

A study of 4-(alkylamino)amino substituted 1,8-naphthalimide fluoroionophores

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Abstract

The fluorescence enhancement (FE) of five 4-(alkylamino)amino-1,8-naphthalimide fluoroionophores upon addition of sub-ppm concentrations of transition, post-transition, and lanthanide metal ions is investigated and the results are reported. Changes in (alkylamino)amine ligand chain length result in significantly different fluorescence enhancement behavior. 4-Diamino substituted 1,8-naphthalimides with two, three, and four carbons between amines exhibit fluorescence enhancement, while substituents of five- and six-carbon spacing between amines exhibit no fluorescence enhancement. Metal ion selectivity as measured by complexation coefficients ($\log \beta$) is observed with the ethylenediamine and propylenediamine substituted compounds for Cu^{2+} , and metal ion selectivity for Pb^{2+} is observed for the butanediamine derivative. Inhibition of photoinduced electron transfer (PET) between the distal nitrogen and the aromatic system by metal ion coordination to the distal amine is the mechanism of fluorescence enhancement for the ethylenediamine, propylenediamine, and butanediamine derivatives. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

There is considerable interest in developing high-sensitivity, high-selectivity fluorescence-based sensors for transition metal ions [1–13]. Fluorescence enhancement (FE) has been identified as a key component for a successful transition metal ion sensor as it allows enhanced sensitivity and reduced interference over quenching methods [1–13]. A major impediment to FE detection of transition metal ions is their inherent quenching of fluorescence [3–5]. Substituted 1,8-naphthalimides have received considerable study as fluorescence sensors for transition metal ions due to FE upon metal ion coordination [1–13]. Enhancement factors of 1.1–1.2 have been reported for alkyl amino derivatives of amino-1,8-naphthalimides [3] as compared to FE factors of up to 55 for phthalimide derivatives [3], hundred's for benzoxadiazole derivatives [4], and up to several thousand for polyamine derivatives of the imide moiety of 1,8-naphthalimide [7]. Photoinduced electron transfer (PET) is proposed as a significant pathway for fluorescence quenching, which is disrupted by coordination to

metal ions, resulting in the observed fluorescence enhancement [1–7]. The largest enhancements are observed for ethylamino substituents of the imide moiety, with significant decreases observed for longer carbon chains, consistent with a conformational component to the amine quenching mechanisms [7]. Kidder has investigated ED4 with a variety of metal ions and measured the wavelength-dependent fluorescence enhancement or quenching [1]. Emission measured at <500 nm is enhanced by a factor of ~1.4, while emission of >500 nm decreases by a similar factor due to the emission hypsochromic wavelength shift [1]. Complexation coefficients were calculated from the emission data and the trend in coordination strength reported as $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Fe}^{2+} > \text{Mn}^{2+}$ [1]. Lifetime data for several naphthalimide derivatives have been reported and clearly show two or more contributing transitions to radiative deactivation [2,7]. Metal ion interaction identified the shorter (3 ns) lived transition as quenched by PET, which when inhibited, allows the longer lived (10 ns), normal or planar, transition to predominate [2,7]. It is generally concluded that FE-based detection can be maximized by designing a fluorophore-spacer-receptor system with maximum PET between the fluorophore and receptor [5]. Kidder reports deconvolutions of emission spectra for 4-ethylenediamine

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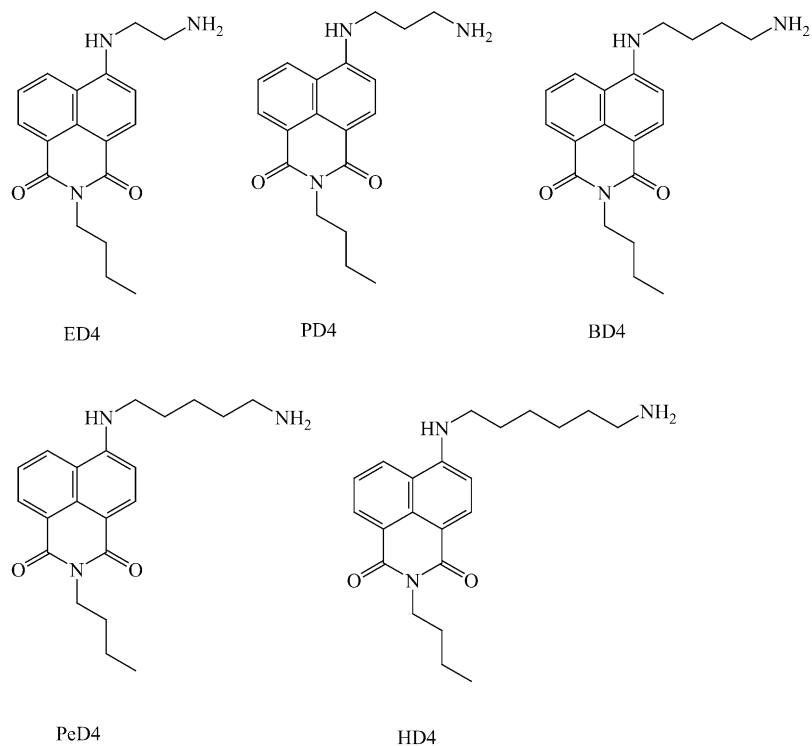


Fig. 1. Naphthalimide derivatives synthesized and studied in this project.

substituted butyl-1,8-naphthalimide that clearly show three significant contributors to the observed band, identified as ICT, TICT, and an aromatic system centered mode emissions [1]. We report here the results of our expanded investigation of the 4-aminoalkyl amine substituted 1,8-naphthalimides (Fig. 1). The series of compounds synthesized probe the aminoalkyl amine chain length effect on the emission properties and coordination strengths of the fluoroionophores as well as the resulting FE. Through these studies we draw conclusions of the relative contributions and competitions of PET and TICT interactions to FE.

2. Experimental

2.1. General methods

4-Bromo-naphthalic anhydride was purchased from Aldrich Chemical Co. and used as received. *N*-butylamine, ethylenediamine, and 1,3-propylenediamine were purchased from Fisher Chemical Co. and used as received. 1,4-Butanediamine, 1,5-pentanediamine, and 1,6-hexanediamine were purchased from Aldrich Chemical Co. and used as received. Solvents were spectrograde, stored over 4 Å molecular sieves, and distilled prior to use.

UV-vis and fluorescence solutions were prepared by dissolving each substituted naphthalimide in isopropanol (iPrOH) or acetonitrile/water (4:1) to a concentration of 1

$\times 10^{-5}$. Solutions for solvent effect studies were prepared as described, but with the solvents listed. Metal ion solutions were prepared at concentrations of 0.1, 1, 10, 50, 100, and 500 ppm in iPrOH and acetonitrile/water (4:1), unless insoluble then isopropanol/water (4:1) was used. HCl (concentrated) was diluted in water to make 0.05 M stock solutions. Solutions of 0.005 and 0.0005 M were prepared by dilution of the stock. NaOH was dissolved in water to make stock solutions of 0.05 M. Solutions of 0.005 and 0.005 M were prepared by dilution of the stock. The effect of acid, base, and metal ion concentration on the absorbance and emission spectra were measured by adding 10, 20, or 50 ml aliquots of the appropriate solutions to a maximum of 100 ml total added. Limiting the volume added decreased the effect of dilution on the measurements to a negligible level. Concentration ranges of the metal ions in the various solutions used for absorbance and emission experiments overlapped to insure consistency when data were merged for chart output. Solutions were freshly prepared prior to measurement and absorption spectra were recorded prior to each fluorescence measurement to monitor for photostability. All samples, solution and solid, were stored in the dark.

Metal salts (chloride or nitrate) were purchased from Baker Chemical Co. or Fisher Chemical Co. as their typical hydrate and used as received.

Absorption spectra were recorded on a Shimadzu UV-vis spectrophotometer. Emission spectra were recorded on a PTI

QuantaMaster Spectrometer and are uncorrected. Quantum yields were calculated using Fluoresceine dianion as an actinometer.

^1H and ^{13}C -NMR were recorded on a GE QE 300 NMR with tecmag AQUERIUS upgrade.

2.2. Synthesis

N-butyl-4-bromo-1,8-naphthalimide was prepared from 4-bromo-1,8-naphthalic anhydride and *N*-butylamine in dry ethanol at 85 °C for 4 h. Cooling the solution resulted in the crystallization of the product, which was isolated by vacuum filtration with a 70% yield and used without further purification. Compounds *N*-butyl-4[(2'-aminoethyl)amino]-1,8-naphthalimide (ED4), *N*-butyl-4[(3'-aminopropyl)amino]-1,8-naphthalimide (PD4), *N*-butyl-4[(4'-aminobutyl)amino]-1,8-naphthalimide (BD4), *N*-butyl-4[(5'-aminopentyl)amino]-1,8-naphthalimide (PeD4), and *N*-butyl-4[(6'-aminohexyl)amino]-1,8-naphthalimide (HD4) (Fig. 1) were synthesized by nucleophilic substitution of *N*-butyl-4-bromo-1,8-naphthalimide by the appropriate diamine, which also served as solvent, heated at 100 °C for 4 days. Each reaction mixture was poured into water and the product isolated by vacuum filtration as a yellow/orange solid. The products were triturated with water and recrystallized from acetic acid for a 75% isolated yield (typical). An overall yield of 53% was typical. Compounds were oven dried to constant weight and stored in a dessicator (Drierite).

N-butyl-4[(2'-aminoethyl)amino]-1,8-naphthalimide (ED4). M.P. 133–135 °C. Elemental analysis calculated for $\text{C}_{18}\text{H}_{21}\text{N}_3\text{O}_2$: C, 69.43; H, 6.80; N, 13.49%. Found: C, 69.29; H, 6.94; N, 13.62%. ^1H -NMR (DMSO- d_6 , TMS ref.) δ 8.72–8.70 (d, 1H, 7 position of aromatic ring), 8.52–8.50 (d, 1H, 5 position of aromatic ring), 8.38–8.35 (d, 1H, 2 position of aromatic ring), 7.64–7.59 (t, 1H, 6 position of aromatic ring), 6.73–6.70 (d, 1H, 3 position of aromatic ring), 4.13–4.08 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.62–3.57 (t, 2H, $\text{NCH}_2\text{CH}_2\text{NH}_2$), 3.22–3.18 (t, 2H, $\text{NCH}_2\text{CH}_2\text{NH}_2$), 3.1 (br-s, 3H, N-H), 1.70–1.62 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.47–1.36 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.99–0.94 (t, 3H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C -NMR δ 163.71, 162.87, 150.64, 134.20, 130.56, 130.01, 129.00, 124.14, 122.03, 120.10, 107.70, 103.60, 41.14, 40.30, 29.78, 23.89, 19.77, 13.68.

N-butyl-4[(3'-aminopropyl)amino]-1,8-naphthalimide (PD4). M.P. 98–100 °C. Elemental analysis calculated for $\text{C}_{19}\text{H}_{23}\text{N}_3\text{O}_2$: C, 70.13; H, 7.12; N, 12.91%. Found: C, 70.00; H, 7.24; N, 13.04%. ^1H -NMR (DMSO- d_6 , TMS ref.) δ 8.67–8.64 (d, 1H, 7 position of aromatic ring), 8.42–8.39 (d, 1H, 5 position of aromatic ring), 8.25–8.22 (d, 1H, 2 position of aromatic ring), 7.68–7.63 (t, 1H, 6 position of aromatic ring), 6.77–6.74 (d, 1H, 3 position of aromatic ring), 4.03–3.98 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.47–3.42 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 3.1 (br-s, 3H, N-H), 2.79–2.74 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.84–1.80 (m, 2H,

$\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.61–1.53 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.37–1.30 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.99–0.94 (t, 3H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C -NMR δ 163.66, 162.80, 150.60, 134.16, 130.51, 129.32, 128.40, 124.10, 121.79, 120.06, 107.35, 103.65, 41.01, 40.32, 30.60, 29.77, 25.32, 19.77, 13.68.

N-butyl-4[(4'-aminobutyl)amino]-1,8-naphthalimide (BD4) M.P. 90–93 °C. Elemental analysis calculated for $\text{C}_{20}\text{H}_{25}\text{N}_3\text{O}_2$: C, 70.77; H, 7.42; N, 12.38%. Found: C, 70.56; H, 7.55; N, 12.50%. ^1H -NMR (DMSO- d_6 , TMS ref.) δ 8.71–8.68 (d, 1H, 7 position of aromatic ring), 8.42–8.40 (d, 1H, 5 position of aromatic ring), 8.25–8.23 (d, 1H, 2 position of aromatic ring), 7.68–7.63 (t, 1H, 6 position of aromatic ring), 6.77–6.74 (d, 1H, 3 position of aromatic ring), 4.03–3.98 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.39–3.34 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 3.1 (br-s, 3H, N-H), 2.64–2.59 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.76–1.30 (m, 6H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.37–1.30 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 0.94–0.90 (t, 3H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C -NMR δ 163.71, 162.87, 150.64, 134.21, 130.55, 129.39, 128.55, 124.12, 121.80, 120.07, 107.40, 103.69, 42.81, 41.26, 30.62, 29.79, 25.38, 19.80, 13.70.

N-butyl-4[(5'-aminopentyl)amino]-1,8-naphthalimide (PeD4) M.P. 77–79 °C. Elemental analysis calculated for $\text{C}_{21}\text{H}_{27}\text{N}_3\text{O}_2$: C, 71.36; H, 7.70; N, 11.89%. Found: C, 71.23; H, 7.85; N, 12.01%. ^1H -NMR (DMSO- d_6 , TMS ref.) δ 8.55–8.52 (d, 1H, 7 position of aromatic ring), 8.41–8.38 (d, 1H, 5 position of aromatic ring), 8.28–8.25 (d, 1H, 2 position of aromatic ring), 7.58–7.56 (t, 1H, 6 position of aromatic ring), 6.77–6.74 (d, 1H, 3 position of aromatic ring), 4.03–3.99 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.43–3.39 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 3.1 (br-s, 3H, N-H), 2.64–2.59 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.76–1.30 (m, 10H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 0.89–0.87 (t, 3H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C -NMR δ 163.70, 162.86, 150.62, 134.21, 130.55, 129.37, 128.53, 124.11, 121.80, 120.08, 107.41, 103.69, 42.80, 41.30, 32.62, 29.79, 27.84, 26.55, 26.00, 19.79, 13.71.

N-butyl-4[(6'-aminohexyl)amino]-1,8-naphthalimide (HD4) M.P. 60–62 °C. Elemental analysis calculated for $\text{C}_{22}\text{H}_{29}\text{N}_3\text{O}_2$: C, 71.90; H, 7.95; N, 11.43%. Found: C, 71.80; H, 8.11; N, 11.54%. ^1H -NMR (DMSO- d_6 , TMS ref.) δ 8.72–8.69 (d, 1H, 7 position of aromatic ring), 8.43–8.41 (d, 1H, 5 position of aromatic ring), 8.26–8.24 (d, 1H, 2 position of aromatic ring), 7.69–7.64 (t, 1H, 6 position of aromatic ring), 6.77–6.74 (d, 1H, 3 position of aromatic ring), 4.03–3.98 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 3.40–3.34 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 3.1 (br-s, 3H, N-H), 2.98–2.95 (t, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 1.79–1.32 (m, 12H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ and $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$), 0.94–0.92 (t, 3H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ^{13}C -NMR δ 163.69, 162.85, 150.61, 134.21, 130.55, 129.40, 128.51, 124.14, 121.83, 120.06, 107.43, 103.69, 42.79, 41.53, 33.24, 29.74, 27.85, 26.55, 26.19, 19.79, 13.69.

3. Results and discussion

3.1. Absorption studies

The absorption spectra of compounds ED4, PD4, BD4, PeD4, and HD4 consist of a structured naphthalimide band with two peaks at 260 and 281 nm and a broad, featureless band centered at 420–440 nm. The long-wavelength bands for ED4–HD4 have extinction coefficients of 16000, 13000, 12000, 11000, and 14000, respectively. The absorption spectra for all compounds studied (ED4, PD4, BD4, PeD4, HD4) behave similarly with the absorbance wavelength maxima shifting to the red 15–20 nm with increasing solvent polarity, as shown in the representative spectra in Figs. 2 and 4 and summarized in Table 1. The large bathochromic shift observed with increasing solvent polarity is characteristic of

an intramolecular charge transfer (ICT) band [6]. A small structured band from 320–340 nm grows in upon storage of isopropanol solutions under room light with an approximate rate of 0.05 mmol per week. This band corresponds to the long-wavelength absorption band of the starting material and indicates photoinstability of the compounds resulting in loss of the 4-diamino group. No photoinstability was observed upon storage of solid samples. UV absorption measurements taken prior to each fluorescence measurement showed no photodecomposition product formed during the measurements. The long-wavelength band of ED4–HD4 occurs with the same wavelength maximum and extinction coefficient as the 4-butylamine derivative (*N*-butyl-4-butylamino-1,8-naphthalimide, acronym 44) [1]. Comparison of the λ_{max} of ED4–HD4 with the λ_{max} of 44 allows the further characterization of the long-wavelength band of ED4–HD4 as an ICT

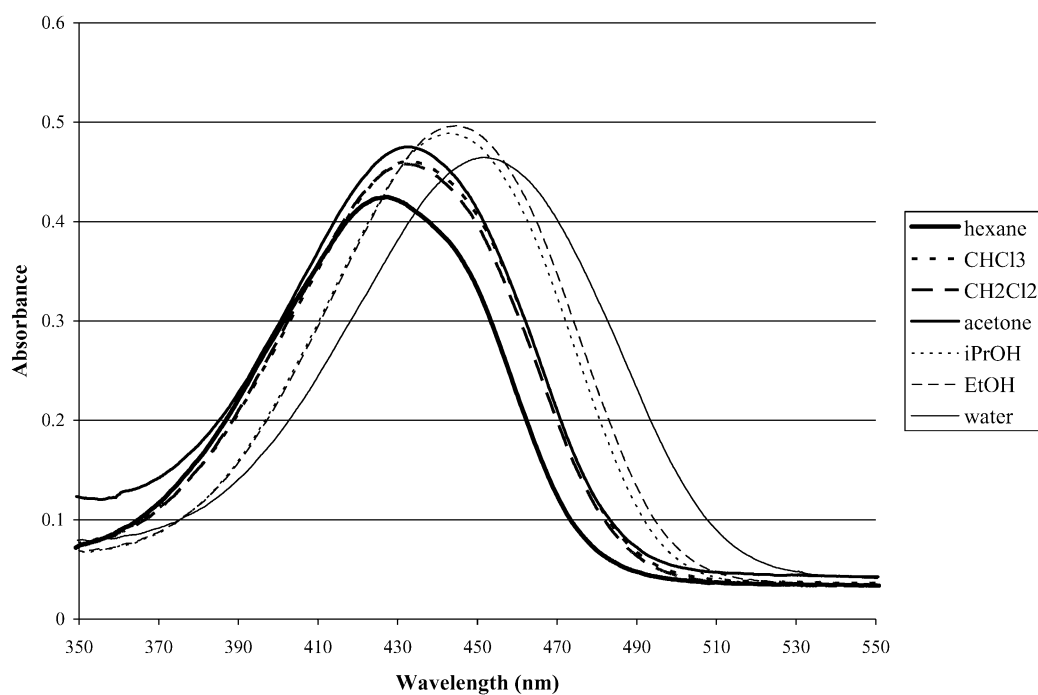


Fig. 2. Solvent effects on absorption properties of PeD4.

Table 1
Wavelength of maximum absorption and emission (nm)

(λ_{max} abs)	Hexane	CHCl ₃	CH ₂ Cl ₂	Acetone	iPrOH	EtOH	Water
ED4	410	420	418	418	432	432	431
PD4	417	436	437		439	442	446
BD4	419	433	425	426	444	445	449
PeD4	426	433	433	431	441	443	451
HD4	416	418	423	425	437	439	449
(λ_{max} em)							
ED4	488	495	501	511	515	520	529
PD4	485	503	509	511	519	522	536
BD4	487	507	500	514	517	521	541
PeD4	496	506	509	511	517	523	548
HD4	489	498	508		515	521	545

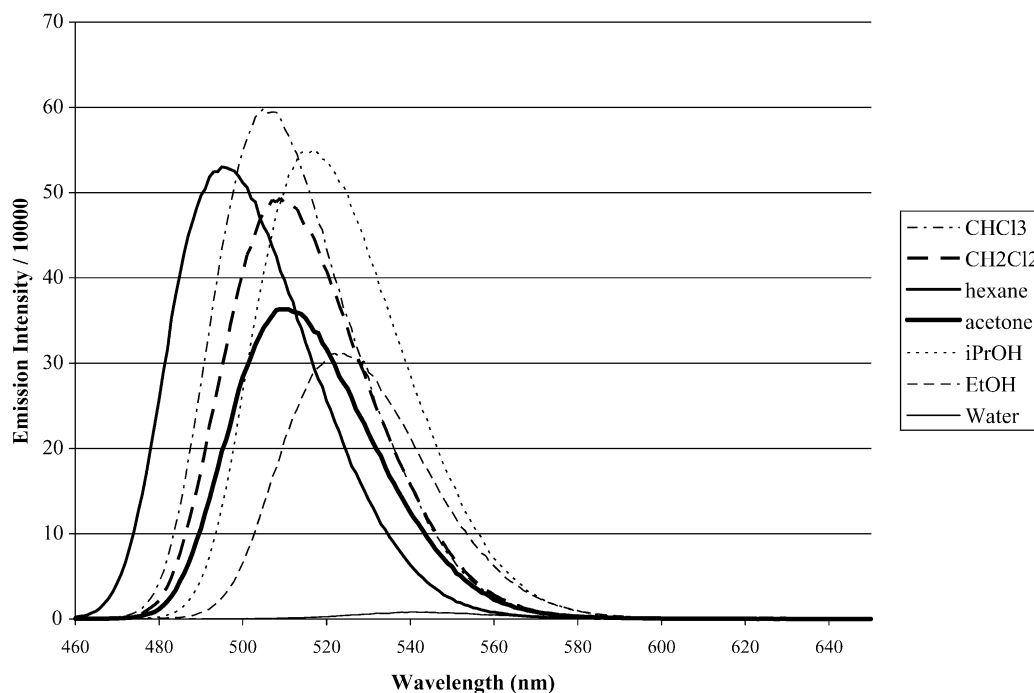


Fig. 3. Solvent effects on emission properties of PeD4.

of the 4-amino-1,8-naphthalimide moiety and not involving electron transfer from the distal amine [1,8]. Out-of-plane twisting of secondary amines of 1,8-naphthalimide systems is typically not observed through the characteristic dual fluorescence of a TICT state [8b]; thus, it is concluded that the normal (planar) ICT mode is responsible for the long-wavelength absorption.

The absorption maxima of ED4, PD4, and BD4 decreased in intensity 10% but did not shift upon complexation with

H^+ . This was also observed and reported by Kidder in her Ph.D. dissertation study of ED4 [1]. Subsequent addition of base (aqueous NaOH) resulted in recovery of the absorbance to the initial levels. The absorption spectra of PeD4 and HD4 show no change when complexed with H^+ . At the concentrations used ($0-10^{-3}$ M), acid will protonate the distal amine preferentially ($pK_a = 9$ versus $pK_a = 3$) [20], having a lesser effect on the absorption spectrum than protonation at the naphthylamine, which is involved with the ICT in-

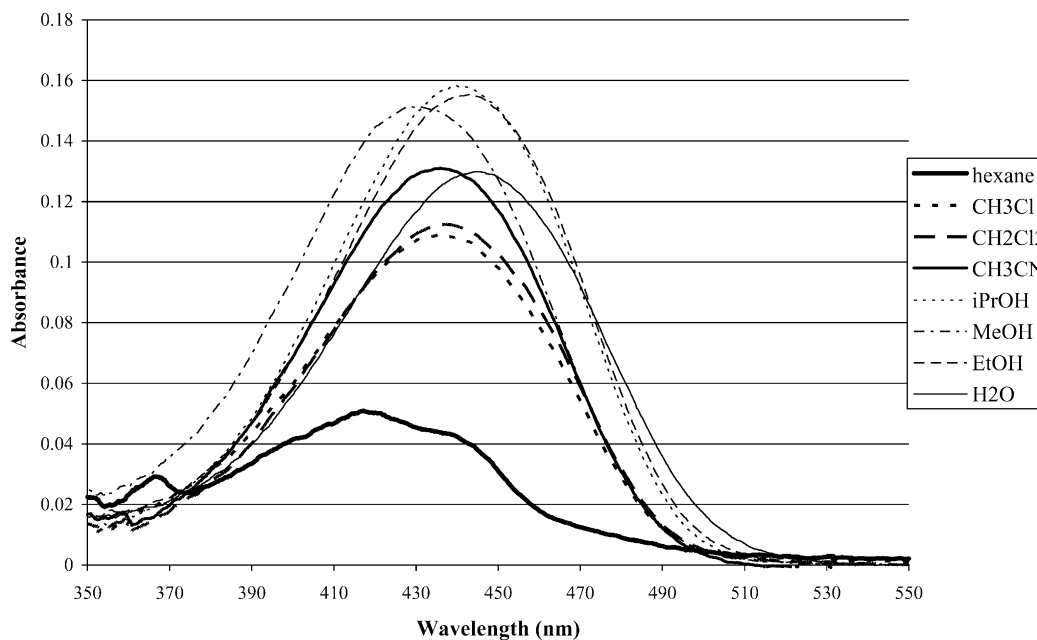


Fig. 4. Solvent effects on absorption properties of PD4.

teraction. Complexation of ED4, PD4, and BD4 with metal ions results in a hypsochromic shift of the absorption λ_{\max} (Table 5). The shift is greatest upon complexation of ED4 with the metal ions studied, is smaller for PD4 complexes, and is smallest for BD4 complexes. This suggests decreasing contribution from bidentate chelation as the metal ion coordination draws electron density away from the naphthylamine nitrogen and aromatic system, lowering the energy of the occupied orbital and increasing the energy of the transition [5,7]. As the chelate ring becomes larger and less stable (ED4 to PD4 to BD4), the shift upon complexation becomes smaller as the metal interacts less with the naphthylamine nitrogen. PeD4 and HD4 exhibit a 1–2 nm shift of the λ_{\max} upon metal ion addition, which is negligible under our experimental conditions. As expected, the eight- and nine-membered rings required for bidentate chelation of PeD4 or HD4 and the metal ions studied appear to be unfavorable. The absorption results support the characterization of the long-wavelength absorption band as an ICT band between the naphthylamine nitrogen and the aromatic system in the planar, or normal, mode. The larger hypsochromic shift observed with those compounds capable of more favorable bidentate chelation (ED4 and PD4), thus bringing the metal ion close to the naphthylamine nitrogen allowing electron withdrawal, supports the characterization of an ICT transition between the naphthylamine nitrogen and the aromatic system as the predominate absorption event represented by the long-wavelength band.

Isopropanol was used as the base solvent in this study due to the best solubility properties of the naphthalimide

and metal ions in isopropanol. Acetonitrile/water (4:1) as well as isopropanol/water mixtures were also used, depending on the solubility of the metal ion in isopropanol with little solvent-induced difference in absorption or emission properties. The only observed difference was the lower quantum yield of emission (ϕ_f) for PeD4 and HD4 (Fig. 3) in water. This is presumably due to greater access of water to the naphthyl amine and the subsequent greater non-radiative decay through vibrational relaxation [19], (Fig. 4).

3.2. Emission studies

The emission spectra recorded for compounds ED4–HD4 upon excitation at 450 nm are structureless bands centered at 500–530 nm, as summarized in Table 1. No significant emission is recorded at wavelengths less than 450 nm regardless of the excitation wavelength. The bands are not symmetrical, but tail to longer wavelength, corroborating the characterization of the bands as combination bands with significant contributions from ICT normal (planar) mode transition as well as other accessible conformers [1–8]. The emission wavelength maxima for all compounds studied shifted to the red ~ 50 nm in solvents of increasing polarity (Table 1). Figs. 3 and 5 show representative spectra of the solvent effect data. Similar to the absorbance results, this is typical of solvent stabilization of more polar excited states and the greater magnitude of the shift compared to the absorption results supports the characterization of the emission as ICT [6].

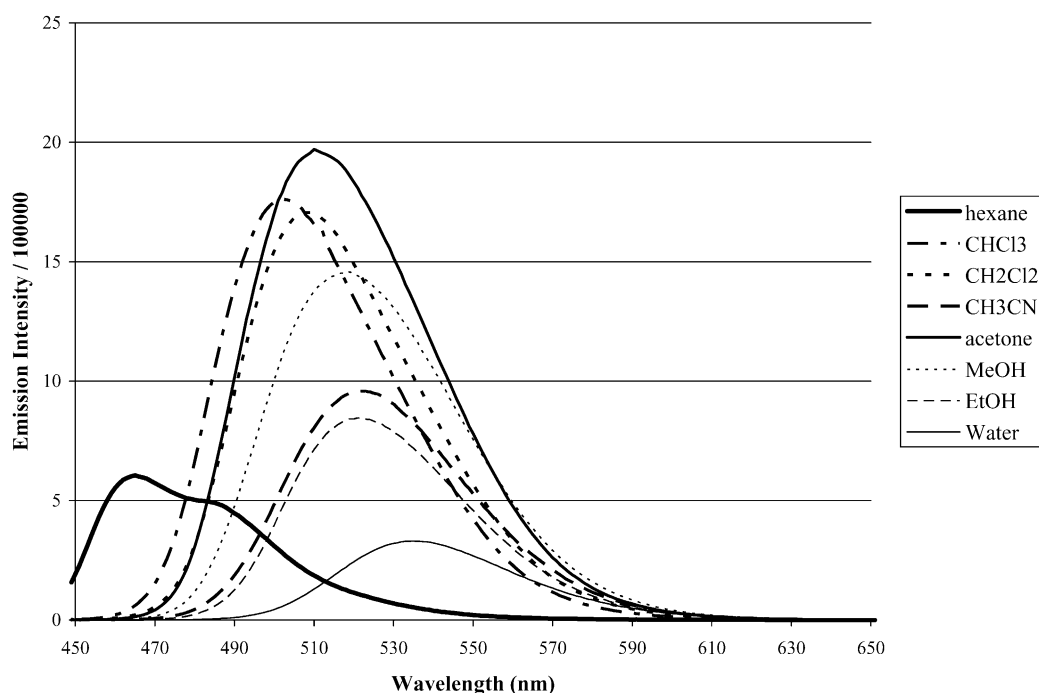


Fig. 5. Solvent effects on emission properties of PD4.

Table 2
Complexation coefficients ($\log \beta$)

	Cu ²⁺	Fe ³⁺	Ni ²⁺	Hg ²⁺	Mn ^{2+(a)}	Pb ²⁺	Zn ^{2+(a)}	Co ²⁺	Cr ^{3+(a)}	Gd ^{3+(a)}	Tb ^{3+(a)}	Tm ^{3+(a)}
ED4	17.2	10.4	7.1	b	b	b	9.4			3.8	4.8	2.8
PD4	17.1	9.4	7.0	b	b	b	c					
BD4	4.3	4.2	4.0	b	b	7.7	3.2	4.8	3.5			

(a) Isopropanol/water (4:1) used instead of 100% isopropanol; (b) $\log \beta$ is not reported for metals that quenched fluorescence as this does not require complexation [ref]; (c) The FE was too small to accurately calculate $\log \beta$

Fluorescence quantum yields for ED4, PD4, BD4, PeD4, and HD4 were calculated from spectra recorded in iPrOH, using fluorescein dianion in 0.1 M NaOH as the actinometer [21]. The absorbances of the solutions were matched at the excitation wavelength (450 nm), and the emission was recorded for samples and actinometer at 515 nm. The ϕ_{fl} for ED4 is 0.15, PD4 is 0.14, and BD4 is 0.13 ± 0.01 . The ϕ_{fl} for PeD4 is 0.23, and the ϕ_{fl} calculated for HD4 is 0.26 ± 0.01 . The difference in quantum yield between ED4, PD4, BD4, which exhibit fluorescence enhancement, and PeD4, HD4, which exhibit no fluorescence enhancement upon complexation with H⁺ or metal ions (see below), provides a measure of the efficiency of quenching by the distal amine of ED4, PD4, and BD4. The lack of interaction between the distal amine and the aromatic system due to conformational constraints in PeD4 and HD4, as observed in the lack of FE, and the resulting quantum yields of 0.23 and 0.26 compared to the quantum yields of ED4, PD4, and BD4 of 0.13–0.15 indicate the quenching interaction is approximately 35–50% effective. We must also conclude from the observed quantum yield of fluorescence of 0.13–0.26 that non-radiative decay is the overall predominate deactivation pathway. This is typical of aromatic systems with conformationally mobile side chains [5,20]. To maximize FE, the fluoroionophore design should include a strongly fluorescent compound that is efficiently quenched. Our low FE numbers (see below), compared to other reports [3–12] are likely due to quenching efficiencies less than 100% (Table 2).

The fluorescence spectra of ED4, PD4, and BD4 were recorded in the presence of metal salts, H⁺, and base. Complexation of ED4 and PD4 by Cu²⁺, Fe³⁺, Ni²⁺, Zn²⁺, Co²⁺, and Cr³⁺ results in quenching of emission at wave-

lengths greater than 500 nm and enhancement of emission at wavelengths less than 500 nm as recorded in Table 3. Fig. 6 shows the plots of emission intensity at 480 and 530 nm of ED4 upon increasing concentration of Fe³⁺. These results are representative of the changes to ED4 emission upon complexation of metal ions causing FE. These results are similar to results reported by Kidder [1]. The other metal ions studied here resulted in emission quenching at all wavelengths. The observed shift in λ_{max} to shorter wavelength upon addition of metal ions is recorded in Table 5 and is larger for ED4 compared to PD4, similar to the absorption measurements. This is consistent with metal ion coordination to the naphthylamine nitrogen, which our observations indicate, is stronger between metals and ED4 compared to PD4. The emission spectra of BD4 complexed with the same metal ions as studied with ED4 and PD4 exhibits a consistent blue shift in λ_{max} of 6 nm, which may indicate the effect of metal ions added to solution in general (an ionic effect) (Table 4).

The magnitude of the FE at 480 nm upon addition of metal ions to ED4 ranged from Ni²⁺ at 1.47 to Fe³⁺ at 4.40 (Table 3). The magnitude of FE of PD4 upon addition of the same metal ions was significantly smaller, ranging from 1.10 (Ni²⁺) to 1.69 (Fe³⁺) (Table 3). The decrease in fluorescence intensity at 530 nm for ED4 and PD4 with the metal ions studied causing FE was approximately 20–30% more than the quenching observed for non-FE ions. The latter is presumably due to paramagnetic effects [2], although Hg²⁺ would be an exception. The greater difference between quenching at 530 nm of those metal ions for which FE is observed and those that quench only, is due to the shifting of emission λ_{max} observed with metal ions causing FE (Table

Table 3
Fluorescence enhancement factors

	H ⁺	Cu ²⁺	Fe ³⁺	Ni ²⁺	Hg ²⁺	Mn ^{2+(a)}	Pb ²⁺	Zn ^{2+(a)}	Co ²⁺	Cr ^{3+(a)}	Gd ^{3+(a)}	Tb ^{3+(a)}	Tm ^{3+(a)}
ED4													
480 nm	0.77	3.30	4.40	1.47	0.83	0.83	0.85	1.70		1.90	1.20	1.20	1.20
530 nm	0.77	0.53	0.59	0.92	0.83	0.83	0.85	1.14		0.77	1.20	1.20	1.20
PD4													
480 nm	0.74	1.49	1.69	1.10	0.84	0.85	0.89	1.10			1.20	1.20	1.20
530 nm	0.74	0.68	0.83	0.91	0.84	0.85	0.89	1.10			1.20	1.20	1.20
BD4													
480 nm	1.52	2.50	2.95	3.00	0.00	0.00	3.10	2.90	3.00	3.00			
530 nm	1.52	1.57	1.50	1.50	0.00	0.00	1.47	1.53	1.47	1.43			

(a) Isopropanol/water (4:1) used instead of 100% isopropanol.

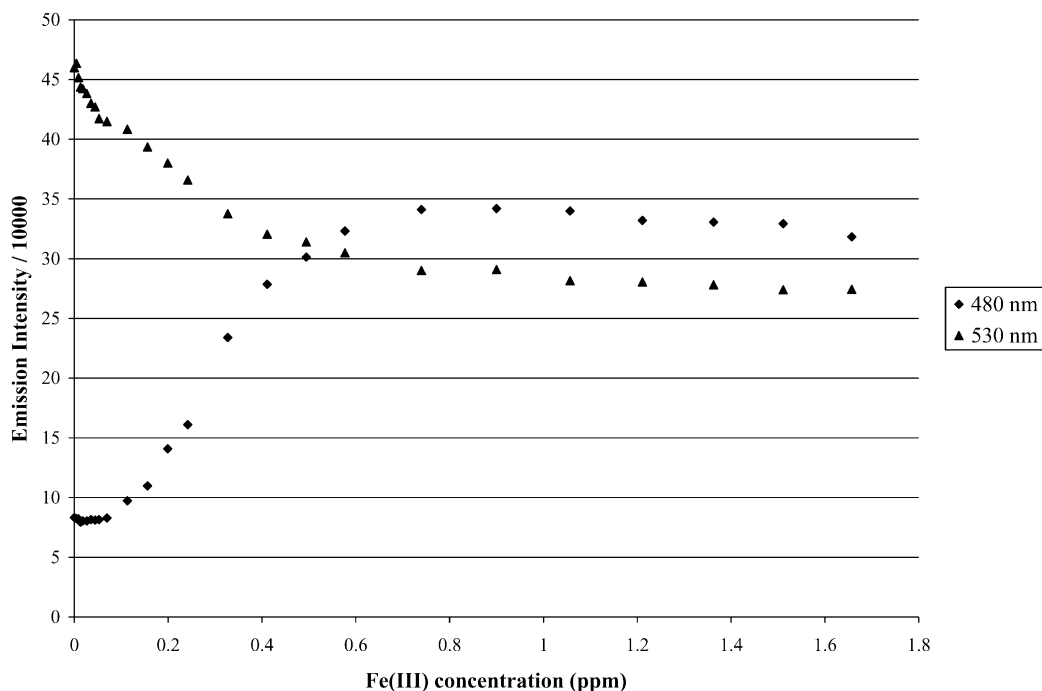


Fig. 6. Plot of change in emission upon metal ion complexation at 480 and 530 nm (ED4 and Fe^{3+}).

Table 4

Concentration in mM of metal ion added (ppm added, equivalents added) for no further emission enhancement

Cu^{2+}	Fe^{3+}	Ni^{2+}	Pb^{2+}	Zn^{2+} (a)	Co^{2+}	Cr^{3+} (a)
ED4						
7.5 (0.5, 0.8)	12 (0.8, 1.4)	7.5 (0.5, 0.9)	b	12 (0.8, 1.2)	6 (0.4, 0.7)	7.5 (0.5, 1)
PD4						
15 (1.0, 1.6)	15 (1, 1.8)	b	b	6 (0.4, 0.6)	15 (1, 1.7)	
BD4						
16 (1.3, 2.0)	26 (1.7, 3.0)	28 (1.9, 3.2)	24 (3.8, 1.8)	38 (2.5, 3.8)	16 (1.3, 2.2)	28 (1.9, 3.7)

(a) Isopropanol/water (4:1) used instead of 100% isopropanol; (b) quenching is observed.

5), and is thus a measure of the interaction of the metal ions with the naphthylamine nitrogen.

N-butyl-4[(4'-aminobutyl)amino]-1,8-naphthalimide exhibits different emission characteristics in the presence of metal ions compared to ED4 and PD. With the exception of Hg^{2+} and Mn^{2+} , complexation with all metal ions studied results in a uniform fluorescence enhancement factor of approximately 1.5 at wavelengths greater than 500 nm and factors of 2.5–3.1 at 480 nm (Table 3). Fig. 7 shows the plots of emission intensity at 480 and 515 nm for BD4 upon increasing concentration of Cu^{2+} . These results are representative of the changes to BD4 emission upon complexation of metal ions causing FE. A fluorescence enhancement factor of 1.50 is also observed for BD4 with increasing acid concentration (decreasing pH). Hg^{2+} and Mn^{2+} may behave differently due to differences in coordination, especially in the case of Hg^{2+} , which forms linear complexes

or complex polymeric chains with ammonia, which would decrease the ability of Hg^{2+} to coordinate to the ligands studied here [22].

The difference in behavior between ED4/ PD4 and BD4 upon addition of H^+ is presumably due to differences in intramolecular hydrogen bonding. ED4 and PD4 are ex-

Table 5

Shifts (nm) of absorption λ_{max} and emission λ_{max} upon addition of metal ions to no further emission change

	Cu^{2+}	Fe^{3+}	Ni^{2+}	Zn^{2+}	Co^{2+}	Cr^{3+} (a)
ED4 (abs)	9	11	7	7	13	8
PD4 (abs)	7	9	5	5	6	5
BD4 (abs)	5	6	5	5	6	5
ED4 (em)	10	19	5	8	17	12
PD4 (em)	4	7	4	4	5	4
BD4 (em)	6	6	6	6	6	6

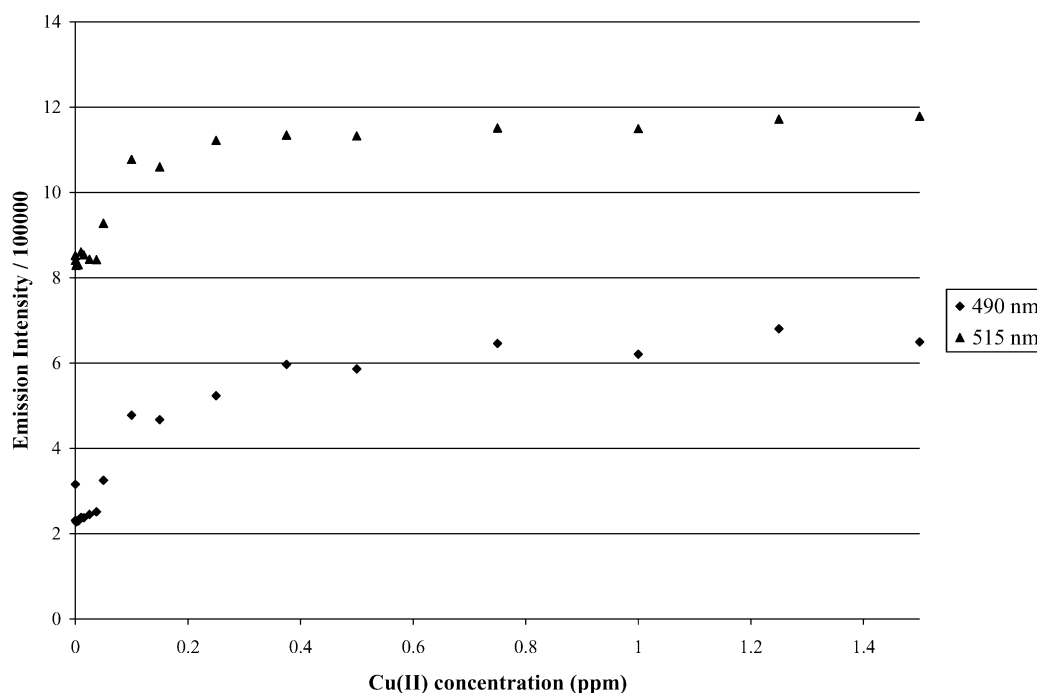


Fig. 7. Plot of change in emission upon metal ion complexation at 490 and 515 nm (BD4 and Cu^{2+}).

pected to form stable intramolecular hydrogen bonds between amines (aliphatic and naphthyl) with ring sizes of five and six members. Intramolecular hydrogen bonding within BD4 is expected to be less favorable due to the conformational requirements of a seven-membered ring. This suggests FE is not observed for ED4 and PD4 upon addition of H^+ because the favorable intramolecular hydrogen bond is not disrupted and no conformational or electronic changes occur to perturb the emissive state. FE is observed for BD4 because complexation with added H^+ disrupts the electronic interaction between the distal amine and the aromatic system, stopping PET.

Stable intramolecular hydrogen bonding within ED4 and PD4 presumably results in decreased PET between the distal amine and the aromatic system as a competing interaction will exist between the naphthyl amine hydrogen donor and the aliphatic amine acceptor. The FE observed for ED4 and PD4, in general, upon coordination with Ni^{2+} , Zn^{2+} , Co^{2+} and Cr^{3+} is therefore less than that observed for BD4 because the intramolecular hydrogen bond interaction decreases PET [5,7]. The increase of 15% in fluorescence quantum yield of ED4 compared to BD4 corroborates this hypothesis. Cu^{2+} and Fe^{3+} , by our observations, form more stable complexes with ED4 and PD4, and thus overcome the favorable hydrogen bonding, resulting in FE of similar or greater magnitude than BD4 (Table 3).

The primary interaction between BD4 and metal ions is coordination at the distal nitrogen, resulting in deactivation of the PET quenching process between the amine and the aromatic group and thus FE. The larger FE factors, except Cu^{2+} and Fe^{3+} , of BD4 upon addition of metal ions recorded

at shorter wavelengths compared to ED4 and PD4 is due to the greater efficiency of PET quenching of the aminonaphthalimide normal-mode emissive transition in the absence of metal ions. The bidentate coordination of metal ions, especially Fe^{3+} , Cu^{2+} , Co^{2+} , and Cr^{3+} , is less than observed for ED4 and PD4, as measured by shifting of the absorption and emission λ_{max} and calculated complexation coefficients (Table 2).

PeD4 and HD4 exhibit no enhancement or quenching upon coordination with any metal ion or acid. Clearly, the distal amine is conformationally isolated from the aromatic system, resulting in insufficient orbital overlap for PET. The conformational constraints of unfavorable ring formation do not allow the distal amine to bring the metal ion close to the lumiphore, thus no observed paramagnetic quenching [7]. The coordinating abilities of the metal ions studied are not great enough to allow strong coordination to the naphthylamine without bidentate chelation, even at higher metal ion concentrations [15,16].

The effect of enhancement is complete for ED4 complexes upon addition of approximately 0.8–1.0 equivalents of metal ion (0.5–0.8 ppm), for PD4 upon addition of approximately 1.7 equivalents of metal ion (1 ppm), and for BD4 with the addition of approximately 2–3 equivalent (1–2 ppm) of metal ion for all metal ions studied (Table 4). The response of emission to added metal ion is curved, but approximately linear over narrow concentration ranges. Fig. 6 shows results for ED4 and added Fe^{3+} . The largest FE is observed at 480 to 490 nm with the onset of detectable change in emission at approximately 70 ppb. The FE levels off after addition of approximately 500 ppb. These results are typical of all metal

ions studied. Addition of 1 equivalent of metal ion (excess) results in no further enhancement. Addition of excess metal ion to ED4 and PD4 solutions results in the onset of quenching of the emission spectra. The response of BD4 to addition of metal ion is also curved for all metal ions studied, approximately linear within narrow concentration ranges, with detectable change beginning at 50 ppb and leveling off after addition of approximately 300–500 ppb. Fig. 7 shows the results of the observed emission change of BD4 upon addition of Cu^{2+} . This is a typical graph for BD4 emission upon addition of metal ions. No quenching is observed upon addition of excess metal ions to BD4 solutions. Preliminary competition studies indicate metal ion interference does occur. These interferences can take the form of higher than expected FE in the case of two high FE metal ions (Cu^{2+} and Fe^{3+}), suggesting the FE of mixed systems is additive. Lower than expected FE of particular metal ions (e.g. Fe^{3+}) from studies of the metal ions alone are observed when non-FE metal ions are present. This is presumably due to non-coordinative quenching and does not necessarily reflect coordination competition. The complexation strength trends produced from patterns of interference generally reproduce the overall trends in complexation coefficients calculated.

Complexation coefficients were calculated from the emission data collected using the following relation [1,14]:

$$\log \left[\frac{(I_{\text{flmax}} - I_{\text{fl}})}{(I_{\text{fl}} - I_{\text{flmin}})} \right] = pM = \log \beta, \quad (1)$$

(where I_{fl} is the emission intensity, M is the metal ion concentration, and b is the complexation coefficient) and are presented in Table 2.

3.3. Linear free energy relationships

Martell and Hancock use linear free energy relationships to examine the complex interactions between free energy measurements ($K_{\text{eq},s}$) and metal ion, ligand, or complex properties and thus provide insight into the factors influencing complex formation [15]. We used this method to look for correlations between our data and the metal ion, ligand, or complex properties. Comparison of our data and trends with literature values allows us to develop a better understanding of the behavior of the ligands studied here. The calculated $K_{\text{eq},s}$ were plotted against a variety of properties, such as ionic radius, affinity for amines (as measured by $K_{\text{eq}}(\text{NH}_3)$, K_{eq} (ethylenediamine), etc. The coefficients calculated for ED4 and PD4 are greater than those reported for simple amines [15], but not as large as reported for diamines capable of full bidentate chelation [16]. The best correlation with the complexation coefficients is found with metal ion ionic radius, as is observed for complexes with NH_3 [15], but our correlation of $\log \beta$ with $\log K(\text{NH}_3)$ is poorer. We believe further refinement of our coefficient measurements by other methods will result in better correlations. No significant correlation is observed with reported ethylenediamine or propylenediamine complexation coefficients [16]. This suggests

ED4 and PD4 complexes have lesser contributions to coordination from bidentate interactions than ethylenediamine or propylenediamine. The coefficient values calculated for BD4 complexes are similar in magnitude to those reported for simple amine complexes [15], but with little correlation to ionic radius, $\log K(\text{NH}_3)$, or $\log K$ for ethylenediamine or propylenediamine, corroborating the expectation of less contribution from bidentate chelation by BD4 compared to ED4 and PD4 due to conformational constraints. Because of the poor correlations and the observed competition between metal ions measured by interference studies, we will be corroborating our coefficients by the method of Carlson et al. [17] and Sawyer et al. [18].

We looked for trends between the complexation coefficients and observed shifts in absorption and emission λ_{max} , and magnitude of FE with metal ion, ligand, and complex properties. The shifting behavior of the complexes follows the general trend in coordination strength for amines [15]. This trend follows the lesser coordinating ability of some metal ions studied toward amines and results in little coordination to the naphthylamine. The emission enhancement observed with the hypsochromic shift is not typical of deactivation of the ICT transition upon coordination to the naphthylamine nitrogen [6,8]. Strong coordination of the naphthylamine nitrogen by a metal ion draws electron density away from the nitrogen raising the energy of the transition, resulting in a decrease in efficiency and intensity of the transition [6,8]. This may be a competitive mechanism that limits the FE observed. The metal ion coordination to the naphthylamine nitrogen decreases as the bidentate chelation ring size, and therefore steric constraints with metal ions typically larger than carbon, increases. As the coordination to the naphthylamine nitrogen decreases, the effect on the ICT state decreases, observed as a decrease in the shift of emission λ_{max} to shorter wavelength. A component of paramagnetic quenching may also be operating as observed by the quenching at all wavelengths when ED4 and PD4 are complexed by Mn^{2+} , and the very low FE of Ni^{2+} and the lanthanides.

The shift in emission λ_{max} observed for complexes of metal ions with BD4 further supports this discussion. A bidentate ring complex involving a seven-membered ring is less favorable than a five- or six-membered ring. Similar shifting of emission λ_{max} is observed for BD4 with all metal ions studied as the weaker bidentate coordination is less metal ion selective.

4. Conclusions

We have investigated a class of compounds that allow detection of transition metal ions at the sub-ppm level by fluorescence enhancement. We observe selectivity for transition metal ions that form strong complexes with amines (e.g., Fe^{3+} , Cu^{2+}), but we also observed competition and interference between metal ions. In particular, we observe the selec-

tivity of ED4 for Cu^{2+} as previously reported [1], selectivity for Cu^{2+} by PD4, similar trends of complexation strengths as ED4 but with significantly lower FE overall (upto 60% lower), and overall higher FE for complexes of BD4 (except Cu^{2+} and Fe^{3+} complexes with ED4) but less selectivity. We do observe possible selectivity of Pb^{2+} by BD4. This is reasonable as Pb^{2+} exhibits less dependence on chelate structure (chain length between amines) than other, smaller metal ions [15,16].

Our results show that bidentate chelation, even when weak, is an important component to metal ion selectivity. Metal ion inhibition of the quenching of the ICT interaction between the naphthylamine nitrogen and the aromatic system by the distal amine accounts for the fluorescence enhancement observed upon metal ion coordination to ED4 and PD4. The generally greater fluorescence enhancement of BD4 upon metal ion coordination appears to be due to greater PET quenching of the ICT transition in the absence of metal ion. Our complexation coefficients are significantly below those reported by Kidder [1]. We believe the differences in absolute value are attributable to differences in the area along the curve the fit is applied. We are continue to investigate this hypothesis.

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