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# Novel Alkali Cation Chemosensors Based on *N*-9-Anthrylaza-crown Ethers[§]

**Bernhard Witulski,*,† Michael Weber,† Uwe Bergsträsser,† Jean-Pierre Desvergne,‡ Dario M. Bassani,‡ and Henri Bouas-Laurent‡**

*Fachbereich Chemie der Universität Kaiserslautern, Erwin-Schrödinger-Strasse,*
*D-67663 Kaiserslautern, Germany, and Laboratoire de Chimie Organique et*
*Organométallique, CNRS UMR 5802, Université Bordeaux 1,*
*F-33405 Talence, France*

*witulski@rhrk.uni-kl.de*

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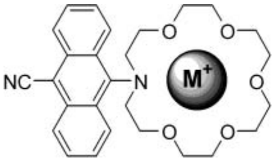
## ABSTRACT

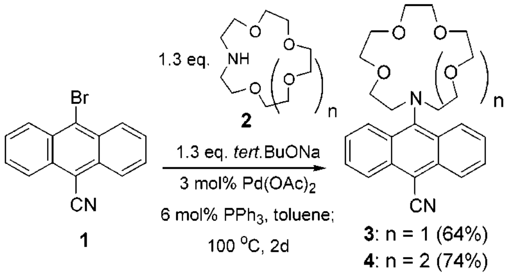


**A novel alkali cation selective probe is described which exhibits unique ICT and binding properties, allowing the ratiometric titration of sodium cations in the presence of other alkali metal ions.**

Considerable interest is devoted to dipolar *donor−spacer−acceptor* compounds in which the spacer is a $\pi$-conjugated system, both for their intramolecular charge transfer (ICT) properties and in connection with nonlinear optics.[1] One of the most extensively studied compounds is *p*-dimethylaminobenzonitrile which displays locally excited (LE) and ICT emission.[2] Incorporating the nitrogen atom into a complexing entity such as a coronand allows the spectroscopic properties to be modulated by metal cations. The resulting systems can then act as chemosensors for selected metal ions, as shown in several examples.[3] We anticipated that anthracene aza-crown analogues of *p*-dimethylaminobenzonitrile would exhibit interesting binding and spectroscopic properties, arising in part from steric constraints imposed by the attached anthracene chromophore.

The 10-cyano-9-*N*-anthryl-aza-crown ethers **3** and **4** were obtained in good yields via a palladium-catalyzed cross-coupling reaction[4] between 9-bromo-10-cyanoanthracene **1** and the corresponding aza-crown ethers **2** following our new approach for the synthesis of *N*-aryl-aza-crown ethers (Scheme 1).[5]

**Scheme 1**



The UV spectra of the free ligands **3** and **4** in acetonitrile are constituted of a structured absorption band in the 350−420 nm region, accompanied by a broad, nonstructured transition at 430−510 nm. Whereas the former is similar to

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[§] Dedicated to Prof. Henning Hopf on the occasion of his 60th birthday.

[†] Universität Kaiserslautern.

[‡] Université Bordeaux.

(1) (a) Wolff, J. J.; Wortmann, R. Organic Materials for Second-Order Nonlinear Optics. *Adv. Phys. Org. Chem.* **1999**, *32*, 121. (b) *Molecular Non-Linear Optics: Materials, Physics, and Devices*; Zyss, J., Ed.; Academic Press: Boston, 1994.

(2) (a) Rettig, W.; Zietz, B. *Chem. Phys. Lett.* **2000**, *317*, 187. (b) Il'ichev, Y.; Künloe, W.; Zachariasse, K. A. *J. Phys. Chem. A* **1998**, *102*, 1670. (c) Rurack, K.; Bricks, J. L.; Reck, G.; Rodeglia, R.; Resch-Genger, H. *J. Phys Chem. A* **2000**, *104*, 3087. (d) Dreyer, J.; Kummrow, A. *J. Am. Chem. Soc.* **2000**, *122*, 2577 and references therein.

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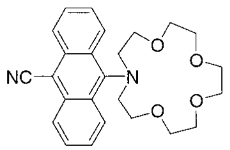
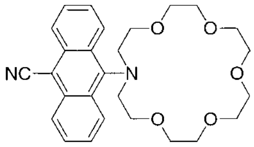
**Table 1.** Spectroscopic Data and Association Constants of **3** and **4** as Free Ligands or in the Presence of Alkali-Metal Cations

| Compound | $M^+ClO_4^-$ | $K_{ass}$[b] | $\lambda_F$[c] [nm] | $\phi$[d] | $\tau$ [ns] |
|---|---|---|---|---|---|
|  **3** | none | - | 585 | 0.03 | 2.2 |
| | $Li^+$ | 1000 | 545 | 0.03[e] | 1.8[e] |
| | $Na^+$ | 110 | 580 | 0.03[e] | 2.8[e] |
| | $K^+$ | 16 | 585 | 0.03[e] | 2.5[e] |
|  **4** | none | - | 570 | 0.09 | 2.9 |
| | $Li^+$ | 190 | 555 | 0.05[e] | 3.1[e] |
| | $Na^+$ | 9500[f] | 540 | 0.12[e] | 3.7[e] |
| | $K^+$ | 710 | 548 | 0.08[e] | 3.2[e] |

[a] In degassed acetonitrile solutions at 297 K. [b] Determined by changes in the absorption spectra using LETRAGROP program;[14] in all cases convergence was found for a 1:1 complex, $K_{ass} = \pm 10\%$. [c] Excitation wavelength $\lambda_{ex} = 420$ nm. [d] Determined using quinine sulfate as reference. [e] In the presence of an excess of metal cation. [f] ±1500.

the $^1La$ band in anthracene, the nonstructured transition at longer wavelengths is attributed to an ICT absorption. In both cases, one observes the disappearance of the ICT band upon protonation, in agreement with the participation of the nitrogen lone pair in the ICT state.

Inhibition of the ICT absorption is also observed for **3** and **4** in the presence of an excess of alkali metal ions ($Li^+$ to $K^+$), with the notable exception of **4** in the presence of $Na^+$. In the latter case, complexation of $Na^+$ is accompanied by an marked *increase* in the intensity of the ICT band, at the expense of the $^1La$ transition (Figure 1).

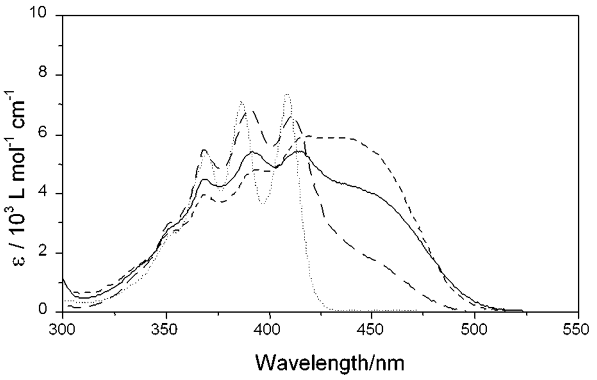


**Figure 1.** Electronic absorption spectra of **4** in acetonitrile (—), with an excess of Na+ (- — -), K+ (— —), or trifluoroacetic acid (....).

Such an increase of the ICT band upon $Na^+$ binding has not been observed with previously reported benzene analogues and is quite unique. To better understand the origins of this intriguing behavior, we proceeded to investigate in more detail the binding properties of compound **4** with certain alkali metal cations and compared them to its smaller-sized analogue **3**.

Addition of alkali metal ions to solutions of **3** and **4** in acetonitrile results in distinct spectral changes of the $^1La$ and ICT bands from which the association constants reported in Table 1 were determined. Interestingly, one notes that **4** displays considerably higher affinity for sodium than potassium, despite the fact that 18-crown-6 macrocyles are tailored for the potassium ion.[6] In this respect, it resembles a 15-crown-5 coronand. Consistent with this observation, compound **3** possesses metal binding properties usually encountered in 12-crown-4 ethers ($Li^+ > Na^+ > K^+$). These trends point to a conformationally constrained or reduced cavity size, presumably a consequence of steric interactions of the crown ether units with the nearby anthracene *peri*-hydrogens.

Suitable crystals for X-ray crystallography were obtained for $3 \subset Na^+$ and $4 \subset K^+$ (Figure 2 and 3).[9]

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(6) (a) Crown Ethers and Cryptands. Gokel, G. W. In *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, 1991. (b) Dietrich, B.; Viout, P.; Lehn, J.-M. *Macrocyclic Chemistry*; VCH: Weinheim, 1993, and references therein.

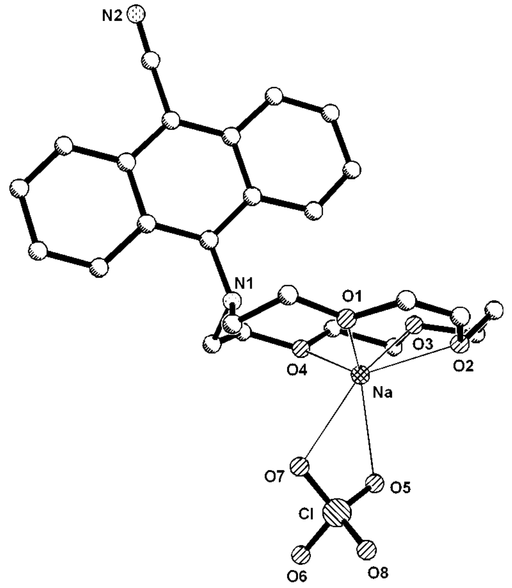

**Figure 2.** Solid-state structures of **3**⊂NaClO$_4$ obtained from X-ray diffraction.[7]

In both complexes the anthracene nucleus is almost perpendicular to the plane defined by the CH$_2$−N−CH$_2$ fragment and the metal cations are essentially situated to one side of the macrocyclic cavity—remote from the nitrogen atoms—and coordinated to the oxygen atoms of the crown ethers: both the Na−N(1) (3.24 Å) and the K−N(1) (3.52 Å) distances exceed the corresponding close contact calculated distances of 2.5 and 2.83 Å, respectively. Such structures are unusual and presumably result from a conformationally constrained complexing entity, as noted above.

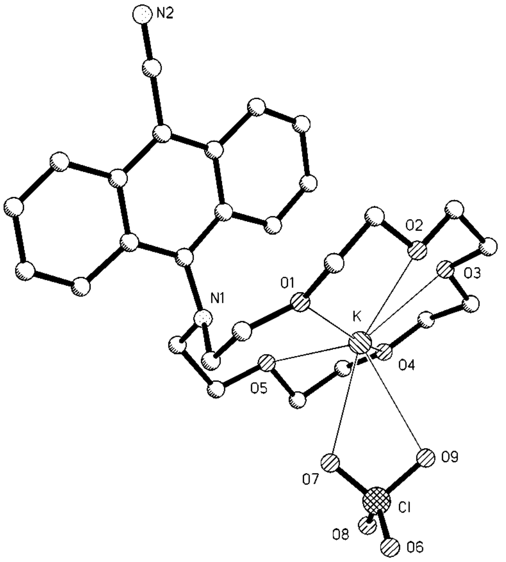

**Figure 3.** Solid-state structures **4**⊂KClO$_4$ obtained from X-ray diffraction.[8]

As noted earlier, addition of Na$^+$ to **4** induces an increase of the ICT band. It is possible to take advantage of this special behavior to determine the Na$^+$ concentration in the presence of other alkali metal cations. An example of such a titration is given in Figure 4, where **4** is titrated with Na$^+$ in the presence of a 30-fold excess of K$^+$ (Figure 4). The significant variations observed in the relative intensities of the $^1$La and ICT band potentially allow the use of **4** in more precise ratiometric Na$^+$/K$^+$ titrations.[10]

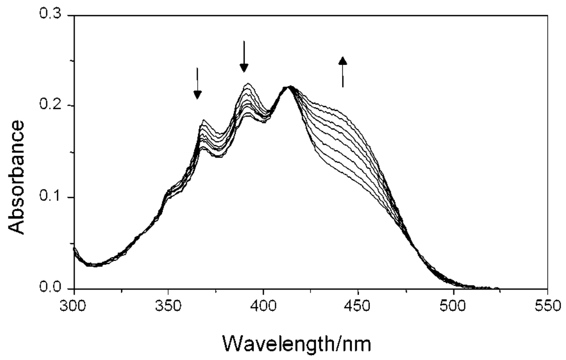

**Figure 4.** Titration of **4** (2.7 × 10$^{-5}$ M) in the presence of K$^+$ (8.2 × 10$^{-4}$ M) with Na$^+$ in acetonitrile. [Na$^+$] = 0, 2.7, 6.6, 13.2, 19.6, 25.9, 44.2, and 61.7 × 10$^{-5}$ M).

ICT absorption of the free ligands **3** and **4** requires partial overlap between the nitrogen lone pair and the anthracene $\pi$-orbitals. We assume, that the observed ICT inhibitions for **3**⊂Na$^+$ and **4**⊂K$^+$ are predominantly induced by conformational changes during cation complexation, causing an increase in rigidity of the macrocycles and forcing the anthracene units into strict orthogonal alignments with the corresponding CH$_2$−N−CH$_2$ fragments. The marked increase in ICT intensity affected by Na$^+$ in the case of **4** should originate from increased oscillator strength of the S$_0$ → CT transition, reflecting a better vibronic coupling between the S$_0$ and CT states, induced by the presence of the Na $^+$ cation.

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(7) Crystal data for **3**⊂NaClO$_4$: C$_{25}$H$_{28}$ClN$_2$NaO$_8$; $M = 542.93$ g mol$^{-1}$; monoclinic; $P2_1/c$ (No. 14); $a = 7.802(2)$ Å, $b = 39.865(8)$ Å, $c = 8.755(2)$ Å, $\beta = 109.13(3)°$, $V = 2572.7(9)$ Å$^3$; $Z = 4$; $T = 293(2)$ K; $2.51 \leq \Theta \leq 25.12°$. A total of 16503 reflections collected, 3846 independent reflections; $R^1 = 0.0965$, wR$^2$ = 0.2022 for 2859 reflections with $I > 2\sigma(I)$ and $R^1 = 0.1211$, wR$^2$ = 0.2364 for all data; CCDC-148378.

(8) Crystal data for **4**⊂KClO$_4$: C$_{27}$H$_{32}$ClKN$_2$O$_9$; $M = 603.10$ g mol$^{-1}$; triclinic; P $\bar{1}$ (No. 2); $a = 7.730(2)$ Å, $b = 10.594(2)$ Å, $c = 17.385(4)$ Å, $\alpha = 93.43(3)°$, $\beta = 92.48(3)°$, $\gamma = 98.34(3)°$, $V = 1404.2(5)$ Å$^3$; $Z = 2$; $T = 293(2)$ K; $1.95 \leq \Theta \leq 24.15°$. A total of 9967 reflections collected, 4175 independent reflections ($R_{\rm int} = 0.0492$); $R^1 = 0.0591$, wR$^2$ = 0.1562 for 2975 reflections with $I > 2\sigma(I)$ and $R^1 = 0.0805$, wR$^2$ = 0.1778 for all data; CCDC-151249.

(9) Data were collected on a STOE-IPDS with Mo Kα radiation ($\lambda$ = 0.710 73 Å). The structures were solved by direct methods using SHELXS-86 and refined against F$^2$ with SHELXL-93. Sheldrick, G. M. SHELXS-86, a program for solution of crystal structures, Göttingen, Germany, 1986. Sheldrick, G. M. SHELXL-93, a program for structure refinement, Göttingen, Germany, 1993.

(10) For examples of Na$^+$/K$^+$ selectivity, see: (a) Dolman, M.; Sutherland, I. O. *Chem. Commun.* **1993**, 1793. (b) Leroy, I.; O'Riley, F.; Habib, J.-L.; Soumillion, J.-Ph.; Valeur, B. *Chem. Commun.* **1999**, 795. For K$^+$/Na$^+$ selectivity, see: (c) Xia, W.-S.; Schmehl, R. H.; Li, C.-J. *Eur. J. Org. Chem.* **2000**, 387.

As such, **3** and **4** clearly differ from previously described benzene analogues, where inhibition of the ICT state was rationalized in terms of a decreased stabilization of the ICT state due to the participation of the nitrogen lone pair in cation complexation.[3]

Broad, structureless fluorescence is observed upon excitation of **3** and **4** characteristic of emission from a CT state.[11] Complexation by $M^+$ induces a hypsochromic shift in all cases (Table 1) which follows the same trend as the association constant. This is evidence that photodecomplexation does not occur in the relaxed singlet excited state, in contrast with other systems investigated previously.[5b,12,13]

In conclusion, we have described novel chemosensors exhibiting unique ICT and cation binding properties, clearly different from those of previously reported benzene analogous.[2,3,12,13] The relative intensities of the ICT and LE bands can serve in the ratiometric titration of metal ions, and the specific interaction of **4** with $Na^+$ allows the determination of $[Na^+]$ in the presence of an excess of other alkali ions. Further investigations are underway to gain a better understanding of the spectroscopic properties of these compounds in view of possible applications.

**Acknowledgment.** We thank the Alexander von Humboldt Foundation for travel fellowships, the Fonds der Chemischen Industrie for financial support, and Dr. R. Lapouyade for helpful discussions.

**Supporting Information Available:** Experimental procedures, characterization for all compounds, and crystallographic data for $\mathbf{3}\subset NaClO_4$ and $\mathbf{4}\subset KClO_4$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) As shown for 9-cyano-10-dimethylaminoanthracene: Druzhinin, S.; Demeter, A.; Niebuer, Tauer, E.; Zachariasse, K. *Res. Chem. Interm.* **1999**, *25*, 531.

(12) (a) Létard, J.-F.; Delmond, S.; Lapouyade, R.; Braun, D.; Rettig, W.; Kreissler, M. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 517. (b) Mathevet, R.; Jonusauskas, G.; Rullière, C.; Létard, J.-F.; Lapouyade, R. *J. Phys. Chem.* **1995**, *99*, 15709.

(13) Martin, M.; Olaza, P.; Meyer, Y. H.; Badaoui, F.; Bourson, J.; Lefèvre, J. P.; Valeur, B. *J. Phys. Chem.* **1996**, *100*, 6879.

(14) Sillen, L. G.; Warnqvist, B. *Arkiv. Kemi* **1968**, *31*, 315 and 377.