# Synthesis, Cation Binding, and Photophysical Properties of Macrobicyclic Anthraceno-cryptands

**Joseph P. Konopelski,[a] Florence Kotzyba-Hibert,[a] Jean-Marie Lehn,[a]* Jean-Pierre Desvergne,[b]* Frédéric Fagès,[b] Alain Castellan,[b] and Henri Bouas-Laurent[b]**

[a] *Laboratoire de Chimie Organique Physique, U.A. 422, Université Louis Pasteur, 4, rue Blaise Pascal, 67000 Strasbourg, France*

[b] *Laboratoire de Chimie Organique, Photophysique et Photochimie Moléculaire, U.A. 348, Université de Bordeaux 1, 33405 Talence Cédex, France*

The new cryptands, (**1a**) and (**1b**), possess remarkable spectroscopic and photophysical properties which are markedly affected by cation binding and by protonation.

Fluorescence quenching of excited aromatic compounds by electron donor or acceptor species may involve energy transfer, charge transfer (leading to an exciplex), electron transfer (generating ion pairs), intersystem crossing, or chemical reactions.[1] Although cations[2] and anions[3] are generally reported to produce fluorescence quenching, moderate enhancements have been observed with dibenzo-18-crown-6 ether[4a,b] and 1,8-naphtho-21-crown-6 ether[5] in the presence of alkali metal cations. In addition, crown ether dyestuffs were found to display cation dependent electronic absorption spectra.[6] Aromatic chromophores incorporated into stronger ligands than monocyclic ethers are expected to exhibit pronounced photophysical responses in the presence of salt. Herein, we report the synthesis and spectroscopic study of new macrobicyclic ligands (**1**) ($n$ = 2,3) designed to combine the specific complexing ability of the cryptands[7] with the photophysical behaviour of the anthracene[8] ring. Moreover, these compounds appear to be well suited to examination of the interaction of the nitrogen lone pairs with the aromatic ring in a given arrangement.

**Table 1.** $^1L_a$ Band u.v. spectral modifications of (**1**) ($\leqslant 10^{-4}$M, methanol, 20 °C) in the presence of salts or $CF_3CO_2H$ (*ca.* $10^{-1}$—$10^{-2}$M).[a]

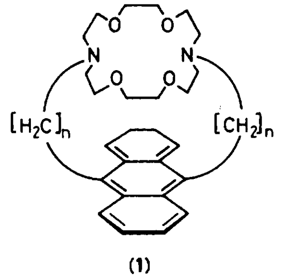
| | | Salt | | | | | |
|---|---|---|---|---|---|---|---|
| | | $LiClO_4$ | $NaClO_4$ | $KClO_4$ | $AgNO_3$ | $TlNO_3$ | $CF_3CO_2H$ |
| (**1a**) | $\Delta\varepsilon$ | — | ↑ 9 | ↑ 12 | ↓ 30 | ↓ 19 | ↑ 15 |
| | $\lambda$ | — | → 2 | ← 1 | → 10 | → 7 | — |
| (**1b**) | $\Delta\varepsilon$ | — | ↓ 13 | ↓ 2 | ↓ 28 | ↓ 4 | ↑ 16 |
| | $\Delta\lambda$ | — | → 1 | → 1 | → 4 | → 2 | ← 1 |

[a] $\Delta\varepsilon$ represents the variation (%) of the absorption intensity and $\Delta\lambda$ the shift (nm) of the $^1L_a \leftarrow ^1A$ transition. Arrows ↑ and ↓ denote hyper-and hypo-chromism respectively. Arrows → and ← indicate batho- and hypso-chromism respectively. The u.v. spectrum of (**2**) is not affected by cations under these conditions.

**Table 2.** Fluorescence quantum yield of (**1**) and (**2**) in degassed methanol ($<10^{-5}$M) in presence of salts or $CF_3CO_2H$ ($\leqslant 10^{-2}$M).

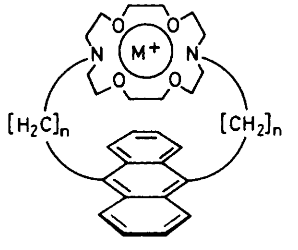
| | $\Phi_F$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | None | $LiClO_4$ | $NaClO_4$ | $KClO_4$ | $AgNO_3$ | $TlNO_3$ | $CF_3CO_2H$ |
| (**1a**) | 0.68 | 0.70 | 0.57 | 0.64 | 0.05 | 0.05 | 0.80 |
| (**1b**) | 0.04[a] | 0.05[a] | 0.17 | 0.30 | 0.23 | 0.07 | 0.70 |
| (**2**) | 0.76 | [b] | [b] | [b] | 0.39 | 0.67 | [b] |

[a] Dual fluorescence emission. [b] *ca.* 0.76 (No cation effect was observed).

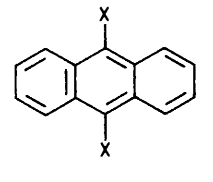


(1)

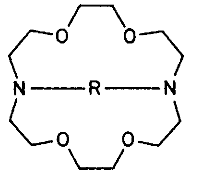
a; $n = 2$
b; $n = 3$



[(1) M$^+$]



(**2**) X = $[CH_2]_2Me$
(**3**) X = $CH_2CO_2H$
(**4**) X = $CH_2COCl$
(**5**) X = $[CH_2]_2CO_2H$
(**6**) X = $[CH_2]_2COCl$



(**1a**) R = $[CH_2]_2$-A-$[CH_2]_2$-
(**1b**) R = $[CH_2]_3$-A-$[CH_2]_3$-
(**7**) R = 2H
(**8**) R = -CO-$CH_2$-A-$CH_2$-CO-
(**9**) R = -CO-$[CH_2]_2$-A-$[CH_2]_2$-CO-
A = 9,10-anthrylidene

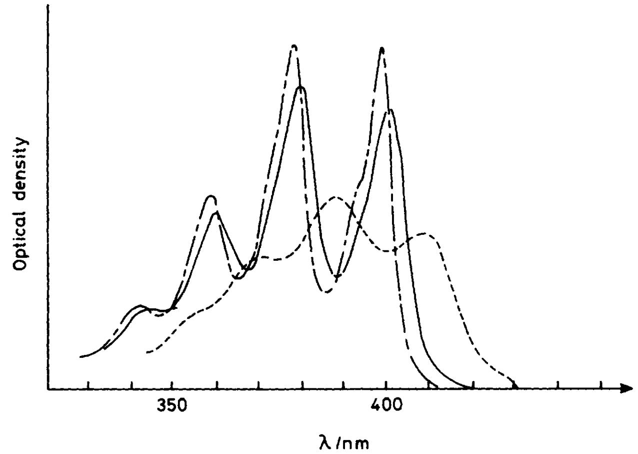


**Figure 1.** Electronic absorption spectrum ($^1L_a$ band) of (**1a**) in methanol ($<10^{-4}$M): —— without salt; — — — with $KClO_4$ ($10^{-1}$ M) - - - - - with $AgNO_3$ ($10^{-1}$ M).

The macrobicyclic cryptands (**1a**) and (**1b**) have been synthesized using the high dilution technique. The diacids (**3**)[9a] and (**5**)[9a] are converted, with thionyl chloride, into the corresponding dichlorides (**4**) (2 h at reflux, 75% yield)[9b] and (**6**) (one night at room temperature, quantitative yield). High dilution condensation of (**4**) with the (2,2) macrocycle (**7**)[10] affords a macrobicyclic diamide (**8**) (m.p. > 260 °C; 61% yield) which gives the anthraceno-macrobicycle (**1a**) by reduction with diborane (m.p. > 260 °C; 65% yield). In a similar way, reaction of (**6**) with the macrocycle (**7**) yields the diamide (**9**) (m.p. > 260 °C; 65% yield) which on reduction affords the macrobicyclic cryptand (**1b**) (m.p. 215 °C; 77% yield).

The binding ability of cryptands (**1**) with $K^+$ and $Ag^+$ cations has been demonstrated by proton n.m.r. experiments (200 MHz). The spectra obtained from equimolar solutions of $AgNO_3$ and (**1**) are markedly different from those of the free ligands. Both spectra are quite complex owing to the non equivalence of the $N_2O_4$ ring protons induced by the proximity of the anthracene ring. The ligand (**1b**) does not bind $MeNH_3^+$ picrate inside its cavity as shown by n.m.r. compared to the previous results obtained on other macropolycycles.[11,12] The *X*-ray crystal structure of the cryptand (**1a**) shows that a preformed cavity exists: the two nitrogen bridgeheads are oriented towards the interior of the molecule, which should facilitate internal cation complexation.[13]

U.v. absorption spectra are characteristic of 9,10-disubstituted alkylanthracenes, presenting slight but signifi-

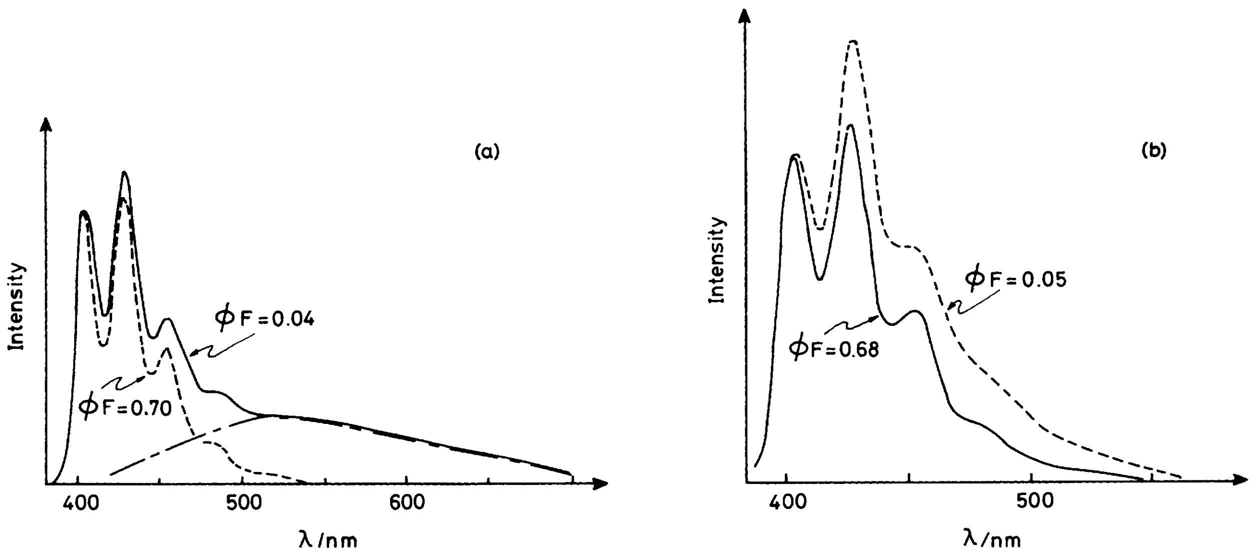
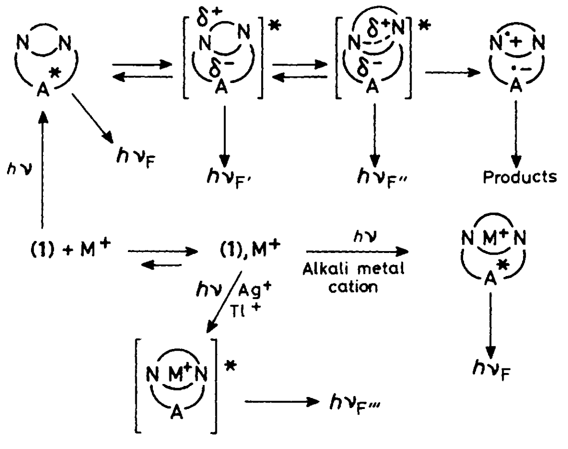


**Figure 2.** Fluorescence emission spectra of (**1**) in degassed methanol (20 °C) ($\ll 10^{-4}$ M); (a) (**1b**) —— without acid; - - - - - with $CF_3CO_2H$ ($10^{-3}$ m); — — — - exciplex; (b) (**1a**) —— without salt; - - - - - with $AgNO_3$ ($10^{-2}$ M). The spectra are normalized to the first vibronic band.



**Scheme 1**

cant modifications in comparison with 9,10-di-n-propylanthracene (**2**); the closer the nitrogen atoms to the anthracene nucleus, the larger are the spectral changes.† The absorption spectra of (**1**) but not of (**2**) are affected by the addition of $CF_3CO_2H$ or of salts (except $LiClO_4$), the perturbation depending on the nature of the added compound (Table 1 and Figure 1). These data are consistent with protonation of the nitrogen sites and formation of complexes between (**1**) and $Na^+$, $K^+$ (but not $Li^+$) cations in which the ion is bound in the 18-$N_2O_4$ macrocycle and held in the vicinity of the π-system.

The stoicheiometry of the complexes can be determined by gradual addition of salt either by u.v. absorption or fluorescence techniques; a 1 : 1 complex was found for $K^+$ and $Tl^+$ but a different stoicheiometry [$Ag_x(\mathbf{1}), x > 1$] was observed for $Ag^+$.

Whereas the fluorescence spectrum of (**1a**) ($\Phi_F = 0.68$) is typical of a *meso*-disubstituted alkylanthracene [(**2**); $\Phi_F = 0.76$], (**1b**) displays a dual fluorescence (Figure 2a) with a low quantum yield ($\Phi_F = 0.04$). Addition of complexable cations ($Na^+$, $K^+$) or protonation strongly reduces the red shifted emission and increases distinctly the fluorescence quantum yield of the structured spectral part; the effect is absent for $Li^+$ (which is expected to bind only weakly to the 18-$N_2O_4$ ring) and largest for $CF_3CO_2H$ addition (Table 2). Thus, involvement of the nitrogen sites in complexation and protonation prevents formation of amine–anthracene exciplexes.‡ Under the same conditions, only small modifications appear for (**1a**), the pure compound displaying an intense fluorescence without any detectable exciplex emission (Table 2); this might be due to conformational factors allowing solvation of the nitrogen sites by methanol, so that the lone pairs are unavailable for exciplex and non fluorescing ion-radical pair formation[14,15] (see Scheme 1). Preliminary experiments in an aprotic solvent (acetonitrile) reveal that both (**1a**) and (**1b**) exhibit almost only exciplex emission ($\Phi_F = 0.20$ and 0.12 respectively). In contrast to protons and alkali metal cations, $Ag^+$ and $Tl^+$ allow rather weak fluorescence§ emission, especially for (**1a**). Fluorescence (Figure 2b) as well as excitation spectra, point to the existence of an association¶ between $Ag^+$ and (**1a**) in the excited state different from the complexes observed by absorption spectroscopy.

The fluorescence decay pattern of pure (**1**) in solution at room temperature has been fitted** to sums of two exponen-

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† λ/nm (ε): (**2**) 260 (176 000) and 398 (11 500); (**1b**) 261 (133 000) and 400 (9 450); (**1a**) 262 (117 000) and 402 (7 700). The first wavelength corresponds to $\lambda_{max.}$ of the $^1B_b$ band and the second to $\lambda_{max.}$ of the onset of the $^1L_a$ band.

‡ The charge transfer character of the excited state leading to this emission is evident from the bathochromic shift upon increasing solvent polarity for (**1b**) ($\lambda_{max.}$: methylcyclohexane: 460; acetonitrole: 505; methanol: 520 nm).

§ The observed fluorescence quantum yield is a compromise between enhancement of the emission due to suppression of the original exciplex and fluorescence quenching resulting from specific interaction between a soft cation and soft ligand system as well as a heavy atom effect.

¶ Observation of an 'exciplex' between perylene and $Ag^+$ was recently reported.[16]

** The measurements were performed using the single photon counting technique (Applied Photophysics). The decay parameters were determined by a non linear least squares deconvolution method.[17]

tials for (**1a**) and three exponentials for (**1b**), indicating the occurrence of several kinetically distinguishable species in the excited state. This can be interpreted in terms of exciplex formation[14,15] involving one or two nitrogen atoms (see Scheme 1). Addition of excess of $CF_3CO_2H$ switches the kinetics towards single exponential functions ($\tau$ *ca.* 14—15 ns) similar to that of the reference compound (**2**) ($\tau$ *ca.* 14 ns) whereas metal cations strongly affect the transient kinetics. This kinetic scheme is proposed to account for the experimental data.

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*Added in proof:* A recent report describes the use of anthracenoyl cryptands as fluorescent probes for membrane studies: U. Herrmann, B. Tümmler, G. Maass, P. K. T. Mew, and F. Vögtle, *Biochem.*, 1984, **23**, 4059.

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