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Convenient syntheses and preliminary photophysical properties of novel 8-aminoquinoline appended diaza-18-crown-6 ligands

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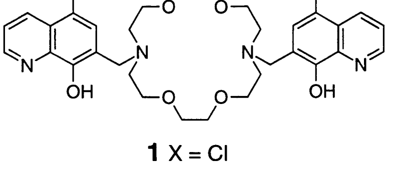
Abstract—Novel 7,16-bis(8-amino-2-quinolinylmethyl)- and 7,16-bis(8-amino-7-quinolinylmethyl)-diaza-18-crown-6 ligands (**12** and **16**) have been synthesized by reductive amination of 8-(di-*tert*-butoxycarbonyl)amino-2-quinolinecarboxaldehyde (followed by removal of the Boc protecting groups) or 8-amino-7-quinolinecarboxaldehyde with diaza-18-crown-6 using triacetoxyborohydride ($NaBH(OAc)_3$) as the reducing agent. The crystal structure of ligand **16** is also given. The absorption spectra of **12** and **16** are dominated by two intense bands at 250±5 and 238±1 nm which are blue shifted upon addition of alkaline earth and heavy metal ions in acetonitrile. In addition, intensities of the fluorescence bands of **12** and **16** are reduced in the presence of metal ions. © 2001 Elsevier Science Ltd. All rights reserved.

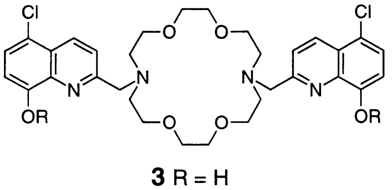
1. Introduction

Considerable attention has recently been focused on the development of compounds capable of selectively responding, via changes in UV absorption or fluorescence spectra, to the presence of specific metal ions.[1–5] In this context, we have prepared and studied several series of macrocyclic ligands with appended chromophores and fluorophores for use as selective metal-ion chemosensors.[6–10] 8-Hydroxy- and 8-methoxyquinoline-substituted diaza-18-crown-6 ligands (**1**–**4**, Fig. 1) developed in our laboratories showed significantly improved ion-complexing and selectivity for certain metal ions compared to unsubstituted diaza-18-crown-6.[9,10] Also these ligands have important luminescent properties when treated with certain metal ions.[3–5,11] Ligand **1** with the two 5-chloro-8-hydroxyquinoline (CHQ) substituents attached through their C-7 positions has a high affinity for Mg^{2+} and lower affinity for the other alkaline earth and alkali metal ions.[10] Ligand **3** with the CHQ groups attached through their C-2 positions, on the other hand, exhibits very strong affinity for Ba^{2+} and no affinity for Mg^{2+}. Ligands **1** and **2** have proven to be effective chemosensors for Mg^{2+} and Hg^{2+}, respectively.[4,5] And as a chemosensor, ligand **4** selectively responds to Cd^{2+}, by an increase in fluorescence.[11]

This paper reports the synthesis of two diaza-18-crown-6 ligands containing two 8-aminoquinoline side arms each attached through their C-2 (**12**) or C-7 (**16**) positions. Since the two soft amino donor groups interact strongly with soft metal ions, we expected these ligands to have enhanced selectivity toward certain transition and post-transition metal ions compared to their hydroxyquinoline analogues **1**–**3**. Also, we expected that the different attachment site of the aminoquinolines to the macrocyclic ligands will influence metal ion affinities of the ligands. The X-ray crystal structure of ligand **16** is also described herein.



1 X = Cl
2 X = NO_2



3 R = H
4 R = CH_3

Figure 1. 5-Chloro(or Nitro)-8-hydroxyquinoline-substituted diaza-18-crown-6 ligands **1**–**4**.

Keywords: diazacrown ether; 8-aminoquinoline; reductive amination.

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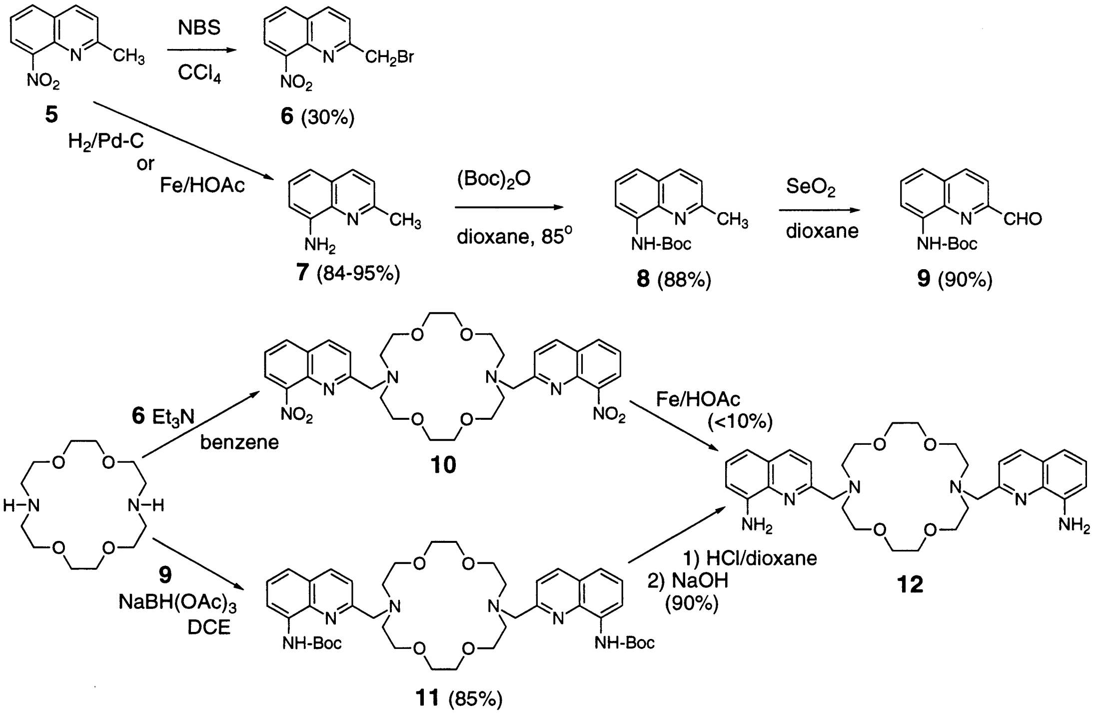
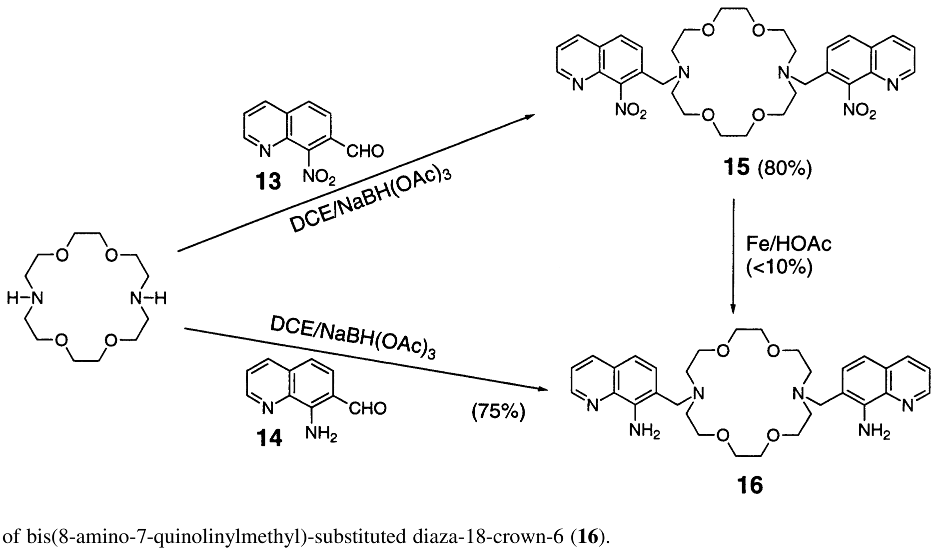


Scheme 1. Preparation of bis(8-amino-2-quinolinylmethyl)-substituted diaza-18-crown-6 (**12**).

2. Results and discussion

Two possible methods for synthesizing 7,16-bis(8-amino-2-quinolinylmethyl)-diaza-18-crown-6 (**12**) were used (Scheme 1). In the first method, the diazacrown was treated with 2-bromomethyl-8-nitroquinoline (**6**) followed by reduction. Intermediate **6** was prepared in 30% yield by bromination of 8-nitroquinaldine (**5**) with *N*-bromosuccinimide in refluxing CCl_4. We tried to reduce the nitro groups of compound **10** to form the desired diamino macrocycle **12** by catalytic hydrogenation using PtO_2 as the catalyst. Unfortunately, no desired products were obtained because the 8-nitroquinoline groups were removed from the diazacrown by hydrogenation. Reduction of **10** was achieved using powdered iron and acetic acid. However, the yield was very low (<10%) due to the formation of an Fe(II)-crown ether complex and it was difficult to effect decomplexation of this complex.

The second method to prepare **12** used reductive amination[12] of Boc-protected 8-amino-2-quinolinecarboxaldehyde (**9**) (Scheme 1). The synthesis of key precursor **9** began with commercially available 8-aminoquinaldine (**7**), which can be easily obtained by reduction of 8-nitroquinaldine (**5**) using powdered iron (84% yield) or by catalytic hydrogenation using Pd–C as catalyst (95% yield). Amine **7** was treated with $(Boc)_2O$ in 1,4-dioxane at 85–90°C to give Boc-protected **8** in 88% yield. Oxidation of **8** was accomplished with SeO_2 in 1,4-dioxane to provide **9** in 90% yield. Reductive amination was carried out by treating



Scheme 2. Preparation of bis(8-amino-7-quinolinylmethyl)-substituted diaza-18-crown-6 (**16**).

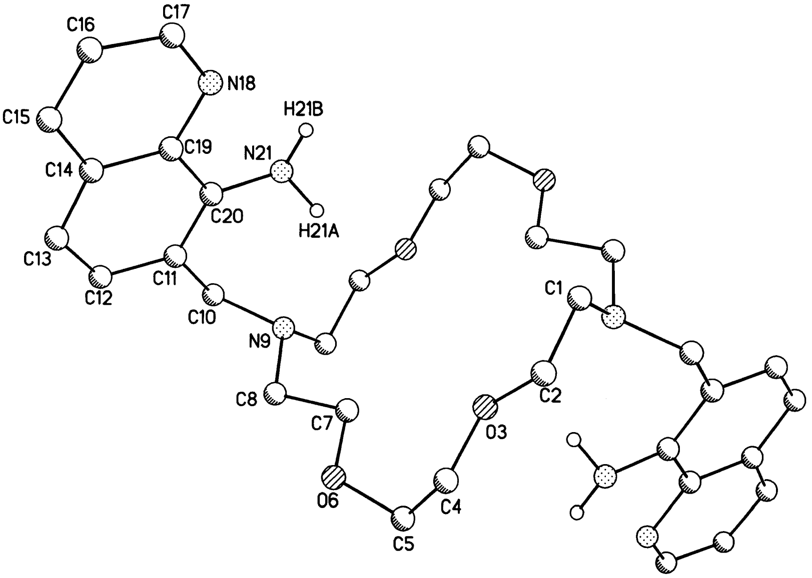


Figure 2. The crystal structure of **16**. All hydrogen atoms were omitted for clarity except those of the primary amines.

diaza-18-crown-6 with **9** in the presence of $NaBH(OAc)_3$ to give Boc-protected macrocycle **11** in an 85% yield. The removal of the Boc groups was accomplished in 90% yield using 4.0 M HCl in 1,4-dioxane to give bis-8-aminoquinoline appended diaza-18-crown-6 ligand **12**.

7,16-Bis(8-amino-7-quinolinylmethyl)-diaza-18-crown-6 **16** was also prepared by reductive amination (Scheme 2). Intermediate aldehydes **13** and **14** were prepared by the published method.[13] Diaza-18-crown-6 was treated with **13** and **14** in the presence of $NaBH(OAc)_3$ to form 8-nitroquinoline- and 8-aminoquinoline-substituted diaza-18-crown-6 ligands **15** and **16** in 80 and 75% yields, respectively. As with the reduction of **10** to **12** (Scheme 1), reduction of **15** to **16** by powdered iron and catalytic hydrogenation occurred in very low yields.

The solid state structure of **16** is shown in Fig. 2. The conformation of the ligand suggests that the side-arms would complex a metal ion guest in the cavity using the primary amine nitrogen atoms. In the absence of a guest cation, the amine nitrogen atom does interact with N9 and O3A of the macroring through a bifurcated H-bond involving H21A. However, the quinoline ring nitrogens do not appear to be available for complexation.

The absorption spectra of ligands **12** and **16** in acetonitrile (Fig. 3) are dominated by two intense bands centered at 245 and 337 nm (**12**) and at 254 and 339 nm (**16**, see Table 1), which are very similar to those observed for **1**, **3**, and **4** in the same solvent.[4,5,11] Compounds **12** and **16** fluoresce intensively at 474 and 490 nm, respectively, in acetonitrile (Table 1), while only very weak signals can be observed in protic solvents such as water and methanol. The lack of fluorescence in protic solvents can be ascribed to proton transfer processes involving solvent molecules, similarly to what was observed for 8-hydroxyquinoline derivatives.[14]

The photophysical properties of **12** and **16** are drastically changed upon addition of alkaline earth and transition metal ions. In particular, the two absorption bands undergo a sizeable blue shift, while the luminescence intensity is typically reduced. In acetonitrile, analysis of the pattern of the absorption and fluorescence intensities as a function of the molar equivalents of metal ions added to the solution (Fig. 4) reveals a marked difference in the ion binding behavior of the two ligands. In particular, with the metal ions studied (with the partial exception of Mg^{2+}) **16** forms stable complexes in acetonitrile ($\log K_a \geq 7.0$) with 1:1 (metal/ligand) stoichiometry. A similar behavior is shown by **12** only with Ca^{2+}, Sr^{2+}, and Ba^{2+}; while with Mg^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+}, it forms complexes with different stoichiometries (see Fig. 4), as can be seen by the lack of isosbestic points in the absorption spectra (Fig. 3 for Hg^{2+}) and the appearance of multiple fluorescence bands during the titration experiments. A complete characterization of all the equilibria involved are in progress in our laboratories.

In conclusion, the synthetic approach presented here could

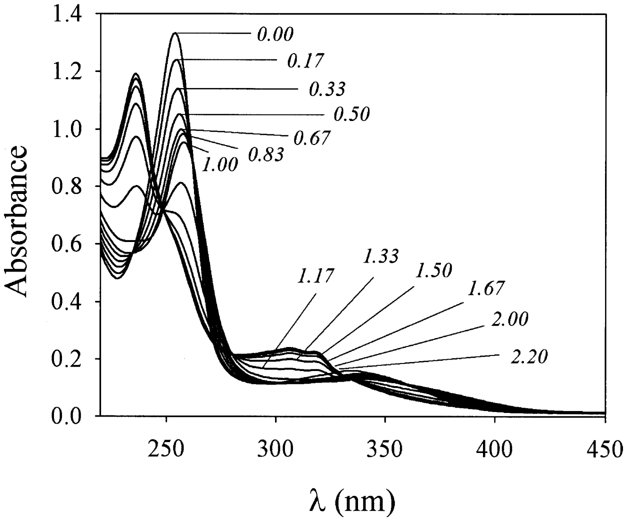


Figure 3. Absorption spectra of acetonitrile solutions of **12** (2×10^{-5} M) and upon addition of up to 2.2 equiv. of $Hg(ClO_4)_2$.

Table 1. Absorbance and fluorescence data of **12** and **16** and their complexes with metal ions

Compound	Absorbance		Fluorescence[a]	
	λ (nm)	ε ($M^{-1}cm^{-1}$)	λ (nm)	I_{rel}
12	245	68,000	474	1000
	337	7000		
12·Mg^{2+}	235	46,000	484	440
	257	41,000		
	316	6000		
12·Ca^{2+}	244	47,000	493	300
	311	6000		
12·Sr^{2+}	245	36,000	488	300
	311	5700		
12·Ba^{2+}	251	38,000	480	80
	311	6000		
16	254	71,000	496	1000
	339	6900		
16·Mg^{2+}	233	48,000	490	250
	254	35,000		
	315	5200		
16·Ca^{2+}	240	83,000	451	180
	303	7400		
16·Sr^{2+}	244	74,000	464	160
	318	6400		
16·Ba^{2+}	245	72,000	451	150
	319	6600		
16·Zn^{2+}	236	80,000	450	10
	303	8500		
16·Cd^{2+}	237	80,000	450	80
	298	9100		
16·Hg^{2+}	234	67,000	–	–
	304	12,000		

[a] Excitation wavelengths were 300 nm for **12** and its complexes and 340 nm for **16** and its complexes.

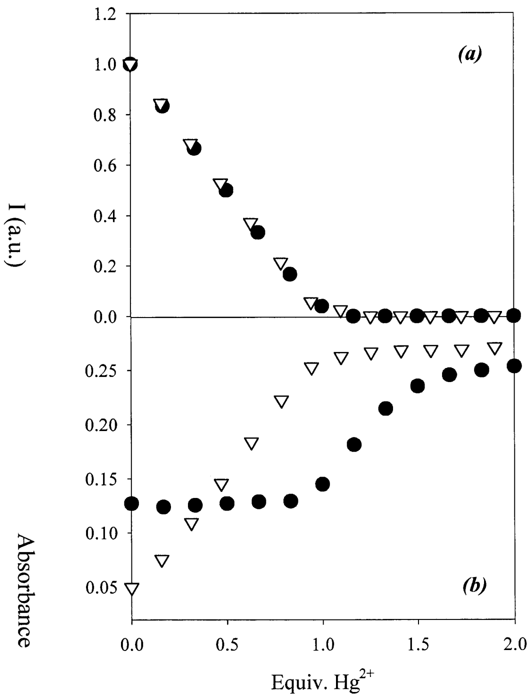


Figure 4. (a) Fluorescence intensity (λ_{exc}=300 nm, λ_{em}=485 nm) recorded after addition of increasing amounts of $Hg(ClO_4)_2$ to a 2×10^{-5} M acetonitrile solution of **12** (●) or **16** (▽). (b) Absorbance (λ=300 nm) recorded after addition of increasing amounts of $Hg(ClO_4)_2$ to a 2×10^{-5} M acetonitrile solution of **12** (●) or **16** (▽).

be applied to the synthesis of any azacrown ether macrocycles bearing 8-aminoquinoline side arms attached either through their positions 2 or 7. The photophysical properties of **12** and **16** indicate that they may be useful as chemical sensors for metal ions.

3. Experimental

The ^1H- and ^{13}C NMR spectra were recorded at 200 or 300 MHz and 50 or 75 MHz in $CDCl_3$ unless otherwise indicated. Melting points are uncorrected. HRMS spectra were determined using fast atom bombardment (FAB), chemical ionization (CI) and electron impact (EI) methods. Solvents and starting materials were purchased from commercial sources were available. Compounds **13** and **14** were prepared as reported.[13] The solvent for photophysical measurements was acetonitrile (Merck, UVASOL) that was used without further purification. Absorption spectra were recorded on a Perkin–Elmer lambda 40 spectrophotometer. Uncorrected emission and corrected excitation spectra were obtained on a Fluorolog spectrofluorimeter equipped with a R928 phototube. In order to allow comparison of emission intensities, corrections for instrumental response, inner filter effects,[15] and phototube sensitivity were performed. A correction for differences in the refraction index was introduced when necessary.

3.1. Synthesis of new ligands

3.1.1. 8-Nitro-2-(bromomethyl)quinoline (6). A solution of 8-nitroquinaldine (**5**) (1.65 g, 8.8 mmol) in 45 mL of CCl_4 was refluxed with *N*-bromosuccinimide (NBS) (1.73 g, 9.7 mmol) in the presence of benzoyl peroxide (0.07 g) for 2 days. The hot solution was filtered. The residue was purified by column chromatography on silica gel using hexane/CH_2Cl_2 (2:1) as eluent to give 0.71 g (30%) of **6** as yellow crystals; mp 144–146°C; ^1H NMR: δ 8.26 (d, *J*=8.7 Hz, 1H), 8.02 (d, *J*=8.1 Hz, 2H), 7.75 (d, *J*=8.7 Hz, 1H), 7.62 (t, *J*=8.1 Hz, 1H), 4.71 (s, 2H); HRMS *m*/*z*: calcd for $C_{10}H_7N_2O_2Br$ (M^+): 265.9691, found: 265.9686. Anal. Calcd for $C_{10}H_7N_2O_2Br$: C, 44.97; H, 2.64. Found: C, 45.12; H, 2.72.

3.1.2. 8-(*t*-Butoxycarbonylamino)quinaldine (8). 8-Aminoquinaldine (**7**) (3.95 g, 25 mmol) was stirred with di-*t*-butyldicarbonate (10.9 g, 50 mmol) in 70 mL of dioxane at 85–90°C for two days. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using CH_2Cl_2/hexane (1:1) as eluent to give 5.68 g (88%) of **8** as white crystals; mp 72–73°C; ^1H NMR: δ 9.06 (s, 1H), 8.38 (d, *J*=7.2 Hz, 1H), 7.99 (d, *J*=8.0 Hz, 2H), 7.47–7.28 (m, 3H), 2.73 (s, 3H), 1.59 (s, 9H); HRMS *m*/*z*: calcd for $C_{15}H_{19}N_2O_2$ $(M+H)^+$: 259.1448, found: 259.1430. Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02. Found: C, 70.00; H, 6.87.

3.1.3. 8-(*t*-Butoxycarbonylamino)-2-quinolinecarboxaldehyde (9). To a stirred suspension of freshly sublimed SeO_2 (3.33 g, 30 mmol) in 150 mL of dioxane at 50–55°C was added a solution of **8** (4.34 g, 16.8 mmol) in 50 mL of dioxane during the course of 3 h. The mixture was heated to 80–85°C overnight, filtered, and the dioxane was removed under reduced pressure. The residue was purified by column chromatography on silica gel with CH_2Cl_2 as eluent to give 4.11 g (90%) of **9** as green crystals; mp 129–131°C; ^{1}H NMR: δ 10.26 (s, 1H), 9.0 (s, 1H), 8.52 (d, *J*=6.6 Hz, 1H), 8.30 (d, *J*=8.8 Hz, 1H), 8.05 (d, *J*=8.4 Hz, 1H), 7.66 (t, *J*=8.0 Hz, 1H), 7.50 (d, *J*=8.4 Hz, 1H); HRMS *m/z*: calcd for $C_{15}H_{17}N_2O_3$ $(M+1)^+$: 273.1240, found: 273.1229. Anal. Calcd for $C_{15}H_{16}N_2O_3$: C, 66.16; H, 5.92. Found: C, 66.06; H, 5.82.

3.1.4. 7,16-Bis(8-nitro-2-quinolinylmethyl)diaza-18-crown-6 (10). A solution of **6** (2.4 g, 9.0 mmol) in 50 mL of benzene was added dropwise to a solution of diaza-18-crown-6 (1.0 g, 3.8 mmol) and triethylamine (1.6 g, 15.8 mmol) in 50 mL of benzene under nitrogen. The mixture was stirred at room temperature for 20 h and then refluxed for 2 h. The solvent was evaporated under reduced pressure. The residue was treated with a mixture of water and CH_2Cl_2 (1:2). The organic layer was separated, washed with water, and dried (Na_2SO_4). After evaporation, the residue was purified by column chromatography on silica gel with acetone as eluent. The product was recrystallized from CH_2Cl_2/EtOH to give 1.98 g (82%) of **10** as white crystals; mp 124–126°C; ^{1}H NMR: δ 8.12 (d, *J*=8.4 Hz, 2H), 7.95–7.89 (m, 6H), 7.51 (t, *J*=7.8 Hz, 2H), 4.07 (s, 4H), 3.68 (t, *J*=5.7 Hz; 8H), 3.62 (s, 8H), 2.93 (t, *J*=5.7 Hz, 8H); ^{13}C NMR: δ 164.6, 148.3, 138.9, 136.1, 131.7, 128.3, 124.6, 123.3, 123.1, 71.0, 70.1, 62.2, 54.8; HRMS *m/z*: calcd for $C_{32}H_{38}N_6O_8Na$ $(M+Na)^+$: 657.2651, found: 657.2656. Anal. Calcd for $C_{32}H_{38}N_6O_8$: C, 60.56; H, 6.03. Found: C, 60.70; H, 5.84.

3.1.5. 7,16-Bis[(8-*t*-butoxycarbonylamino)-2-quinolinylmethyl]diaza-18-crown-6 (11). A mixture of diaza-18-crown-6 (393 mg, 1.5 mmol) and **9** (898 mg, 3.3 mmol) in 25 mL of dichloroethane was stirred with $NaBH(OAc)_3$ (848 mg, 4.0 mmol) under nitrogen at room temperature for 5 h. The reaction was then quenched with saturated Na_2CO_3 (15 mL) and the mixture was extracted with CH_2Cl_2 (3×10 mL). The combined CH_2Cl_2 extracts were dried (Na_2SO_4), filtered, and concentrated on a rotary evaporator. The residue was purified by column chromatography on silica gel with acetone as eluent to give 987 mg (85%) of **11** as white crystals; mp 48–50 °C; ^{1}H NMR: δ 9.0 (s, 2H), 8.40 (d, *J*=7.2 Hz, 2H), 8.08 (d, *J*=8.4 Hz, 2H), 7.75 (d, *J*=8.4 Hz, 2H), 7.44 (m, 4H), 4.06 (s, 4H), 3.70 (t, *J*=5.6 Hz), 3.64 (s, 8H), 2.96 (t, *J*=5.6 Hz), 1.61 (s, 18H); ^{13}C NMR: δ 159.1, 152.9, 137.2, 136.5, 134.8, 127.0, 126.7, 121.5, 119.9, 114.3, 70.8, 70.1, 62.2, 54.5, 28.4; HRMS *m/z*: calcd for $C_{42}H_{58}N_6O_8Na$ $(M+Na)^+$: 797.4217. found: 797.4196. Anal. Calcd for $C_{42}H_{58}N_6O_8$: C, 65.09; H, 7.54. Found: C, 65.10; H, 7.57.

3.1.6. 7,16-Bis(8-amino-7-quinolinylmethyl)diaza-18-crown-6 (12). Compound **11** (774 mg, 1.0 mmol) was treated with 4.0 M HCl in 50 mL of dioxane and the mixture was allowed to stir for 12 h. A chilled solution of 3N NaOH (80 mL) was added dropwise to the mixture. Solid **12** was filtered and recrystallized from CH_2Cl_2/EtOH (1:1) to give a 90% yield of the pure product; mp 114–115°C; ^{1}H NMR: δ 8.01 (d, *J*=8.4 Hz, 2H); 7.65 (d, *J*=8.4 Hz, 2H); 7.34–7.26 (m, 2H); 7.12 (d, *J*=7.2 Hz, 2H); 6.91 (d, *J*=7.2 Hz, 2H); 4.98 (s, 4H), 4.02 (s, 4H); 3.69 (t, *J*=5.6 Hz, 8H); 3.64 (s, 8H); 2.95 (t, *J*=5.6 Hz, 8H); ^{13}C NMR: 158.0, 143.7, 137.5, 136.s2, 127.8, 126.7, 121.4, 115.9, 110.0, 70.8, 70.1, 62.3, 54.5; HRMS *m/z*: calcd for $C_{32}H_{42}N_6O_4Na$ $(M+Na)^+$: 597.3169, found: 597.3146. Anal. Calcd for $C_{32}H_{42}N_6O_4$: C, 66.88; H, 7.37. Found: C, 66.70; H, 7.15.

3.1.7. 7,16-Bis(8-nitro-7-quinolinylmethyl)diaza-18-crown-6 (15). Macrocycle **15** was prepared as above for **11** from diaza-18-crown-6 (393 mg, 1.5 mmol) and **13** (666 mg, 3.3 mmol). Crude compound **15** was purified by column chromatography on silica gel with acetone as eluent to give an 80% yield of pure **15**; mp 141–143°C, ^{1}H NMR: 8.94 (d, *J*=3.0 Hz, 2H), 8.18 (d, *J*=8.4 Hz), 7.86 (d, *J*= 3.0 Hz, 4H), 7.47 (dd, *J*=4.0 and 8.4 Hz), 3.93 (s, 4H), 3.65 (t, *J*=5.6 Hz, 8H), 3.60 (s, 8H), 2.87 (t, *J*=5.6 Hz, 8H); ^{13}C NMR: δ 152.0, 147.7, 139.4, 135.6, 132.9, 129.1, 127.8, 127.7, 122.3, 70.7, 69.7, 55.1, 54.1; HRMS *m/z*: calcd for $C_{32}H_{38}N_6O_8Na$ $(M+Na)^+$: 657.2651, found: 657.2649. Anal. Calcd for $C_{42}H_{38}N_6O_8$: C, 60.56; H, 6.03. Found: C, 60.40; H, 6.18.

3.1.8. 7,16-Bis(8-amino-7-quinolinylmethyl)diaza-18-crown-6 (16). Macrocycle **16** was prepared as above for **11** from diaza-18-crown-6 (393 mg, 1.5 mmol) and **14** (567 mg, 3.3 mmol). Crude compound **16** was purified by column chromatography on silica gel with acetone/Et_3N (10:1) as eluent to give a 75% yield of the pure product; mp 150–152°C; ^{1}H NMR: δ 8.74–8.72 (m, 2H), 8.02 (dd, *J*=1.8 and 8.4 Hz, 2H), 7.30 (dd, *J*=4.4 and 8.4 Hz, 2H), 7.19 (d, *J*=8.6 Hz, 2H), 7.03 (d, *J*=8.6 Hz, 2H), 6.20 (s, 4H), 3.82 (s, 4H), 3.62 (t, *J*=5.4 Hz, 8H), 3.54 (s, 8H), 2.80 (d, *J*=5.4 Hz, 8H); ^{13}C NMR: δ 147.2, 144.5, 138.4, 135.8, 129.7, 128.1, 120.8, 118.4, 113.9, 70.6, 96.6, 59.1, 54.2; HRMS *m/z*: calcd for $C_{32}H_{42}N_6O_4Na$ $(M+Na)^+$: 597.3169, Found: 597.3172. Anal. Calcd for $C_{32}H_{42}N_6O_4$: C, 66.88; H, 7.37. Found: C, 66.77; H, 7.43.

3.2. X-Ray crystallography data

Crystal data and experimental details are listed in Table 2.

Table 2. Crystal data and experiment details for **16**

Formula	$C_{32}H_{42}N_6O_4$
Formula weight	574.72
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	7.0482(13)
b (Å)	19.629(4)
c (Å)	11.233(2)
β (°)	98.03(2)
V (Å^3)	1538.9(3)
Z	2
$F(000)$	616
D_x (g cm^{-3})	1.240
Crystal size (mm)	0.40×0.35×0.20
μ (mm^{-1})	0.083
Temperature (K)	293
$2\theta_{max}$ (°)	50.0
Total data	2941
Independent data	2710 (R_{int}=0.0171)
Total parameters	191
Goodness of fit on F^2	1.015
$R[I>20\text{-}(I)]$	0.0450
R (all data)	0.0776
Largest diff peak and hole (eÅ^{-3})	0.129, −0.139

Single crystal data were collected using a Bruker P4 automated diffractometer which utilized graphite monochromated MoKα radiation. The structure was solved using the direct method and refined on F^2 using a full matrix, least-squares procedure. All non-hydrogen atoms were refined anisotropically. Positions for hydrogen atoms, except for the two amine hydrogens, were calculated based on geometrical factors. The positions for the amine hydrogen atoms were obtained from a difference map. All hydrogens were allowed to ride on their neighboring heavy atoms during refinement. The structure was solved, refined and displayed using SHELXTL PC[16] computer program package.

3.3. Experimental data for UV–Vis and fluorescence titration experiments

In a typical experiment, a solution of ligand (concentration 2×10^{-5} M) in dry acetonitrile was titrated by increasing amounts of a solution of the perchlorate salt of the cation of interest (concentration 5×10^{-3} M) at room temperature. After each addition of aliquots, the UV–Vis and fluorescence spectra of the solution were recorded. When the titration was completed, the spectra were implemented into the Specifit software.[17]

Acknowledgements

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