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6. AUTHOR(S) R. Todd Bronson, Jerald S. Bradshaw, Paul B. Savage, Saowarux Fuangswasdi, Sang Chul Lee, and Reed M. Izatt
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The preliminary photophysical properties of a diazatrithia-15-crown-5 and diazatrithia-16-crown-5 ligands containing two 8-hydroxyquinoline side arms (**15**, **16**, **18** and **19**) are reported. The studies show that ligands **16** and **19** exhibit increased fluorescence in the presence of Zn<sup>2+</sup> indicating that these ligands could be chemical sensors for Zn<sup>2+</sup>.

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15-Crown-5 and Diazatrithia-16-Crown-5 Ligands**

by

**R. Todd Bronson, Jerald S. Bradshaw, Paul B. Savage,  
Saowarux Fuangswasdi, Sang Chul Lee, and Reed M. Izatt**

**Department of Chemistry and Biochemistry  
Brigham Young University, Provo, UT 84602-4678**

**April 17, 2001**

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# Photophysical Properties of Bis-8-Hydroxyquinoline-Armed Diazatrithia-15-Crown-5 and Diazatrithia-16-Crown-5 Ligands

R. Todd Bronson, Jerald S. Bradshaw, Paul B. Savage,  
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Brigham Young University

## Results and Discussion

**UV-Visible Studies.** Due to the low solubilities of the ligands in methanol, stability constants of **15**, **18**, and **19** could be determined by UV-Vis spectrophotometry. Addition of metal ions to solutions of these ligands caused a decrease in intensity of the UV-Vis absorption as well as formation of a new peak leading to at least one isosbestic point. Spectral variations in the UV-Vis of **19** exhibited evidence of the formation of a second complex. In the case of  $\text{Zn}^{2+}$  and **19** (Figure 2), the first series of spectral lines passed through two isosbestic points at 226.5 and 253 nm until  $C_M/C_L \approx 1$ , then a new isosbestic point at 261 nm was observed at higher values of  $C_M/C_L$ . These spectral changes were interpreted as the result of formation of both mono- and binuclear complexes. The stoichiometry of complexation was found from interpretation of the spectrophotometric data and is given in Table 1. Whenever there was ambiguity in choosing the best stoichiometry, the simplest one was chosen if there is no other clear evidence to support another one.

All three ligands formed strong mononuclear complexes ( $\log \beta \geq 5$ ) with the metal ions studied. The complexes of **18**, for example, were of sufficient thermodynamic stability that equilibrium constants for their formation could not be determined accurately by UV-Vis spectrophotometry. Only a lower limit of  $\log \beta$  values could be given ( $\log \beta \geq 7$ ).

Among the three ligands studied, **18** possesses the highest affinity towards transition metal ions. The higher constants for the formation of complexes of **18** over those of **15** with a given cation can be explained by participation of quinoline nitrogen atoms in complexation. This demonstrates how the attachment site of the quinoline to the crown can effect complexation. When attached at the 7-position, the quinoline nitrogen atoms may not bind metal ions as effectively. Crown size effects can be seen by comparison of **18** and **19**. Although complexes formed by **19** with  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  are less stable than those formed by **18**, **19** can accommodate two cations. No comparison between **18** and **19** can be made for the other cations as only the lower limit of  $\log \beta$  can be assigned.

**Preliminary Fluorescence Studies.** Among the transition metal ions studied, complexes of ligands **15**, **16**, **18**, and **19** with  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{2+}$  gave emission wavelengths as shown in Table 2. Compounds **15** and **16** containing CHQ groups attached at the quinoline 7-positions, formed strongly fluorescent complexes of the type  $\text{ML}_2$  with  $\text{Cd}^{2+}$ . However, the  $\text{Cd}^{2+}$  complexes of **18** and **19** with the 8-HQ side arms

attached through quinoline 7-positions, exhibited weaker fluorescence intensities at longer wavelengths and formed complexes of the type ML. Presumably, the fluorescence properties of the  $\text{Cd}^{2+}$  complexes were influenced by side arm orientation.

Complexes with  $\text{Zn}^{2+}$  gave different results. Compounds **16** and **19** containing 16-membered rings gave strong emission bands, but **15** and **18** with 15-membered rings showed relatively weak fluorescence intensities with  $\text{Zn}^{2+}$ . Figures 3 and 4 illustrate the fluorescence spectra of the complexes formed by the interactions of  $\text{Zn}^{2+}$  with **16** and **19**, respectively. Interestingly, Figures 3 and 4 show that ML and  $\text{M}_2\text{L}$  complexes have emission maxima at different wavelengths (540 and 500 nm, respectively). Figures 5 and 6 illustrate the titration curves of **16** and **19** with  $\text{Zn}^{2+}$  showing a sharp endpoint for **16** at a 2:1 metal/ligand ratio. Figure 6 shows that **19** forms more than one type of complex with  $\text{Zn}^{2+}$ . It appears that **19** does not bind the second  $\text{Zn}^{2+}$  as strongly as does **16**. The fluorescence spectra of the **18**- $\text{M}^{2+}$  complexes were similar to those of 8-HQ with the same metal ions. These results suggest a lack of crown participation in complexation by **18**. Complexes of  $\text{Pb}^{2+}$  with all ligands gave weak fluorescent responses while forming ML complexes. 8-Hydroxyquinoline and 5-chloro-8-hydroxyquinoline exhibited low fluorescence intensities with  $\text{Cd}^{2+}$ ,  $\text{Zn}^{2+}$ , and  $\text{Pb}^{2+}$  relative to the ligands studied.

Table 1. Stability Constants for the Formation of Metal Ion Complexes ( $\log \beta_x$ )<sup>a</sup> in MeOH<sup>b</sup>

	15	18	19	19	8-HQ <sup>c</sup>	8-HQ <sup>c</sup>	8-HQ <sup>c</sup>	CHQ <sup>d</sup>	CHQ <sup>d</sup>
Log $\beta$	ML	ML	ML	M2L	ML	ML	ML <sub>2</sub>	ML	ML <sub>2</sub>
Co <sup>2+</sup>	≥ 7	≥ 7	≥ 7		4.5±0.2	11.6±0.3	11.7±0.1	5.6±0.3	11.7±0.1
Ni <sup>2+</sup>	6.82±0.03	≥ 7	5.93±0.06	12.7±0.2		11.8±0.2			11.7±0.1
Cu <sup>2+</sup>	6.7±0.2	≥ 7	6.72±0.05	11.4±0.2	5.7±0.1	13.3±0.4	≥ 7	≥ 7	≥ 14
Zn <sup>2+</sup>	6.8±0.1	≥ 7	≥ 7	≥ 11	6.1±0.2	10.4±0.1	6.17±0.07	10.8±0.05	
Cd <sup>2+</sup>	5.18±0.06	≥ 7	≥ 7		4.24±0.06	9.2±0.2		9.5±0.2	
Hg <sup>2+</sup>	4.92±0.02	≥ 7 <sup>e</sup>	≥ 7	≥ 14	4.30±0.01	8.60±0.01	4.50±0.03	9.29±0.06	
Pb <sup>2+</sup>	5.44±0.01	≥ 7	≥ 7		5.58±0.01		5.3±0.3		

<sup>a</sup> Corresponding to the general equilibrium:  $xM^{n+} + yL \rightleftharpoons M_xL_y^{xn+}$  (room temperature, I = 0.01 M NaOAc).

<sup>b</sup> Mean values of n ≥ 2 independent determinations, with the standard deviation  $\sigma_{n-1}$  on the mean.

<sup>c</sup> 8-HQ = 8-Hydroxyquinoline. <sup>d</sup> CHQ = 5-Chloro-8-hydroxyquinoline. <sup>e</sup> Value of one determination only.

Table 2. Fluorescence Properties of 8-Hydroxyquinoline, 5-Chloro-8-hydroxyquinoline, **15**, **16**, **18**, and **19** in Methanol Containing 0.01 M NaOAc.

Ions	Cd <sup>2+</sup>						Zn <sup>2+</sup>					
	8-HQ <sup>a</sup>	CHQ <sup>a</sup>	<b>15</b>	<b>16</b>	<b>18</b>	<b>19</b>	8-HQ <sup>a</sup>	CHQ <sup>a</sup>	<b>15</b>	<b>16</b>	<b>18</b>	<b>19</b>
Ligand	8-HQ <sup>a</sup>	CHQ <sup>a</sup>	<b>15</b>	<b>16</b>	<b>18</b>	<b>19</b>	8-HQ <sup>a</sup>	CHQ <sup>a</sup>	<b>15</b>	<b>16</b>	<b>18</b>	<b>19</b>
Wavelength (nm) <sup>b</sup>	540	548	513	511	544	540	541	545	515	511	541	500
Maximum Intensity <sup>c</sup>	17	29	335	265	15	36	15	22	74	188	20	240
Complexation	1:1	1:1	1:2	1:2	1:1	1:1	1:1	1:1	2:1	2:1	1:1	2:1

Ions	Pb <sup>2+</sup>					
	8-HQ <sup>a</sup>	CHQ <sup>a</sup>	<b>15</b>	<b>16</b>	<b>18</b>	<b>19</b>
Ligand	8-HQ <sup>a</sup>	CHQ <sup>a</sup>	<b>15</b>	<b>16</b>	<b>18</b>	<b>19</b>
Wavelength (nm) <sup>b</sup>	531	552	517	521	520	530
Maximum Intensity <sup>c</sup>	3	6	9	11	3	8
Complexation	<sup>d</sup>	<sup>d</sup>	1:1	1:1	1:1	1:1

<sup>a</sup>8-HQ and CHQ are defined in Table 1. <sup>b</sup>Wavelength of maximum intensity. <sup>c</sup>Intensity of 10 μM of each ligand. <sup>d</sup>Could not be determined from the fluorescence data.

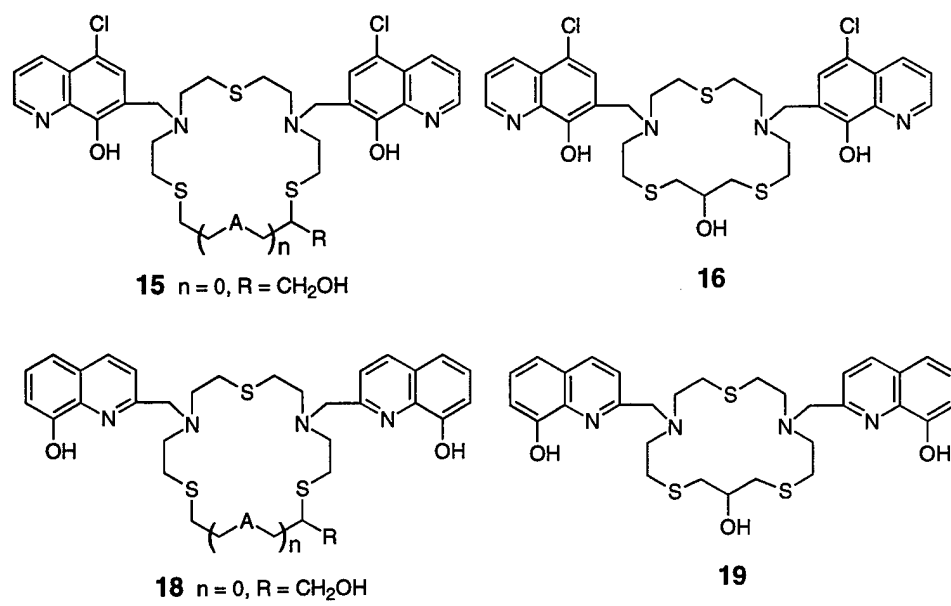


Figure 1. Structures of Ligands

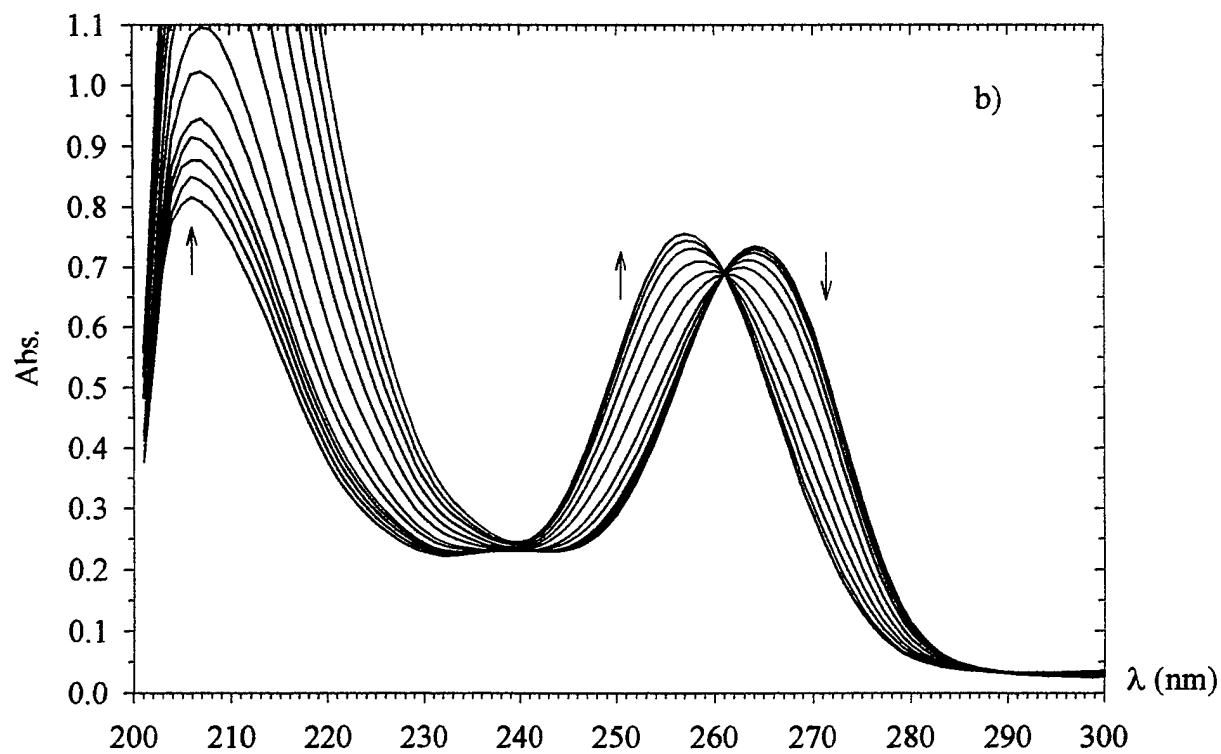
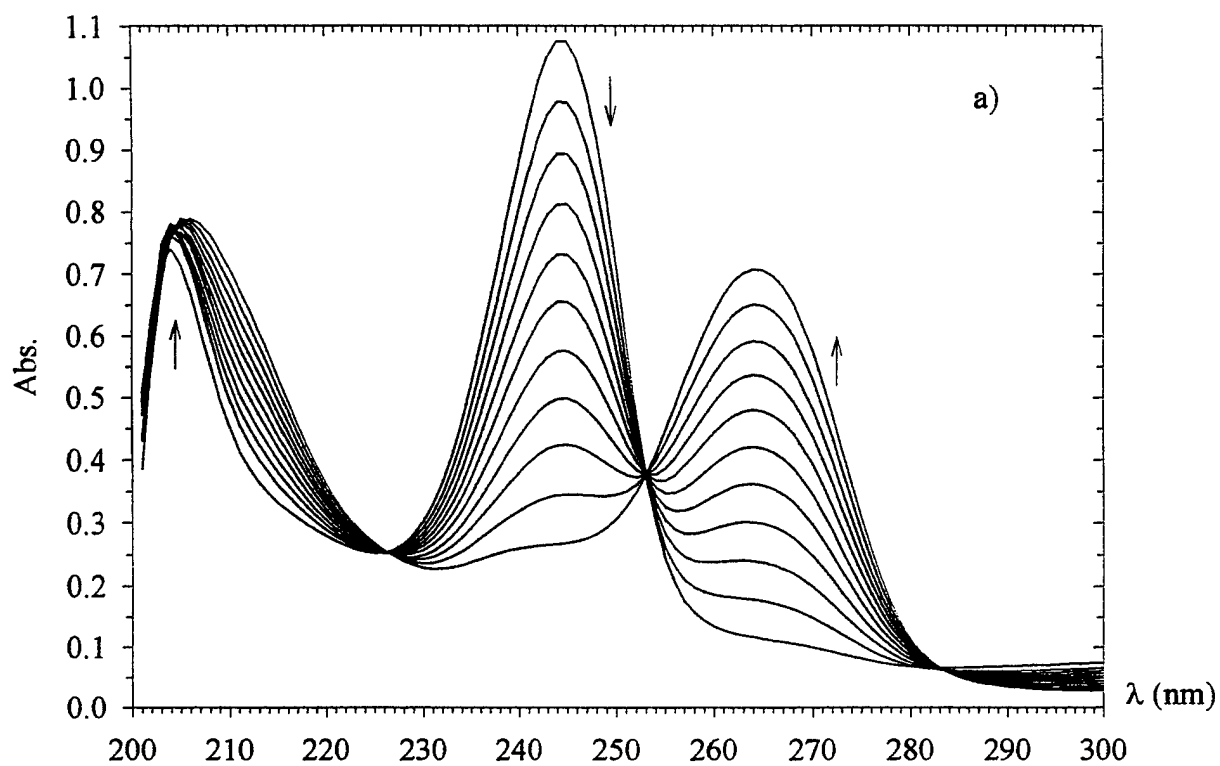


Figure 2. Spectral changes in the UV-Vis absorption of **19** ( $C_L = 1 \times 10^{-5}$  M) upon addition of  $\text{Zn}(\text{NO}_3)_2$  in MeOH: a)  $0 < C_M / C_L < 1$  b)  $1.2 < C_M / C_L < 10.1$ .

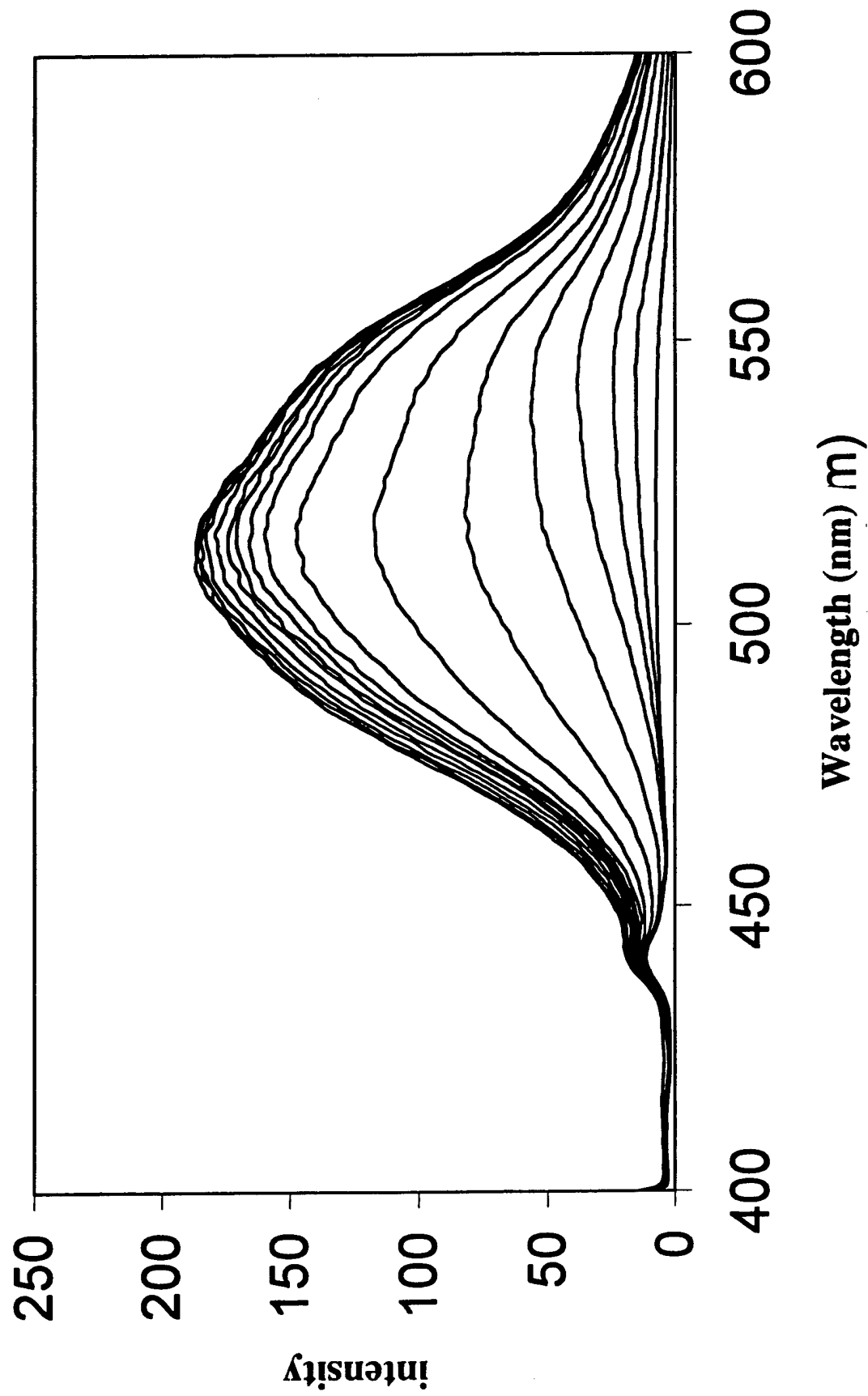


Figure 3. Fluorescence spectra of the 16-Zn<sup>2+</sup> complex; [16] = 10  $\mu$ M, Zn<sup>2+</sup> = 0.25-5 eq.

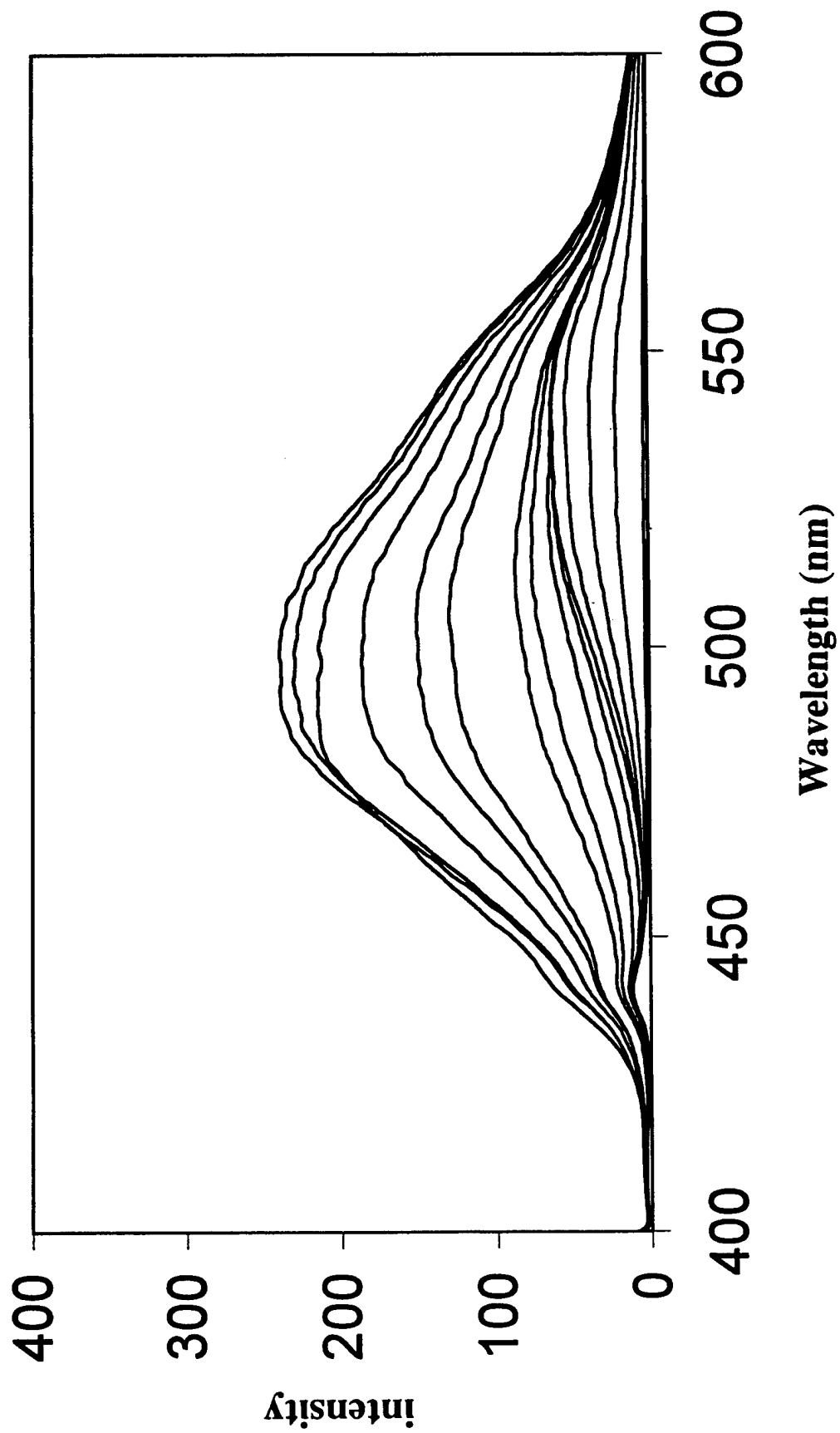
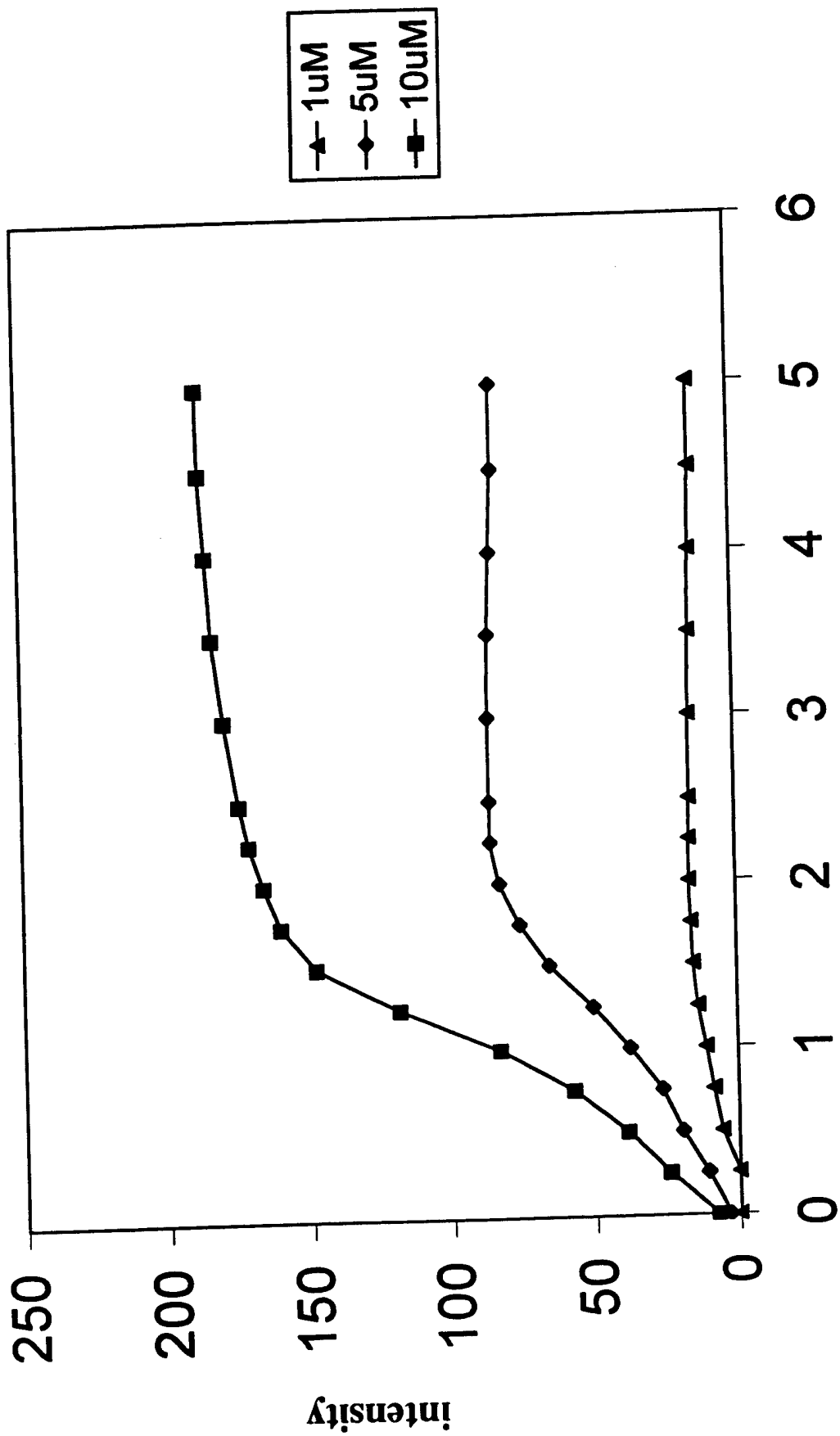
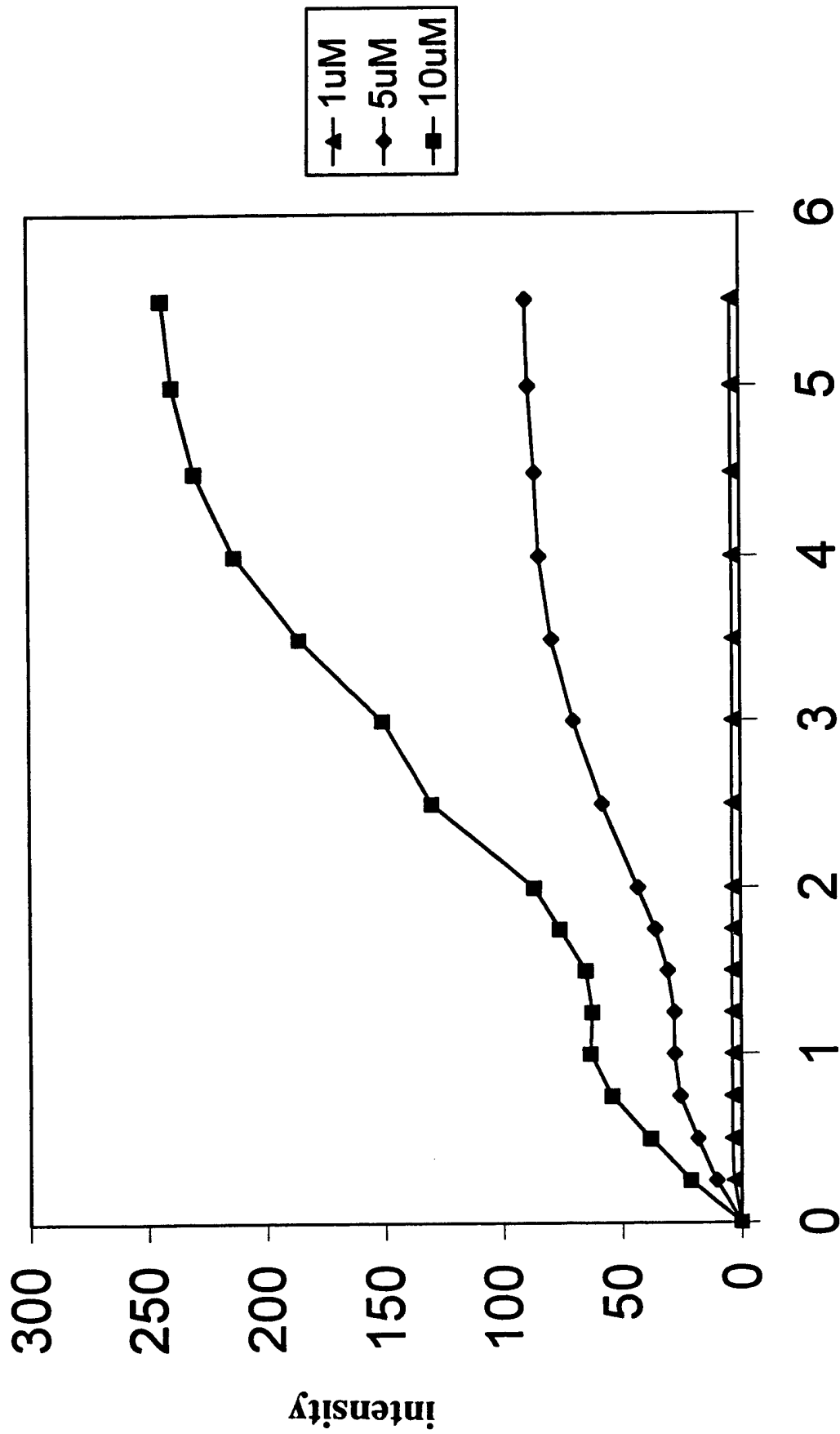


Figure 4. Fluorescence spectra of the 19-Zn<sup>2+</sup> complex; [19] = 10  $\mu$ M, Zn<sup>2+</sup> = 0.25-5 eq.



ratio (Zn<sup>2+</sup>/ligand)

Figure 5. Fluorescence intensity (550 nm) of **16** (1-10 μM) titrated with Zn<sup>2+</sup> (10-100 μM) in MeOH containing 0.01 M NaOAc.



ratio (Zn<sup>2+</sup>/ligand)

Figure 6. Fluorescence intensity (550 nm) of **19** (1-10 μM) titrated with Zn<sup>2+</sup> (10-100 μM) in MeOH containing 0.01 M NaOAc.