

Poly(amide amine) Dendrimer with Naphthyl Units as a Fluorescent Chemosensor for Metal Ions

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Poly(amide amine) dendrimer with naphthyl units (**N8**) as a fluorescent chemosensor for metal ions was synthesized. We investigated the metal ion recognition of **N8**. Large changes in the fluorescence spectra of **N8** were observed upon the addition of cadmium and zinc ions.

Dendrimer chemistry is a rapidly expanding field for both basic and applicative reasons.^{1,2} An important property of dendrimers is the presence of dynamic cavities.³ This feature, coupled with the presence of coordinating moieties, has been exploited to host metal ions in the interior of dendrimers.⁴ Research on such host-guest systems has been performed for a variety of purposes, which include investigations of the dendrimer structure,⁵ preparation of encapsulated metal nanoparticles,⁶ ion transportation,⁷ ion sensing,⁸ light harvesting,⁹ and reversible metal complex assembly.¹⁰ Our interest is to design fluorescent sensors that undergo photophysical changes as marked as possible upon cation binding. Recently, we synthesized a poly(amide amine) dendrimer with naphthyl units (**N8**) as a fluorescent chemosensor for metal ions. We now wish to report on the preliminary results of our study on metal ion recognition by **N8**. Structural formulas of **N8** and its reference compounds (**N1** and **N4**) are shown in Fig. 1.

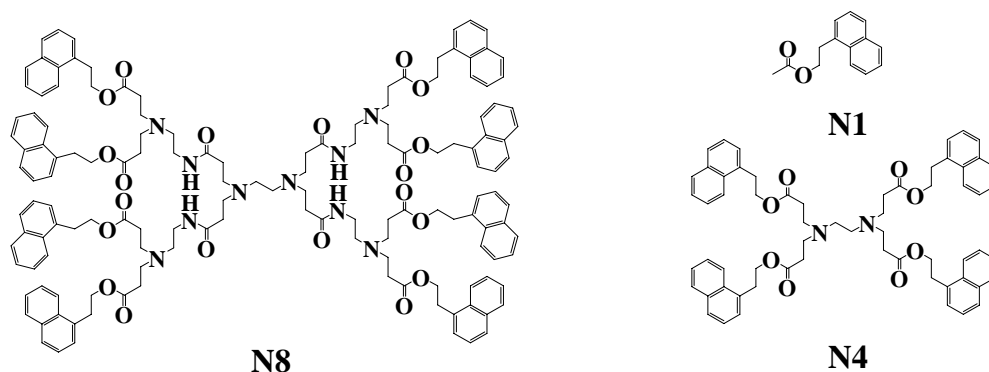


Fig. 1 Structural formulas of **N8**, **N4**, and **N1**.

N8 was obtained by the Michael reaction of 2-(1-naphthyl)ethyl acrylate and poly(amide amine) dendrimer (Generation 0), and **N4** was prepared from 2-(1-naphthyl)ethyl acrylate and ethylenediamine. **N1** was obtained by the esterification of acetyl chloride and 2-(1-naphthyl)ethyl alcohol. The MS spectra of **Nn** ($n = 1, 4, 8$) showed corresponding molecular ion peaks, and the NMR spectra were suitable.¹¹ The **Nn**'s stock solutions were prepared by the dissolution of a weighed amount of the **Nn** in acetonitrile. Titrations of the **Nn** ($[\text{Nn}] = 5\mu\text{M}$, $M = \text{mol dm}^{-3}$) by metal ion solutions were performed in a spectrophotometric cell of 1cm path length. The resulting spectra were recorded from 200 nm to 600 nm at room temperature with a Hitachi U-2001 spectrophotometer after each addition of the metal salts ($\text{Zn}(\text{ClO}_4)_2$, $\text{Cd}(\text{ClO}_4)_2$, $\text{Co}(\text{ClO}_4)_2$ and $\text{Mg}(\text{ClO}_4)_2$). Fluorescence spectra were measured using $\lambda_{\text{ex}} = 280$ nm at a wavelength of between 300 and 600 nm with a Hitachi F-4500 fluorometer. The fluorescence intensities were measured in acetonitrile. The titrations were performed with a titrant (metal ions, 1-10000 μM) and titrate (**Nn**, 5 μM). The metal-ion sources were identical to those used to perform the UV-vis studies. The UV-vis absorption spectra of **N8** or **N4** are essentially identical with **N1**. The ground-state intramolecular interactions, such as charge transfer (CT), were excluded by the absence of a new band at longer wavelength **N8** and **N4**. In contrast, the fluorescence spectra of **N8** and **N4** showed a difference from that of **N1**. Although **N1** showed only emission from the naphthalene chromophore in acetonitrile, structureless broad emissions were observed in the longer wavelength region for **N8** and **N4**. The observed excitation spectra of **N8** and **N4** are identical of the absorption spectra, indicating that these new longer wavelength emissions are due to excited-state intramolecular interactions: naphthyl-amine interactions (exciplex) and/or interactions between naphthyl units (excimer). We examined the change in the absorption and fluorescence spectra after adding some metal ions to a solution of **N8** and **N4**. When Zn^{2+} , Cd^{2+} , Co^{2+} , or Mg^{2+} were added to an acetonitrile solution of **N8** and **N4**, the shape and absorbance of the absorption spectra were not changed. However, the shape and intensity of the fluorescence spectra of **N8** and **N4** changed with the addition of metal ions. The fluorescence spectra of **N8** in the presence of several concentrations of $\text{Zn}(\text{ClO}_4)_2$ are shown in Fig. 2 as a typical example. The intensity of the naphthyl emission (340 nm) increases and reaches a plateau at $[\text{Zn}^{2+}]/[\text{N8}] = 2$, as shown in inset of Fig. 2a; after that, it keeps increasing gently, as shown in inset of Fig. 2b. This result shows that **N8** forms a 2:1 complex (M_2L) with Zn^{2+} first. The association constants (K) were determined from the fluorescence intensity changes at 340nm by using the program NMRTIT.¹²

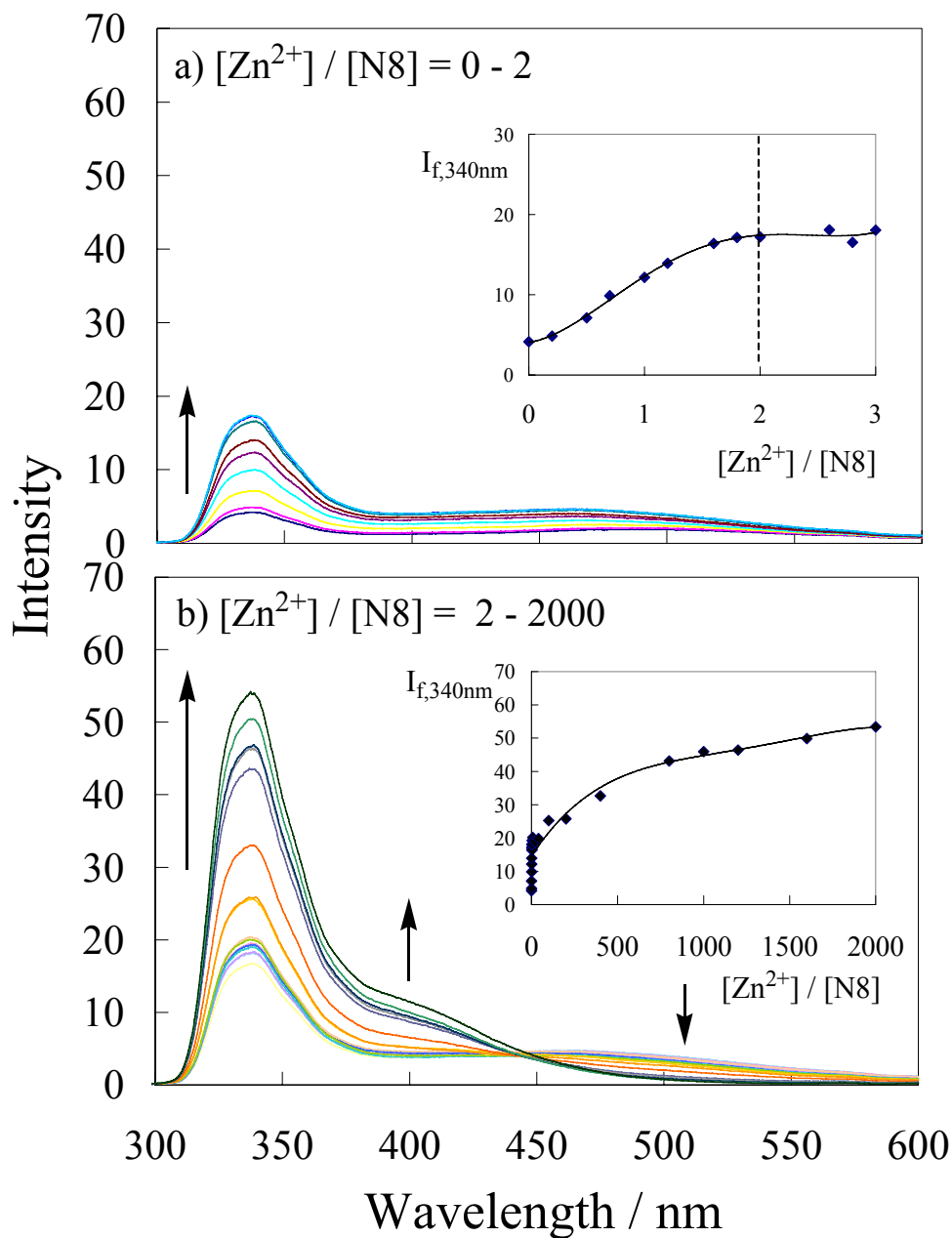


Fig. 2 Fluorescence spectra of a titration of **N8** with Zn²⁺ when excited at 280 nm: [N8] = 5 μ M, a) [Zn²⁺]/[N8] = 0, 0.2, 0.5, 0.7, 1, 1.0, 1.6, 1.8, 2; b) [Zn²⁺]/[N8] = 2, 2.6, 2.8, 3, 4, 5, 7, 10, 20, 40, 100, 200, 400, 800, 1000, 1200, 1600, 2000. The inset is the fluorescence intensity at 340nm ($I_{f,340nm}$) vs [Zn²⁺]/[N8].

The values of $\log K_1$ and $\log K_2$ of **N8** with Zn²⁺ are 8.2 and 5.6, respectively. While the exciplex contribution to the emission intensity at 490 nm decreased and finally disappeared upon the addition of Zn²⁺, and the excimer contribution to the emission

intensity at 390 nm increased. A similar behavior was observed for **N8** with Cd^{2+} . However, the behaviors of **N8** with Co^{2+} or Mg^{2+} and **N4** with Zn^{2+} , Cd^{2+} , Co^{2+} , or Mg^{2+} were different. Titration curves of the fluorescence intensity at 340 nm indicate a sharp endpoint at $[\text{M}^{2+}]/[\text{Nn}(\text{n} = 8, 4)] = 2$ for **N8** with Co^{2+} or Mg^{2+} and **N4** with Zn^{2+} , Cd^{2+} , Co^{2+} , or Mg^{2+} . The maximum values of the fluorescence intensity ($I_{\text{f,max}}$) of **N8** and **N4** at 340 nm are shown in Fig. 3.

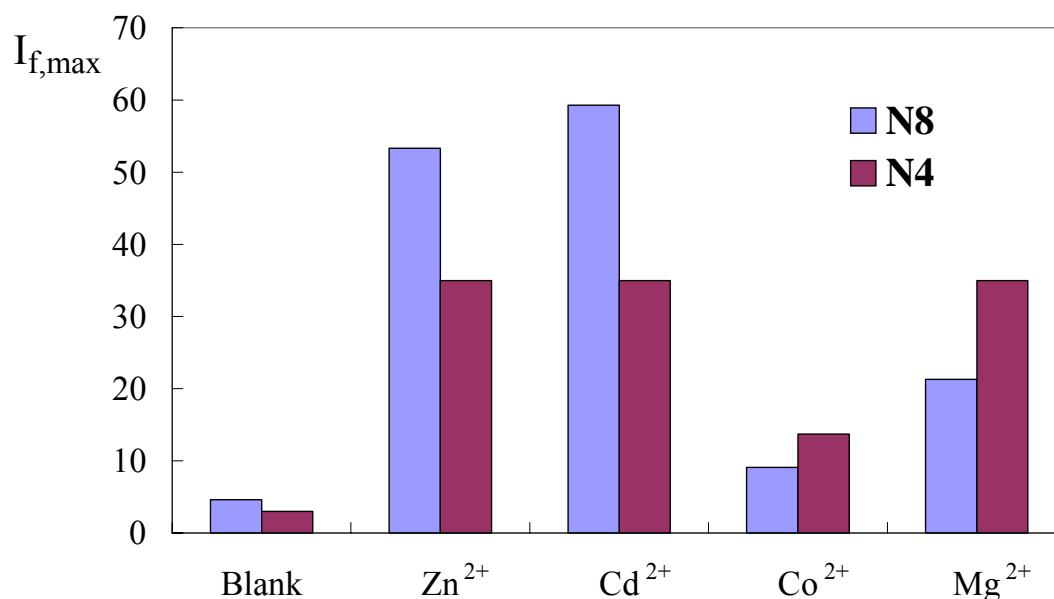


Fig. 3 Maximum values of the fluorescence intensity ($I_{\text{f,max}}$) of **N8** and **N4** at 340nm.

The saturation points of fluorescence intensity are $[\text{M}^{2+}]/[\text{N8}] = 2000$ for Zn^{2+} , Cd^{2+} , $[\text{M}^{2+}]/[\text{N8}] = 2$ for Co^{2+} , Mg^{2+} and $[\text{M}^{2+}]/[\text{N4}] = 2$ for Zn^{2+} , Cd^{2+} , Co^{2+} , Mg^{2+} .

The order of the $I_{\text{f,max}}$ for **N4** is $\text{Zn}^{2+} = \text{Cd}^{2+} = \text{Mg}^{2+} > \text{Co}^{2+}$, but that for **N8** is $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Mg}^{2+} > \text{Co}^{2+}$. This result shows that there is selectivity for metal ions on **N8**. **N8** will become good fluorescent chemosensors for metal ions.

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References

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11. **N8**: ¹H NMR (270MHz, CDCl₃) δ 2.25-2.39(36H, m), 2.66(24H, t), 3.20(8H, m), 3.35(16H, t), 4.36(16H, t), 7.28-7.50(32H, m), 7.69(8H, d), 7.81(8H, d), 8.04(8H, dd); ¹³C NMR (70MHz, CDCl₃) δ 32.1, 32.7, 33.8, 37.3, 49.2, 50.1, 52.9, 64.5, 123.5, 125.5, 125.6, 126.1, 126.9, 127.4, 128.8, 132.1, 133.6, 133.9, 172.3, 172.5; ESI-MS m/z 2325 ([M]⁺).
N4: ¹H NMR (270MHz, CDCl₃) δ 2.39(8H, t, *J*=7.0Hz), 2.45(8H, s), 2.71(8H, t, *J*=7.0Hz), 3.37(8H, t, *J*=7.6Hz), 4.39(8H, t, *J*=7.6Hz), 7.30-7.52 (16H, m), 7.71(4H, dd), 7.82(4H, dd), 8.05(4H, dd); ¹³C NMR (70MHz, CDCl₃) δ 32.2, 32.9, 49.8, 52.3, 64.4, 123.6, 125.5, 125.7, 126.2, 126.9, 127.4, 128.8, 132.1, 133.7, 133.9, 172.5; ESI-MS m/z 964 ([M]⁺).
N1: ¹H NMR (270MHz, CDCl₃) δ 2.05(3H, s), 3.41(2H, t), 4.41(2H, t), 7.35-7.43(2H, m), 7.46-7.55(2H, m), 7.76(1H, d), 7.86(1H, d), 8.09(1H, dd); ¹³C NMR(70MHz, CDCl₃) δ 20.9, 32.2, 64.4, 123.6, 125.5, 125.6, 126.1, 126.9, 127.4, 128.8, 132.1, 133.7, 133.9, 170.0.
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