



N-(9-Anthryl) aza-18-crown-6: Palladium-catalysed Synthesis, Photophysical Properties and Cation Binding Ability

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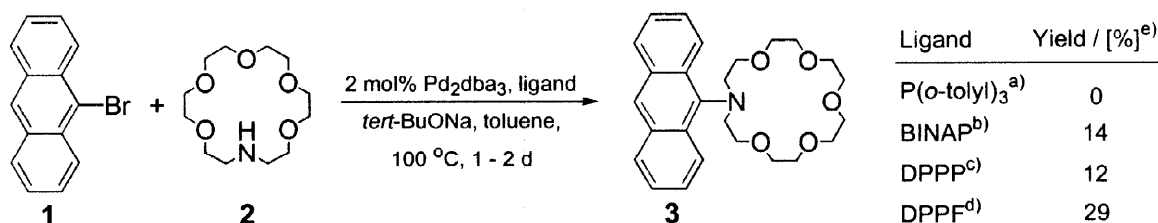
Abstract:

N-(9-Anthryl) aza-18-crown-6 (**3**) was synthesised via the palladium-catalysed cross-coupling of 9-bromoanthracene (**1**) and aza-18-crown-6 (**2**). Its photophysical properties include an intramolecular charge-transfer absorption band ($\lambda_{\text{max}} \approx 425$ nm) in polar and non-polar solvents, which disappears upon protonation or binding of K^+ ($\log K_{\text{ass}} = 3.7$ in acetonitrile). © 1998 Elsevier Science Ltd. All rights reserved.

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N-Aryl-aza-crown ethers have often been combined with photoactive subunits in the design of metal-cation-selective detection systems.¹ Several of these supramolecular systems incorporate the anthracene ring to harness its unique photophysical properties,^{1,2} but none has the simplicity of the so far unknown *N*-(9-anthryl) aza-18-crown-6 (**3**), in which the nitrogen is directly linked to the anthracene chromophore.

The synthesis of **3** was achieved by a palladium(0)-catalysed amination reaction³ of 9-bromoanthracene (**1**) with the macrocyclic secondary amine aza-18-crown-6 (**2**). Amongst several palladium/ligand catalysts tested, the catalyst based on $\text{Pd}(\text{DPPF})\text{Cl}_2/\text{DPPF}$ was the most efficient giving the anticipated coupling product **3** in 29 % yield (Scheme 1).⁴



Scheme 1: Palladium(0)-catalysed arylation of 9-bromoanthracene (**1**) with aza-18-crown-6 (**2**).

a) $\text{P}(o\text{-tolyl})_3$: tris-(*ortho*-tolyl) phosphine, $\text{Pd}(0)$:ligand = 1:2; b) BINAP:2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, $\text{Pd}(0)$:ligand = 1:1.5; c) DPPP:diphenylphosphinopropane, $\text{Pd}(0)$:ligand = 1:1.5; d) Reaction was carried out in THF with 3 mol% $\text{Pd}(\text{DPPF})\text{Cl}_2$ as palladium source, DPPF: 1,1'-bis[diphenylphosphino]ferrocene, Pd :ligand = 1:3; e) isolated yields after chromatography.

The UV absorption spectrum of **3** was recorded in three different solvents: methylcyclohexane (MCH), acetonitrile, and methanol at ambient temperature. All show a typical anthracene-like spectrum in the region 300–400 nm, followed by a long wavelength band between 400 and 460 nm. The latter can be assigned to an $n\text{-}\pi^*$ intramolecular charge transfer (ICT) band ($\lambda_{\text{max}} \approx 425$ nm). The spectrum of **3** in acetonitrile is represented

in Fig. 1. Addition of excess trifluoroacetic acid (TFA) results in the disappearance of the ICT band and a bathochromic shift ($\Delta\lambda \approx 5$ nm; $\Delta\nu \approx -330$ cm⁻¹) of the vibronic bands in the anthracene absorption. Whereas the protonation of the amino group is expected to inhibit charge transfer, the bathochromic shift of the π - π^* transition is surprising and deserves further investigation. The CT wavelength maximum does not vary significantly in the three solvents investigated, which is consistent with a relatively small dipole moment in the ground state.

The fluorescence emission spectra of **3** recorded in solvents of increasing polarity as characterised by Lippert's solvent polarity factor f are represented in Fig. 2. A Lippert-Mataga plot⁵ of emission energy vs. $f = (\epsilon-1)/(2\epsilon+1) - (n^2-1)/(2n^2+1)$ yields an excited-state dipole moment of ca. 7 D (assuming a solvent cavity radius of 5 Å). Identical emission spectra were obtained using different excitation wavelengths (370, 390, or 420 nm) and the excitation spectra were found to be superimposable with the absorption spectra when scanned at 550 nm or 450 nm. In degassed acetonitrile samples, the fluorescence quantum yield (Φ_F) of **3** was found to be 0.18 ($\lambda_{exc.} = 367$ nm) and 0.31 (with excess TFA, $\lambda_{exc.} = 370$ nm); these results are consistent with the measured singlet lifetimes: $\tau = 9.7$ ns and 16.7 ns, respectively. In the presence of an excess of light metal cations, which strongly affect the UV absorption spectra (*vide infra*), the fluorescence spectra were observed to be similar to those of the free ligand; this is an indication of a decrease of complexing ability in the excited singlet state.^{6,7}

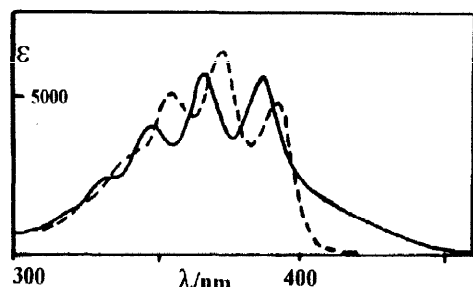


Fig. 1 UV spectra of **3** in pure CH₃CN (—) and in CH₃CN + TFA (---), conc. = 2.3×10^{-4} M. Similar spectra are observed in MCH and in MeOH.

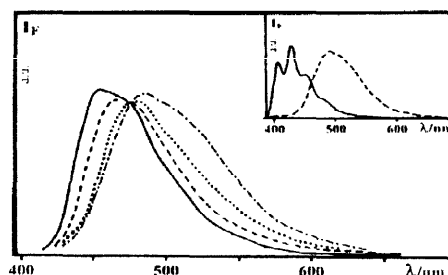


Fig. 2: Fluorescence emission spectra of **3** in MCH (—), di-*n*-butylether (---), dichloromethane (•••), and acetonitrile (-•-). Insert: spectra of **3** in acetonitrile (---) and in acetonitrile + TFA (—).

Variations in λ_{max} and ϵ were the basis for the determination of the association constants using the LETAGROP-SPEFO programme.⁸ Among the metal cations studied (Li⁺, Na⁺, K⁺, Cs⁺, Tl⁺, and Mg²⁺ in CH₃CN and CH₃OH), K⁺ and Tl⁺ gave the largest spectral shifts. For K⁺ and Tl⁺ the best fits were found for a 1:1 stoichiometry [$\log K_{ass}(K^+) = 3.7$ in CH₃CN,⁹ $\log K_{ass}(Tl^+) = 3.9$ in CH₃OH].

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References and Notes

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- The values of $\log K_{ass}$ for K⁺ is somewhat lower than those reported by others in CH₃OH: 4.18 for aza-18-crown-6; 4.65 for *N*-*n*-octylaza-18-crown-6¹⁰ and 4.40 for *N*-(9-anthrylmethyl)aza-18-crown-6.¹¹
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