Synthesis and Photophysical Properties of Polyazacrown Ethers with Appended Naphthyl or Anthracenyl Units

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Polyazacrown ethers containing one, two, and four appended naphthyl or anthracenyl units have been synthesized. The absorption spectra and photophysical properties of the novel compounds have been investigated in CH_2Cl_2 solution. Acid titration of the amine nitrogens of the polyazacrown ethers causes strong changes in the absorption and fluorescence spectra. In the unprotonated compounds of the naphthalene family, the naphthalene-type emission is completely quenched and a weak, unstructured, and broad fluorescence band with maximum at 440 nm is observed. Upon addition of trifluoroacetic acid, the absorption maximum is displaced to the red by a few nanometers, and a revival of the strong naphthalene-type emission at 340 nm is observed. These results are accounted for by the change in the nature of the lowest excited state (CT to π-π*) upon protonation. In the compounds of the anthracene family, the deprotonated forms of the species containing the polyazacrown groups show an absorption around 300 nm and a long wavelength tail at lower energies, neither of which are present in the 9-[(methylamino)methyl]anthracene. In all cases a weak, anthracene-type fluorescence is present, increasing in intensity on protonation. Furthermore, the emission spectra of the compounds with two or four anthracene moieties show an excitation-dependent, broad emission band at lower energies, which almost disappears upon protonation. This behaviour can be accounted for by the quenching of the anthracene-type emission caused by lower lying charge-transfer levels and, in the case of the compounds containing two and four anthracene moieties, of conformers where an anthracene-anthracene interaction is present. In all cases, each equivalent of added acid causes protonation of one equivalent of crown nitrogen. However, in the azacrown with four appended naphthyl units the revival of the naphthalene-type fluorescence does not parallel the number of added protons. This shows that the higher energy π-π* levels of the protonated units are quenched by the lower energy CT levels of the units involving the not yet protonated crown nitrogens.

Introduction

The molecular recognition process between a receptor and a substrate can be revealed by several types of signals. Fluorescence signalling offers many advantages, including high sensitivity and relatively cheap equipment.[1] Naphthalene and anthracene are well-known fluorescent molecules,[2] often used as luminophores in supramolecular systems.[3,4] Azacrown ethers are known to play the role of receptors for protons, ammonium ions and metal cations.[5] In an attempt to design new luminescent sensors, we have synthesized two families of polyazacrown ethers containing one, two, and four appended anthracenyl or naphthyl units, respectively. Similar compounds have recently been proposed as sensors for metal cations.[6−9] In this paper we report the synthesis, the absorption and fluorescence properties of the prepared compounds, and the effect of protonation on these properties. The results obtained have allowed us to elucidate the nature of the electronic interaction that causes the different fluorescence behaviour of the unprotonated and protonated forms of these compounds. The formulas of the investigated compounds (including 9-[(methylamino)methyl]anthracene, **MAA**, for comparison purposes) and the abbreviations used are shown in Schemes 1 and 2.

Results and Discussion

Synthesis of Compounds

Compounds **1A**, **1N**, **2A**, and **2N** have been prepared according to Scheme 1. Starting compounds **6** and **8** have been obtained, in quantitative yield, by reductive detosylation of known products **5** [10] and **7** [10] by $LiAlH_4$ in refluxing THF. Condensation of **6** and **8** with commercially available 9-(chloromethyl)anthracene and 1-(chloromethyl)-naphthalene, carried out in refluxing CH_3CN in the presence of solid Na_2CO_3 as base, afforded **1A** (61%), **1N** (70%), **2A** (89%) and **2N** (73%) after column chromatography.

Analogous condensation conditions have been used in the preparation of fluorescent receptors based on tetraoxa-

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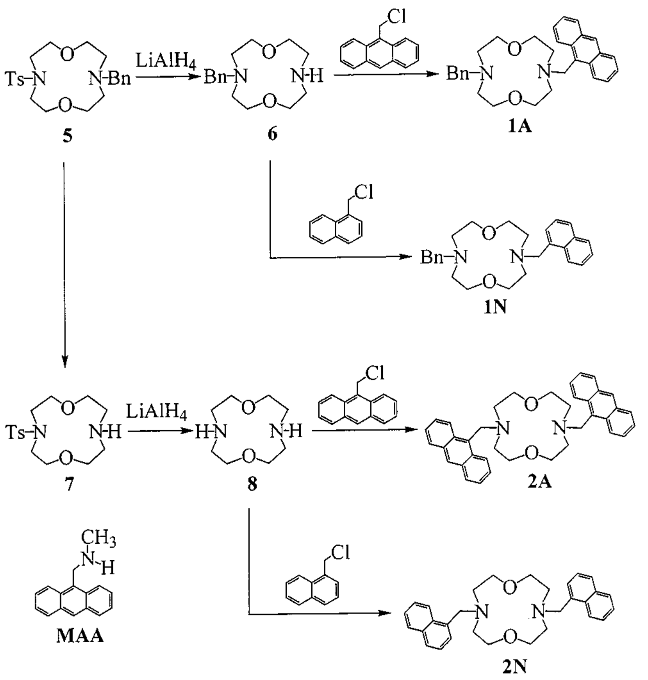
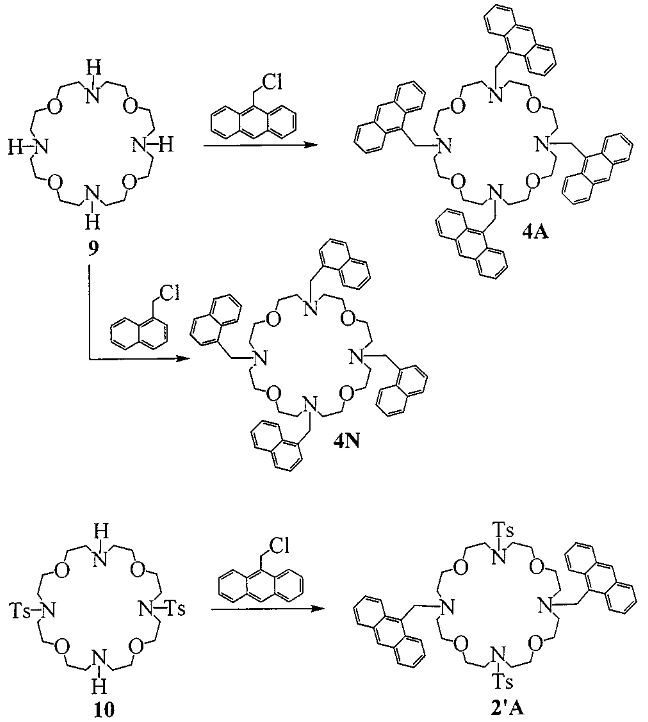


Scheme 1. Synthesis of fluorescent receptors based on tetraoxatetraaza-24-crown-8



Scheme 2. Synthesis of fluorescent receptors based on dioxa-diaza-12-crown-4

tetraaza-24-crown-8, starting from known compounds **9**[11] and **10**.[11] Compounds **4A**, **4N**, and **2′A** were isolated in 30%, 51%, and 48% yields, respectively, after column chromatography (Scheme 2).

Naphthyl derivatives **2N** and **4N** have also been characterized by single-crystal X-ray structure analysis.[12]

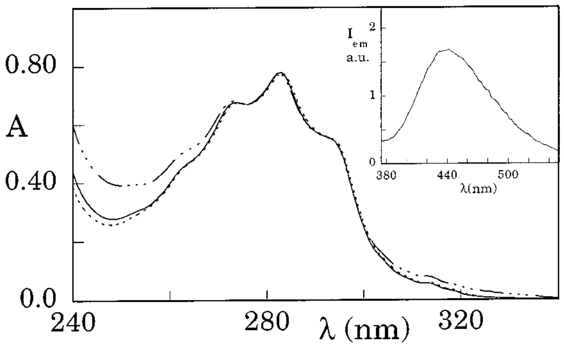


Figure 1. Absorption spectra of **1N** (– · · · –), **2N** (- - - -), **4N** (——); the inset shows the emission spectrum of **2N**

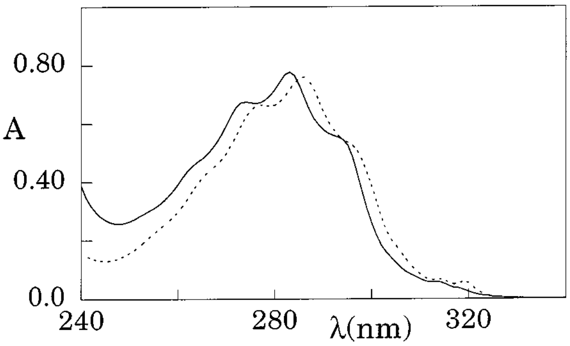


Figure 2. Absorption spectra of **2N** (——) and **2NH⁺** (- - - -)

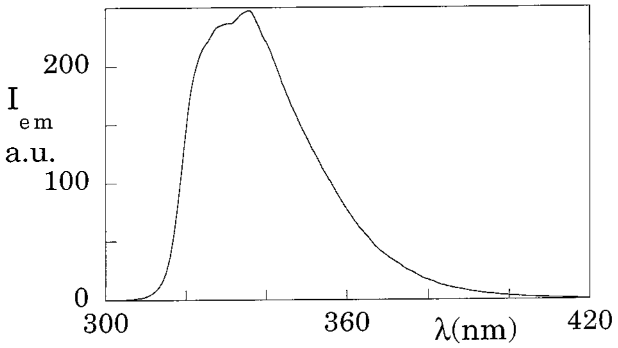


Figure 3. Emission spectrum of **2NH⁺**

Photophysical Properties of Compounds Containing Naphthyl Units

The absorption and emission spectra of compounds **1N**, **2N**, and **4N** are shown in Figure 1, Figure 2, and Figure 3, respectively, and some relevant data are collected in Table 1. The absorption spectra show the characteristic, structured

Table 1. Absorption and emission data of the naphthyl compounds

Compound	Absorption[a] λ (nm)[b]	ε	Emission[a] λ (nm)[c]	τ(ns)[d]	Φ_{em}[e]
Naphthalene	275	6000	338	5.0	0.023
1N	282	5500	440	0.4, 7.2	$<10^{-3}$
1NH⁺	285	4800	336	5.0	0.02
2N	282	10500	441	0.5, 7.0	$<10^{-3}$
2NH⁺	285	9500	336	5.4	0.025
4N	282	21000	440	0.6, 7.2	$<10^{-3}$
4NH⁺	285	19000	336	6.5	0.03

[a] Dichloromethane, room temperature. – [b] Wavelength of the highest intensity absorption feature. – [c] Wavelength of the emission maximum. – [d] Emission lifetime. – [e] Emission quantum yield.

naphthalene-type band in the near UV spectral region. Compared to naphthalene, the absorption maximum is red shifted by 7 nm and the minimum around 240 nm is less deep. The naphthalene-type fluorescence is strongly quenched and a very weak, broad and unstructured emission appears with λ_{max} = 440 nm. The emission decay is biexponential, with one component much shorter and one longer than the monoexponential decay observed for naphthalene. The absorption and emission spectra of compounds **2N** and **4N**, containing two and four naphthyl units per molecule respectively, are practically identical (except, of course, for the molar absorption coefficient) to those of compound **1N**, indicating that there is no ground or excited state interaction between the naphthyl units.

Upon addition of trifluoroacetic acid, protonation of the crown nitrogens causes spectral changes in compounds **1N**, **2N**, and **4N**. At the end of the acid titration the maximum of the absorption spectrum of the azacrown compounds is displaced to the red by a few nanometers and there is a substantial decrease in absorption in the 240−260 nm region. In the fluorescence spectrum, the very weak, broad, and unstructured emission with λ_{max} = 440 nm disappears, and a strong, slightly structured band, very similar to that exhibited by naphthalene, is formed. In all cases the excited state decay is monoexponential and the lifetime is very close to that for naphthalene.

The above results can be rationalized as follows. In the unprotonated crown-type compounds, an important role is played by charge transfer (CT) excited states (involving a nitrogen n orbital and a naphthalene π* orbital) which lie at relatively low energies. In particular, the lowest CT level lies below the π-π* level of the naphthalene moiety, as already shown for similar compounds.[13] Therefore, the naphthalene-type fluorescence is strongly quenched, as one can see from the very low quantum yield compared to naphthalene (Table 1).

The short component observed in the emission decay can be assigned as the lifetime of the quenched π-π* level. The longer component can be assigned to the lowest CT excited state, which is also responsible for the very weak, broad and unstructured emission with λ_{max} = 440 nm. Another CT excited state lies at higher energy and contributes to the absorption in the 240−260 nm region. On protonation, the CT excited states move to much higher energies [13] and therefore the absorption in the 240−260 nm region decreases and the very weak, broad and unstructured emission with λ_{max} = 440 nm disappears. Furthermore, the π-π* naphthalene-type level becomes the lowest energy spin-allowed excited state and the protonated compounds exhibit the same fluorescence properties as naphthalene (Table 1).

The titration curves of the above compounds reveal another interesting aspect. When protonation is monitored by changes in absorption, a linear plot is obtained in all cases until a plateau is reached when a stoichiometric amount of protons, relative to the number of nitrogen present in the crown, is added. For **1N**, the titration curve obtained following the change in the emission intensity at 338 nm coincides with the curve obtained from the changes in absorption. This, however, is not the case for compounds **4N** (Figure 4) and **2N**.

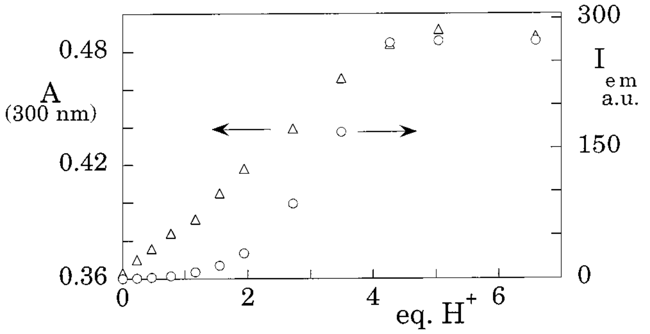


Figure 4. Changes in absorption (300 nm, Δ) and emission intensity (335 nm, O) upon addition of CF_3COOH to a CH_2Cl_2 solution of **4N**

As can be seen, at the beginning of the titration the increase in the number of protonated chromophoric units, as indicated by the changes in absorption, is not followed by a parallel increase in the emission intensity of such units. This effect is most probably due to the quenching of the (upper lying) π-π* levels of the protonated units by the (lower lying) CT levels of the unprotonated ones.[13]

Photophysical Properties of Compounds Containing Anthracenyl Units

The absorption and emission spectra of compounds **MAA**, **1A**, **2A**, **2′A**, and **4A** are shown in Figures 5−8. Some relevant data for all the examined compounds are collected in Table 2. Luminescence lifetimes (in the 10−20 ns range) are not reported because the decay was always multiexponential and difficult to analyze. The spectra of **MAA** (Figure 5) are quite similar to those of anthracene, with the absorption and emission maxima slightly red shifted, similarly to what happens for 9-methyl-anthracene.[2] The absorption spectrum of **1A** (Figure 6) is almost coincident with that of **MAA**, except for the presence of a weak, long wavelength absorption tail. The absorption spectra of **2A**, **2′A**, and **4A** are very similar to those of **1A**, except, of course, for the molar absorption coefficient.

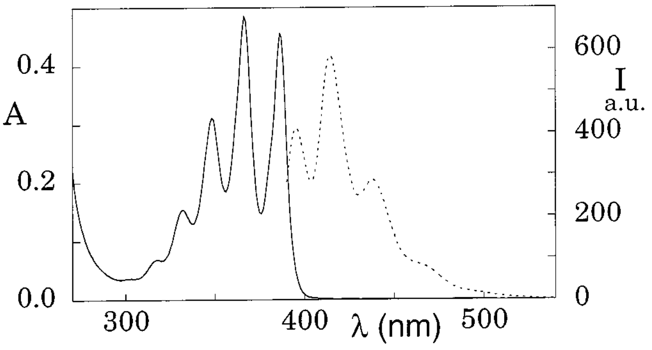


Figure 5. Absorption (——) and emission (- - - -) spectra of **MAA**

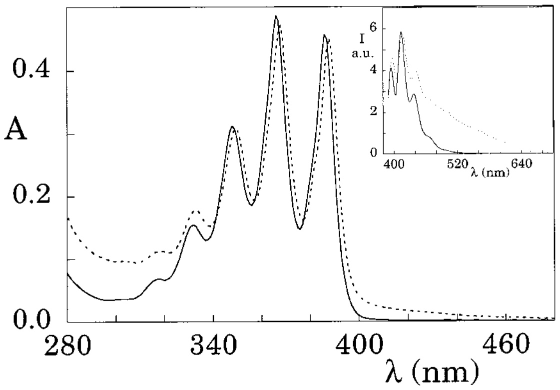


Figure 6. Absorption spectra of **MAA** (——) and **1A** (- - - -); the inset shows the normalized emission spectra of the two compounds

The structured anthracene-type fluorescence of **MAA** is strongly quenched in the polyazacrown ethers (Table 2). It can also be seen that, contrary to what happened for **MAA** (Figure 5) a broad emission band is present at longer wavelengths in **2A**, **2′A**, and **4A** (Figure 7), particularly when excitation is performed at 290 nm. **1A** shows a long wavelength tail (Figure 6). For compounds **2A**, **2′A**, and **4A**, the ratio between the intensity of the longer wavelength emission and the anthracene-type emission decreases when excitation is performed at 368 nm instead than at 290 nm.

Table 2. Absorption and emission data of the anthracenyl compounds

Compound	Absorption[a] λ (nm)[b]	ε	Emission[a] λ (nm)[c]	Φ_{em}[d]
Anthracene	356	10000	403	0.3
9-MAA	366	8700	415	0.13
9-MAAH$^+$	370	7500	420	0.41
1A	368	–	417	0.014
1AH$^+$	374	–	424	0.1
2A	368	13000	418, 490	0.03
2AH$^+$	374	11500	423	0.1
2A′	368	14200	418, 480	0.006
2A′H$^+$	374	12000	425	0.3
4A	368	27000	417, 480	0.009
4AH$^+$	374	22000	424	0.1

[a] Dichloromethane, room temperature. – [b] Wavelength of the highest intensity absorption feature. – [c] Wavelength of the emission maximum. – [d] Emission quantum yield.

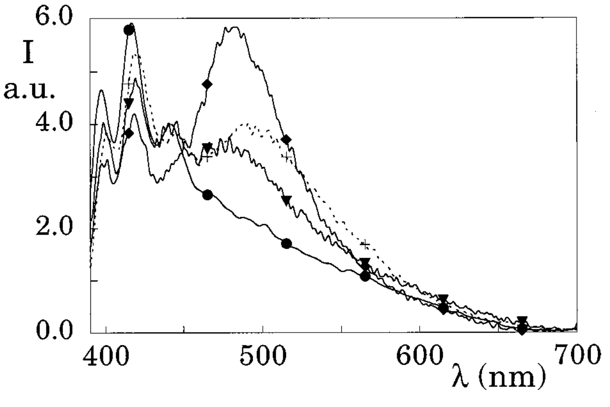


Figure 7. Normalized emission spectra of **1A** (–•–•–) **2′A** (–◆–◆–), **2A** (- - + - - + - -), **4A** (–▼–▼–) upon excitation at 290 nm

Upon addition of trifluoroacetic acid, some spectral changes are observed for all the examined compounds (see, e.g., Figure 8). At the end of the acid titration, the maximum of the absorption spectrum is red shifted by a few nanometers for all compounds (Table 2), but no decrease in absorption in the UV minimum is observed, contrary to what happens for the naphthalene compounds above. Also, the weak absorption tail at longer wavelength does not disappear. In the fluorescence spectrum, the structured anthracene-type band increases in all cases (Figure 8, inset). For **MAA**, the form of the spectrum does not change. For **2A**, **2′A**, and **4A** (Figure 7), the broad, lower energy emission present in the spectra of the unprotonated crown-type compounds decreases in intensity on protonation, but it does not completely disappear in **2A**.

The results obtained with the anthracene-bearing polyaza crowns are more difficult to rationalize than those obtained for the analogous naphthalene-bearing compounds.[14] A very important point to be noted is that the behaviour of compound **1A**, which contains the azacrown and only one appended anthracene unit, is different from the behaviour of **MAA**, which contains one anthracene unit but not the azacrown, and also from that of compounds **2A**, **2′A**, and **4A**, which contain the azacrown and more than one anthracene unit. The difference in behaviour between **MAA** and **1A** – namely the long wavelength tail in the fluorescence spectrum of **1A** and the much lower fluorescence quantum yield of the unprotonated forms of **1A** – can be attributed to the presence of a CT excited state involving the remote N atom in the azacrown at slightly lower energy than the fluorescent π-π* anthracene-type level. The interaction leading to this CT excited state can be favoured by the intramolecular hydrogen bond between the α-hydrogen of anthracene and the proximate oxygen atom of the macrocycle recently observed in similar compounds.[15] This kind of interaction could also be responsible for the slight spectral differences between **MAA** and **1A**. The difference in behaviour between **1A** and the azacrown compounds containing two or four anthracene moieties can be assigned to the presence, in the latter compounds, of conformers in which an anthracene-anthracene interaction is present (even in the ground state), which accounts for the presence of the broad, excimer-type emission with maximum around 480 nm.

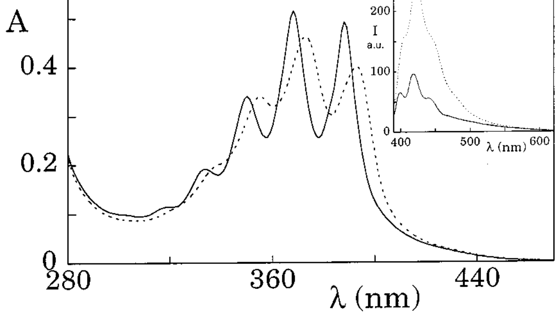


Figure 8. Absorption and emission spectra of **2A** (——) and **2AH$^+$** (- - - -)

Experimental Section

General Remarks: Solvents were purified by standard methods and dried if necessary. Compounds 10-benzyl-4-[(4-methylphenyl)sulfonyl]-1,7-dioxa-4,10-diazacyclododecane (**5**),[10] 4-[(4-methylphenyl)sulfonyl]-1,7-dioxa-4,10-diazacyclododecane (**7**),[10] 1,7,13,19-tetraoxa-4,10,16,22-tetraazacyclotetracosane (**9**)[11] and 4,16-di-[(4-methylphenyl)sulfonyl]-1,7,13,19-tetraoxa-4,10,16,22-tetraazacyclotetracosane (**10**) [11] were synthesized according to the literature procedures. All commercially available reagents were used as received. TLC was carried out on silica gel 60-F_{254}. Column chromatography was carried out on silica gel Si 60, mesh size 0.040−0.063 mm (Merck, Darmstadt, Germany). ^{1}H NMR (300 MHz) spectra were recorded with a Bruker AC 300 spectrometer. − Elemental analyses were performed by the Departmental Service of Microanalysis (University of Milan). Melting points (uncorrected) were determined with a Büchi SMP-20 capillary melting point apparatus.

Photophysical experiments were carried out in air-equilibrated CH_2Cl_2 solution. The equipment used to obtain the absorption spectra and the excited state properties (fluorescence spectra, quantum yields, and excited state lifetimes) have been described elsewhere.[13] In the acid titration experiments the changes in the fluorescence intensity were measured upon excitation at an isosbestic point of the unprotonated and protonated forms. The estimated experimental errors are ±2 nm on the band maximum, ±5% on the molar extinction coefficient, ±30% on the fluorescence quantum yield, and ±10% on the fluorescence lifetime.

Synthesis

4-Benzyl-1,7-dioxa-4,10-diazacyclododecane (6): A solution of **5** (1.1 g, 2.5 mmol) in 30 mL of dry THF was slowly added to a magnetically stirred suspension of $LiAlH_4$ (0.47 g, 12.5 mmol) in 30 mL of dry THF in an inert atmosphere. After the addition was complete, the reaction mixture was refluxed and stirred for 2 d, then allowed to cool to room temp. and excess $LiAlH_4$ was decomposed with the stoichiometric amount of H_2O. The aluminium oxide was filtered off and carefully washed with 50 mL of THF and the solvent evaporated from the combined filtrates to afford 0.65 g (quantitative yield) of **6** as a pale yellow viscous oil. − ^{1}H NMR ($CDCl_3$) δ 2.55−3.10 (m, 9 H), 3.40−3.60 (m, 8 H), 3.65 (s, 2 H), 7.10−7.45 (m, 5 H). − MS-FAB(+) *m/z*: 264 [M^+], calcd. for $C_{15}H_{24}N_2O_2$ 264. − $C_{15}H_{24}N_2O_2$: calcd. C 68.14, H 9.17, N 10.59; found C 68.35, H 9.40, N 10.25.

10-Benzyl-4-(9-methylanthracenyl)-1,7-dioxa-4,10-diazacyclododecane (1A): Solid Na_2CO_3 (424 mg, 4 mmol) was added to a solution of **6** (264 mg, 1 mmol) and 9-(chloromethyl)anthracene (227 mg, 1 mmol) in 50 mL of CH_3CN, and the resulting suspension was stirred at reflux for 20 h. The reaction mixture was allowed to cool to room temp. and filtered through Celite and the solvent evaporated to afford 532 mg of the crude product, as an orange viscous oil. Purification by column chromatography (SiO_2, $CHCl_3/CH_3OH$ = 98:2 v/v) afforded 250 mg (61%) of pure **1A** as a thick viscous oil. − ^{1}H NMR ($CDCl_3$) δ = 2.75 (t, *J* = 4.8 Hz, 4 H), 2.93 (t, *J* = 4.8 Hz, 4 H), 3.47 (t, *J* = 5.0 Hz, 4 H), 3.51 (t, *J* = 5.0 Hz, 4 H), 3.66 (s, 2 H), 4.64 (s, 2 H), 7.24−7.40 (m, 5 H), 7.42−7.58 (m, 4 H), 8.01 (d, *J* = 8.1, 2 H), 8.44 (s, 1 H), 8.64 (d, *J* = 8.6, 2 H). − MS-FAB(+) *m/z:* 454 [M^+], calcd. for $C_{30}H_{34}N_2O_2$ 454. − $C_{30}H_{34}N_2O_2$: calcd. C 79.25, H 7.55, N 6.16; found C 79.41, H 7.80, N 5.95.

10-Benzyl-4-(1-methylnaphthyl)-1,7-dioxa-4,10-diazacyclododecane (1N): Prepared as reported for **1A** in 70% yield as a thick brownish oil. − ^{1}H NMR ($CDCl_3$) δ = 2.77 (t, *J* = 4.6 Hz, 4 H), 2.87 (t, *J* = 4.6 Hz, 4 H), 3.53−3.58 (m, 8 H), 3.68 (s, 2 H), 4.11 (s, 2 H), 7.24−7.60 (m, 9 H), 7.75−7.90 (m, 2 H), 8.43 (d, *J* = 8.9 Hz, 2 H). − MS-FAB(+) *m/z:* 404 [M^+], calcd. for $C_{26}H_{32}N_2O_2$: 404. − $C_{26}H_{32}N_2O_2$: calcd. C 77.18, H 7.99, N 6.92; found C 76.95, H 8.20, N 6.70.

1,7-Dioxa-4,10-diazacyclododecane (8): A solution of **7** (820 mg, 2.5 mmol) in 30 mL of dry THF was slowly added to a magnetically stirred suspension of $LiAlH_4$ (0.47 g, 12.5 mmol) in 30 mL of dry THF in an inert atmosphere. After the addition was complete, the reaction mixture was refluxed and stirred for 2 d, allowed to cool to room temp. and excess $LiAlH_4$ was decomposed with the stoichiometric amount of H_2O. The aluminium oxide was filtered off and carefully washed with 50 mL of THF and the solvent evaporated from the combined filtrates to afford 430 mg (quantitative yield) of **8** as a pale yellow waxy solid. − ^{1}H NMR ($CDCl_3$) δ = 2.33−2.55 (br s, 2 H, D_2O exchange), 2.78 (t, *J* = 4.8 Hz, 8 H), 3.59 (t, *J* = 4.8 Hz, 8 H). − MS-FAB(+) *m/z*: 174, calcd. for $C_8H_{18}N_2O_2$: 174. − $C_8H_{18}N_2O_2$: calcd. C 55.14, H 10.43, N 16.07; found C 54.92, H 10.27, N 16.35.

4,10-Bis(9-methylanthracenyl)-1,7-dioxa-4,10-diazacyclododecane (2A): Solid Na_2CO_3 (152 mg, 1.44 mmol) was added to a solution of **8** (100 mg, 0.6 mmol) and 9-(chloromethyl)anthracene (260 mg, 1.1 mmol) in 30 mL of CH_3CN, and the resulting suspension was stirred at reflux for 20 h. The reaction mixture was allowed to cool to room temp., filtered through Celite and the solvent evaporated to afford 335 mg of the crude product. Purification by column chromatography (SiO_2, CH_2Cl_2/CH_3OH = 95:5 v/v) afforded 282 mg (89%) of pure **2A** as a yellow solid. − M.p. 82−84 °C. − ^{1}H NMR ($CDCl_3$) δ = 2.83 (t, *J* = 5.0 Hz, 8 H), 3.35 (t, *J* = 5.0 Hz, 8 H), 4.56 (s, 4 H), 7.42−7.52 (m, 8 H), 7.95−8.05 (m, 4 H), 8.40 (s, 2 H), 8.55 (d, *J* = 8.2, 4 H). − MS-FAB(+) *m/z*: 554 [M^+], calcd. for $C_{38}H_{38}N_2O_2$: 554. − $C_{38}H_{38}N_2O_2$: calcd. C 82.27, H 6.92, N 5.05; found C 81.95, H 6.81, N 4.97.

4,10-Bis(1-methylnaphthyl)-1,7-dioxa-4,10-diazacyclododecane (2N): Prepared as reported for **2A** in 73% yield as a pale yellow solid. − M.p. 139−140 °C. − ^{1}H NMR ($CDCl_3$) δ = 2.80 (t, *J* = 4.8 Hz, 8 H), 3.45 (t, *J* = 4.8 Hz, 8 H), 4.05 (s, 4 H), 7.36−7.52 (m, 8 H), 7.76 (d, *J* = 8.1 Hz, 2 H), 7.81−7.85 (m, 2 H), 8.36−8.40 (m, 2 H). − MS-FAB(+) *m/z*: 454 [M^+], calcd. for $C_{30}H_{34}N_2O_2$: 454. − $C_{30}H_{34}N_2O_2$: calcd. C 79.24, H 7.55, N 6.16; found C 79.01, H 7.35, N 5.94.

4,10,16,22-Tetrakis(9-methylanthracenyl)-1,7,13,19-tetraoxa-4,10,16,22-tetraazacyclotetracosane (4A): Solid Na_2CO_3 (360 mg, 3.4 mmol) was added to a solution of **9** (236 mg, 0.7 mmol) and 9-(chloromethyl)anthracene (629 mg, 2.7 mmol) in 50 mL of CH_3CN, and the resulting suspension was stirred at reflux for 2 d. The reaction mixture was allowed to cool to room temp., filtered through Celite and the solvent evaporated to afford 720 mg of the crude product, as a brown viscous oil. Purification by column chromatography (SiO_2, CH_2Cl_2/CH_3OH = 98:2 v/v) afforded 226 mg (30%) of pure **4A** as a pale brownish solid. − M.p. 88−89 °C. − ^{1}H NMR ($CDCl_3$) δ = 2.79 (t, *J* = 5.7 Hz, 16 H), 3.43 (t, *J* = 5.7 Hz, 16 H), 4.50 (s, 8 H), 7.33−7.40 (m, 16 H), 7.89−7.94 (m, 8 H), 8.33 (s, 4 H), 8.46−8.50 (m, 8 H). − MS-FAB(+) *m/z*: 1130 [M + Na^+], 1108 [M^+], calcd. for $C_{76}H_{74}N_4O_4$: 1108. − $C_{76}H_{74}N_4O_4$: calcd. C 82.27, H 6.92, N 5.05; found C 82.01, H 6.72, N 4.85.

4,10,16,22-Tetrakis(1-methylnaphthyl)-1,7,13,19-tetraoxa-4,10,16,22-tetraazacyclotetracosane (4N): Prepared as reported for **4A** in 51% yield as a white solid. − M.p. 112−114 °C. − ^{1}H NMR ($CDCl_3$) δ = 2.83 (t, *J* = 5.8 Hz, 16 H), 3.51 (t, *J* = 5.8 Hz, 16 H), 4.09 (s, 8 H), 6.74−7.48 (m, 16 H), 7.74 (d, *J* = 8.1 Hz, 4 H), 7.79−7.84 (m, 4 H), 8.33−8.36 (m, 4 H). − MS-FAB(+) *m*/*z*: 930 [M + Na$^+$], 908 [M$^+$], calcd. for $C_{60}H_{68}N_4O_4$: 908. − $C_{60}H_{68}N_4O_4$: calcd. C 79.24, H 7.55, N 6.16; found C 78.96, H 7.12, N 6.01.

10,22-Bis(9-methylanthracenyl)-4,16-bis[(4-methylphenyl)sulfonyl]-1,7,13,19-tetraoxa-4,10,16,22-tetraazacyclotetracosane (2′A): Solid Na_2CO_3 (159 mg, 1.5 mmol) was added to a solution of **10** (200 mg, 0.3 mmol) and 9-(chloromethyl)anthracene (138 mg, 0.6 mmol) in 30 mL of CH_3CN, and the resulting suspension was stirred at reflux for 2 d. The reaction mixture was allowed to cool to room temp., filtered through Celite and the solvent evaporated to afford 370 mg of the crude product, as an orange viscous oil. Purification by column chromatography (SiO_2, CH_2Cl_2/CH_3OH = 95:5 v/v) afforded 150 mg (48%) of pure **2′A** as a yellow solid. − M.p. 191−193 °C. − ^{1}H NMR ($CDCl_3$) δ = 2.32 (s, 6 H), 2.76 (t, *J* = 5.6 Hz, 8 H), 3.23 (t, *J* = 5.6 Hz, 8 H), 3.39−3.48 (m, 16 H), 4.54 (s, 4 H), 7.15 (d, *J* = 8.2 Hz, 4 H), 7.39−7.49 (m, 8 H), 7.59 (d, *J* = 8.2 Hz, 4 H), 7.97 (d, *J* = 9.0 Hz, 4 H), 8.38 (s, 2 H), 8.49 (d, *J* = 8.7 Hz, 4 H). − MS-FAB(+) *m*/*z*: 1058 [M + Na$^+$], 1036 [M$^+$], calcd. for $C_{60}H_{68}N_4O_8S_2$: 1036. − $C_{60}H_{68}N_4O_4$: calcd. C 69.47, H 6.62, N 5.40; found C 69.04, H 6.84, N 5.10.

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