [Pb**1** + K]$^+$), as well as peaks with *m*/*z* values matching the Pb^{2+}-complex of a doubly ionized ligand **4**: *m*/*z* 1231.13 for [Pb**4** + H]$^+$, 1253.16 for [Pb**4** + Na]$^+$, 1269.03 for [Pb**4** + K]$^+$, and also low-intensity peaks with *m*/*z* of 2483.11 for [Pb_2**4**$_2$ + Na]$^+$ and 2716.59 for [Pb_2(**1**)(**4**) + Na]$^+$. Evidently,

Table 2. Selected Bond Distances (Å) and Angles (°) for $[Pb\mathbf{4}(CH_3CN)(H_2O)]_4$

Bond Distances			
Pb(1)−O(11D)	2.546(5)	Pb(2)−O(21D)	2.522(5)
Pb(1)−O(1C)	2.582(5)	Pb(2)−O(2G)	2.618(6)
Pb(1)−O(1G)	2.421(5)	Pb(2)−O(2C)	2.429(5)
Pb(1)−O(1B)	2.700(5)	Pb(2)−O(1H)	2.723(5)
Pb(1)−O(1A)	2.767(5)	Pb(2)−O(1E)	2.823(5)
Pb(1)−O(1D)	2.833(5)	Pb(2)−O(1F)	2.868(5)
Pb(1)−O(3C)	2.777(5)	Pb(2)−O(3G)	2.709(5)
Pb(1)−O(1W)	2.451(5)	Pb(2)−O(2W)	2.424(5)
Bond Angles			
O(1C)−Pb(1)−O(11D)	139.8(3)	O(2G)−Pb(2)−O(21D)	139.17(18)
O(1G)−Pb(1)−O(1C)	79.81(18)	O(2C)−Pb(2)−O(2G)	79.0(3)
O(1G)−Pb(1)−O(11D)	74.85(16)	O(2C)−Pb(2)−O(21D)	75.70(17)
O(1C)−Pb(1)−O(1W)	73.5(3)	O(2G)−Pb(2)−O(2W)	71.9(3)
O(1G)−Pb(1)−O(1W)	88.35(19)	O(2C)−Pb(2)−O(2W)	86.7(3)
O(1W)−Pb(1)−O(11D)	74.99(19)	O(2W)−Pb(2)−O(21D)	75.1(3)
O(1A)−Pb(1)−O(11D)	62.0(2)	O(1E)−Pb(2)−O(21D)	60.3(2)
O(1B)−Pb(1)−O(1D)	113.61(16)	O(1H)−Pb(2)−O(1F)	115.85(15)
O(1A)−Pb(1)−O(1D)	71.0(2)	O(1E)−Pb(2)−O(1F)	69.31(15)
O(1A)−Pb(1)−O(3C)	115.97(16)	O(1E)−Pb(2)−O(3G)	116.4(2)
C(1G)−O(1G)−Pb(1)	135.7(5)	C(1C)−O(2C)−Pb(2)	139.1(5)

a prolonged reaction of **1** with $PbCO_3$ resulted in a partial hydrolysis of its pendent dansylcarboxamide groups yielding the corresponding monoacid.



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It should be noted at this point that the subsequent testing performed for **1** and **2** revealed no indication of their dansylcarboxamide group hydrolysis upon the reaction with Pb^{2+} in acidic medium, as well as upon a shorter-time (1–2 days) contact of these ligands with $PbCO_3$ in MeCN or $CHCl_3$. Moreover, hydrolysis of **1** to **4** was not observed during a month-long interaction of the calixarene with HgO or Na_2CO_3. However, the unexpected finding discussed in this section suggests that Pb^{2+} has a potential of acting as a catalyst of basic hydrolysis of the dansylcarboxamide group. Further investigation of basic hydrolysis of **1** was beyond our interests.

Meanwhile, slow evaporation of CD_3CN from the sample used in the ^1H NMR study of the partially hydrolyzed complex yielded colorless, strongly fluorescent crystals which were analyzed by X-ray diffraction. As is obvious from the crystal structure presented in Figure 7, this compound is a tetrameric Pb^{2+}-complex with $\mathbf{4}^{2-}$, $[Pb\mathbf{4}(CH_3CN)(H_2O)]_4$. Selected bond distances and angles for the structure are presented in Table 2. Besides the evidence of partial basic hydrolysis of **1** supposedly catalized by Pb^{2+}, the structure revealed several other interesting features that are worth mentioning:

(i) The asymmetric unit consists of a dimer formed by two isostructural $[Pb\mathbf{4}(CH_3CN)(H_2O)]$ molecular units connected via bridging carboxylate groups of **4** (Figure 7a). Likewise, the dimers are further assembled into the tetramers (Figure 7b), two of which make the unit cell. The tendency of Pb^{2+}-complexes for polymerization by means of formation of carboxylate bridges is not uncommon (for example, see ref 21b).

(ii) Each of the Pb^{2+} ions is octa-coordinated with six oxygen atoms of the di-ionized **4**, one water molecule, and a bridging carboxylate oxygen of the ligand in the neighboring complex unit. Nitrogen atoms of the deprotonated dansylcarboxamide groups are not involved in coordination of Pb^{2+}. Instead, the bonding takes places via adjacent carbamoyl oxygen atoms, as well as oxygens of the carboxylate and phenolic groups.

(iii) All of the calixarene units within the complex are fixed in the *cone* conformation, with a molecule of acetonitrile entrapped inside of the cavity. The spatial orientation of the encapsulated MeCN molecules within the hydrophobic calixarene cups is analogous, with the methyl group oriented inward, which is typical for the calixarene−acetonitrile complexes.[16]

Detailed crystallographic information for $[Pb\mathbf{4}(CH_3CN)(H_2O)]_4$, as well as additional diagrams, are provided in the Supporting Information.

Therefore, in coordination with the dansyl-containing calixarene, Pb^{2+} demonstrated a clear preference for oxygen over nitrogen donor atoms. The crystals of $[Pb\mathbf{4}(CH_3CN)(H_2O)]_4$ were dissolved in $MeCN-H_2O$ (1:1 v/v) at pH 3.5, and the fluorescence spectrum was measured with excitation at 330 nm. The emission band for this complex was observed at the same wavelength, 515 nm, as the emission of **1** in the presence of a large excess of Pb^{2+} under the identical conditions of solvent and pH. As discussed in section Pb^{2+} Recognition Studies of **2**, this λ_{em} is also significantly longer than the wavelength for the uncomplexed $\mathbf{1}^{2-}$ projected from the fluorescence pH-profile. Addition of $PbNO_3$ to the solution of Pb**4** to suppress possible complex dissociation produced no further blue shift of the emission maximum. This supports the assumption made above that a relatively small λ_{em} observed for Pb^{2+}-complexed $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ should be attributed to the electronic factor (decreased electron density on the dansyl naphthalene ring because of metal ion coordination with adjacent C═O group) rather than equilibrium effects.

Conclusions

A new fluorescent calixarene described in this paper demonstrated remarkable sensitivity and selectivity toward lead(II) in acidic aqueous acetonitrile medium. This tremendous result was achieved because of the preorganization of the calix[4]arene moiety of the fluoroionophore in the *paco* conformation preferred by Pb^{2+} and disfavored by the competing metal ion, Hg^{2+}.

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Supporting Information Available: ^1H NMR spectra, MALDI-TOF mass-spectra, plot of I/I_0 (496 nm) vs C_{Pb} for **2**, and additional structure diagrams for $[Pb\mathbf{4}(CH_3CN)(H_2O)]_4$ obtained with Mercury 1.4.2 software (PDF). X-ray crystallographic file (CIF) for $[Pb\mathbf{4}(CH_3CN)(H_2O)]_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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