1474 *J. Am. Chem. Soc.* **1998,** *120,* 1474−1478

Effect of Solvent Polarity, pH, and Metal Complexation on the Triple Fluorescence of 4-(*N*-1,4,8,11-tetraazacyclotetradecyl)benzonitrile

Greg E. Collins,* Ling-Siu Choi, and John H. Callahan

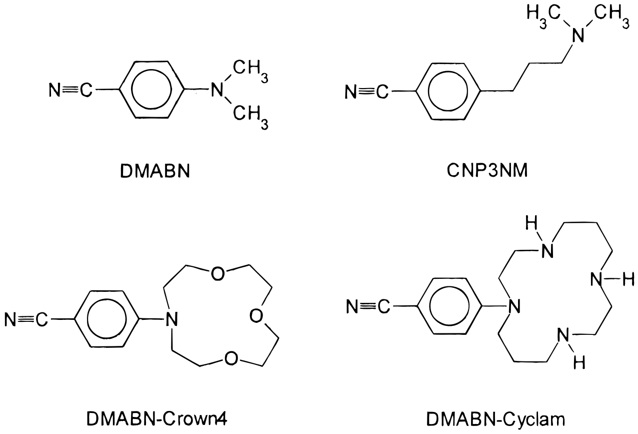
Contribution from the Naval Research Laboratory, Chemistry Division, Code 6116,
Washington D.C. 20375-5342

Received June 30, 1997

Abstract: Triple fluorescence is observed for 4-(*N*-1,4,8,11-tetraazacyclotetradecyl)benzonitrile (DMABN-Cyclam) in ethanol, corresponding to a locally excited (LE) singlet state, a twisted intramolecular charge-transfer (TICT) state, and an intramolecular exciplex (E). The LE state emission dominates the spectrum in nonpolar solvents such as *n*-hexane, while polar solvents stabilize the charge-transfer states, TICT and E. Optimal intramolecular exciplex emission, however, was observed in toluene, while the TICT band was maximal in water. The influence of pH on the fluorescent properties of DMABN-Cyclam were studied, indicating that protonation of cyclam strongly influences the equilibria existing between the three excited-state species, as well as the extent of quenching apparent for each excited-state band. DMABN-Cyclam uniquely responded to the addition of micromolar quantities of transition metal cations with varying changes in the triple fluorescence emission.

Introduction

Since Lippert's initial discovery[1] of the dual fluorescent behavior of 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN) in polar solvents (Figure 1), various models and theoretical explanations have been proposed to explain the anomalous, long wavelength fluorescence, including bending of the cyano group,[2] solute−solvent exciplex formation,[3] and twisted intramolecular charge transfer (TICT).[4] The concept put forward by Grabowski et al. of a TICT state where a charge transfer is accompanied by a twisting motion and orbital decoupling of the phenyl acceptor ring from the dimethyl amino donor group, is generally favored.[5−7] DMABN is thought to possess a double-minimum potential in the excited state. Excitation of DMABN forms a delocalized excited (DE) state which bears a partial charge transfer due to significant π overlap and mesomeric interaction between the donor (D) and acceptor (A) moieties in the planar geometry. There is an additional, lower lying S_1 minimum for the perpendicularly twisted geometry (TICT state), accessible via an adiabatic photoreaction that combines an excited-state intramolecular twist, electron transfer, and solvent reorganization. Decoupling of the phenyl ring from the dimethylamino donor group theoretically results in a full separation of charge, although Zachariasse et al. have noted a significant degree of electronic coupling between the A^- and D^+ moieties.[8]



DMABN CNP3NM

DMABN-Crown4 DMABN-Cyclam

Figure 1. Structure of molecules identified and discussed in text.

Our interest has been in the design of new, fluorescent sensor molecules capable of sensitively and selectively monitoring heavy metal ion concentration. The covalent attachment of benzonitrile to the aza group of a metal binding ionophore such as 1,4,8,11-tetraazacyclotetradecane (Cyclam), creates a fluorescent ionophore (DMABN-Cyclam) that uniquely combines the properties of DMABN with the metal binding properties of cyclam (Figure 1). Because one of the aza binding sites of cyclam is directly coupled to benzonitrile, we can expect that the complexation of a metal cation will have a dramatic influence upon both the localized excited (LE) state and TICT state emission.

Recently, Létard et al. reported the dual fluorescence of two compounds structurally similar to DMABN-Cyclam, 4-(1-aza-4,7,10-trioxacyclododecyl)benzonitrile (DMABN-Crown4) and 4-(1-aza-4,7,10,13-tetraoxacyclopentadecyl)benzonitrile (DMABN-

---

* To whom all correspondence should be addressed.

(1) Lippert, E.; Lüder, W.; Moll, F.; Nagele, H.; Boos, H.; Prigge, H.; Siebold-Blankenstein, I. *Angew. Chem.* **1961**, *73*, 695−706.

(2) Sobolewski, A. L.; Domcke, W. *Chem. Phys. Lett.* **1996**, *250*, 428−436.

(3) de Lange, M. C. C.; Thorn Leeson, D.; Van Kuijk, K. A. B.; Huizer, A. H.; Varma, C. A. G. O. *Chem. Phys.* **1993**, *177*, 243−256.

(4) Rotkiewicz, K.; Grellmann, K. H.; Grabowski, Z. R. *Chem. Phys. Lett.* **1973**, *19*, 315−318.

(5) Rettig, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 971−988.

(6) Grabowski, Z. R.; Dobkowski, J. *Pure Appl. Chem.* **1983**, *55*, 245−251.

(7) Siemiarczuk, A.; Grabowski, Z. R.; Krowczynski, A.; Asher, M.; Ottolenghi, M. *Chem. Phys. Lett.* **1977**, *51*, 315−320.

(8) Von der Haar, T.; Hebecker, A.; Il′ichev, Y.; Jiang, Y.-B.; Kühnle, W.; Zachariasse, K. A. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 430−442.

S0002-7863(97)02169-0 CCC: $15.00

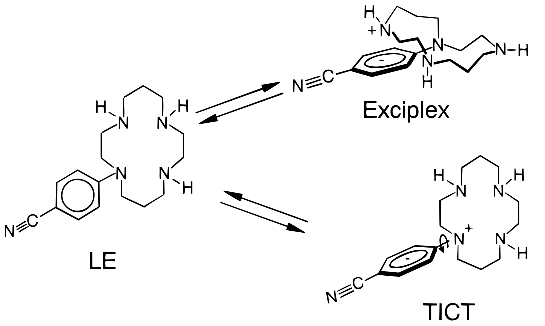


Figure 2. Proposed structures and equilibria existing between the three excited-state species, LE, TICT, and E, generating the observed triple fluorescence of DMABN-Cyclam.

Crown5) (Figure 1).[9] There are two primary differences between DMABN-Cyclam and the DMABN-Crowns: (1) cyclam contains four aza binding sites that promote complexation of transition metal ions,[10] in contrast to the ether linkages of DMABN-Crown4 and DMABN-Crown5 that favor complexation of alkali and alkaline earth cations;[11] and, (2) the three additional aza binding sites of DMABN-Cyclam give this molecule the capability for forming an intramolecular exciplex, a feature not found in the crown ether compounds. Benzonitriles bearing flexible, alkyl amino chains, e.g., 3-(4-cyanophenyl)-1-(*N*,*N*-dimethylamino)propane (CNP3NM, Figure 1), can form intramolecular exciplexes which arise due to the conformational flexibility of the alkyl amino chain, and its ability to form a sandwich configuration promoting excited state, charge transfer.[12] The propensity for intramolecular exciplex formation in CNP3NM is indicated by the strong, red-shifted fluorescence observed, and the complete absence of LE emission. In contrast to TICT state formation, the large distance and minimal mesomeric interaction apparent between D and A causes a localized excited (LE) state precursor to be formed, wherein the excited state is primarily localized on either D or A, depending upon which gives the lower S_1 energy. Van der Auweraer *et al.*[13] observed a correlation between intramolecular exciplex formation and Hirayama's rule,[14] which states that the most stable sandwich conformation will arise when $n = 3$ for a phenyl-$(CH_2)_n$-NMe_2 system.

We report here the triple fluorescence of 4-(*N*-1,4,8,11-teraazacyclotetradecyl) benzonitrile (DMABN-Cyclam), corresponding to the LE state, a TICT state, and an intramolecular exciplex (E) (Figure 2). Particular attention is devoted to understanding the effect of solvent, pH, and metal complexation on the triple fluorescence of DMABN-Cyclam.

Experimental Section

Upon the basis of the general procedure given by Suhr,[15] DMABN-Cyclam was prepared via the nucleophilic aromatic substitution of 4-fluorobenzonitrile with 1,4,8,11-tetraazacyclotetradecane (Cyclam) in DMSO at 130 °C under argon for 4 days. Following room-temperature filtration, DMSO was removed under vacuum and the resulting yellow solid redissolved in toluene and purified via silica gel column chromatography. Sequential elution of the compound with toluene, 2-propanol, and 20% concentrated NH_4OH in ethanol separated the product: UV $\lambda_{max} = 295$ nm; ^1H NMR (CD_3CN) δ 1.68 (m, 4, $CH_2CH_2CH_2$), 2.65 (s, 3, N*H*), 2.72 (m, 12, CH_2NH), 3.47 (m, 4, CH_2-NAr), 6.66 (d, 2, Ar*H*), 7.38 (d, 2, Ar*H*); ^{13}C NMR (CD_3CN) δ 27.83, 28.05, 45.72, 47.18, 47.80, 48.29, 48.72, 48.89, 49.21, 51.33, 96.85, 112.60, 121.16, 133.93, 152.57; electrospray MS ($M + H^+$) 302.4, calcd for $C_{17}H_{27}N_5 + H^+$, 302.4.

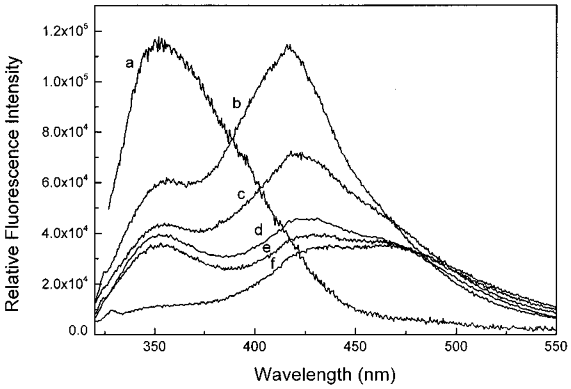


Figure 3. Solvent effect on the triple fluorescence of DMABN-Cyclam: (a) hexane, (b) toluene, (c) THF, (d) 2-propanol, (e) ethanol, and (f) water. All concentrations were 25 μM, with the exception of *n*-hexane, whose low solubility made this concentration unattainable (the hexane emission has been normalized to that seen in toluene).

A Spex Fluorolog $\tau 2$ spectrofluorimeter was used for making all fluorescence measurements, and a double-beam Hitachi U3000 spectrophotometer was used for all absorbance measurements. The excitation wavelength used was 295 nm. The solvents were of spectral grade quality and used as received from the supplier (Aldrich or Fischer Scientific). All metal salts contained chloride anions and were of the highest purity available (Aldrich or Alfa). Buffers (0.1 M) were prepared using H_3PO_4 (pH 1−3), acetic acid (pH 4−5), NaH_2PO_4 (pH 6−8), $NaHCO_3$ (pH 9−11), Na_2HPO_4 (pH 12), and NaOH (pH 13), with the pH being adjusted using either HCl or NaOH while monitoring with a pH meter. Intensity contributions from the three individual excited states were estimated using the Voigt Amplitude function of Jandel's PeakFit 4.0.

Results and Discussion

Solvent Dependence of Triple Fluorescence for DMABN-Cyclam. The UV spectra for DMABN-Cyclam in ethanol shows a single absorption peak at 295 nm. Excitation at this wavelength leads to three emission peaks: 352, 429, and 473 nm (Figure 3e). The fluorescence excitation spectra for these three emission wavelengths overlap at 295 nm, further indicating the purity of this compound and that each of these emission bands arise from excitation of the same ground-state species. Intensity contributions and wavelength placement of the three excited-state species were determined using a peak fitting protocol discussed in the Experimental Section. Because of the spectral overlap apparent between these three species, only qualitative information such as relative intensity trends and approximate peak positions have been derived from this analysis. The peak at 352 nm is attributed to the LE state emission of DMABN-Cyclam and compares favorably to that found for DMABN in THF ($\lambda_{max} = 354$ nm).[9] Identification of the two additional, red-shifted emission peaks was accomplished by comparison to structural analogues of DMABN-Cyclam, DMABN-Crown5, and CNP3NM. Létard *et al.* reported that DMABN-Crown5 exhibits a TICT emission that red shifts and increases in intensity as the solvent polarity is increased from hexane (where the emission band was too weak to be measured accurately), to toluene ($\lambda_{max} = 406$ nm), to acetonitrile ($\lambda_{max} = 466$ nm).[9] Similarly, DMABN-Cyclam, which differs from DMABN-Crown5 primarily in the replacement of nitrogen

---

(9) Létard, J.-F.; Delmond, S.; Lapouyade, R.; Braun, D.; Rettig, W.; Kreissler, M. *Recl. Trav. Chim. Pays-Bas* **1995**, *114*, 517−527.

(10) Hancock, R. D. *J. Chem. Educ.* **1992**, *69*, 615−621.

(11) Hancock, R. D. *Chem. Rev.* **1989**, *89*, 1875−1914.

(12) Grabowski, Z. R. *Pure Appl. Chem.* **1992**, *64*, 1249−1255.

(13) Van der Auweraer, M.; Grabowski, Z. R.; Rettig, W. *J. Phys. Chem.* **1991**, *95*, 2083−2092.

(14) Hirayama, F. *J. Chem. Phys.* **1965**, *42*, 3163−3171.

(15) Suhr, H. *Liebigs Ann.* **1965**, *687*, 175−182.

binding sites for the oxygen atoms of the crown ether, reports a similar trend in the emission spectra (Figure 3): hexane (λ_{max} = 390 nm ± 10 nm), toluene (λ_{max} = 413 ± 10 nm) and ethanol (λ_{max} = 473 ± 3 nm). We, therefore, attribute the third emission band in ethanol at 473 nm to a TICT state. Unlike DMABN-Crown5, however, DMABN-Cyclam has two additional amine goups linked by a short chain (n = 3 and n = 4) to the benzonitrile acceptor. Petrov et al. have shown that aza crown ethers can readily form intermolecular exciplexes with pyrene, for example.[16] Despite the cyclic nature of the cyclam functional group in DMABN-Cyclam, this molecule exhibits sufficient flexibility to form a sandwich complex in the excited state that gives rise to an intramolecular exciplex peak (E) (Figure 2). The peak position identified for the exciplex peak of DMABN-Cyclam in hexane (λ_{max} = 392 nm ± 10 nm) compares favorably with that found for CNP3NM in isopentane (λ_{max} = 390 nm).[17]

Several trends are evident from Figure 3 with regard to the effect of solvent polarity on the triple fluorescence of DMABN-Cyclam. The TICT emission band red shifts by more than 80 nm and increases in intensity relative to the LE emission as solvent polarity is increased. The relative intensity of the TICT band increases with solvent polarity due to a stabilization of the charge separation. This type of behavior was also reported for DMABN-Crown4.[9] The exciplex emission does not red shift quite as severely (43 nm), due to a smaller dipole moment compared with the TICT configuration. The intensity of the TICT emission band increases relative to the exciplex emission with increasing solvent polarity. This feature can be attributed to (1) increased stabilization of the larger dipole moment evident in the TICT state; and (2) increased radiationless decay of the exciplex by internal conversion in the more polar solvents. In fact, the intensity of the intramolecular exciplex emission band is maximal in toluene, decreasing in intensity as the solvent polarity is increased. This type of behavior has been observed for other amine intramolecular exciplexes, including ((*N*,*N*-dimethylamino)alkyl)phenanthrenes[18] and *ω*-(1-pyrenyl)-α-(*N*,*N*-dimethylamino)alkanes.[19] Weller was the first to propose that the decrease in intermolecular exciplex fluorescence intensity with increasing solvent polarity was due to ionic dissociation and the formation of nonfluorescent radical ions in polar solvents.[20] Because ionic dissociation is not possible in intramolecular exciplexes, Mataga and co-workers suggested that a compact folded geometry is favored in nonpolar solvents, and looser, more open geometries are apparent in polar solvents.[21] The loose geometry is akin to the solvent-separated radical ion pair which is formed in intermolecular exciplexes, thereby explaining the quenching effect observed in more polar solvents. In a similar fashion, we can expect that prior to excitation DMABN-Cyclam will conform to a unique conformation in solvents of differing polarity. We can presume that DMABN-Cyclam optimally conforms to a compact folded configuration in toluene, fostering enhanced intramolecular exciplex formation and emission. As the polarity of the solvent is increased, solvation of the aza groups on the cyclam moiety is enhanced, allowing DMABN-Cyclam to attain a more open configuration that decreases intramolecular exciplex formation and emission. We have reported similar behavior in other dye-linked aza crown ethers.[22]

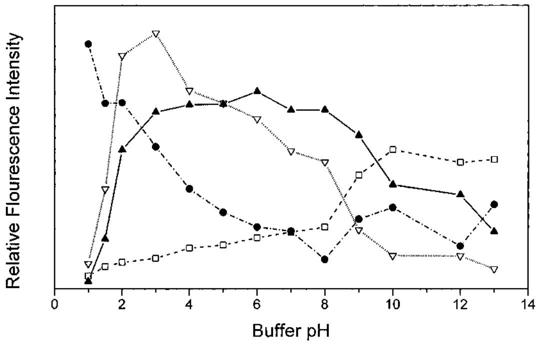


Figure 4. Effect of pH on the triple fluorescence of DMABN-Cyclam in water: solid circles, LE; open squares, TICT/E; open triangles, E/LE; and solid triangles, TICT/LE.

The LE band exhibits an intensity minima in water because of the high polarity of this solvent, and its capability for stabilizing the two charge-transfer complexes. The small hypsochromic shift evident in the LE band (5 nm) with decreasing solvent polarity indicates that minimal charge transfer exists for this excited-state species prior to formation of the charge-transfer states. It is possible that steric hindrance introduced by the cyclam moiety forces the diethylamino group to rotate out of the plane of the phenyl acceptor group, resulting in lower mesomeric interaction between D and A. Support for this contention was found by Létard et al., who reported a calculated twist angle for DMABN-Crown5 of 18° (compared to 1° for DMABN) which was attributed to the repulsion of the large ring of the 5-azacrown ether by the ortho hydrogens.[9]

pH Dependence of Triple Fluorescence for DMABN-Cyclam. An improved understanding of the interplay between the three excited-state species can be achieved by examining the change in fluorescence emission for DMABN-Cyclam with pH (Figure 4). Examining first the effect of pH on intramolecular exciplex emission (open triangles), we note that emission from this band is maximal at pH 3, dropping off rapidly at more acidic pH, and decreasing in a nearly linear fashion at more basic pH values. The pK_a values for cyclam have been measured by several workers, and are summarized by Bianchi et al.[23] At 25 °C, there is reasonable agreement between the different measurements for pK_1 (11.6 ± 0.16), pK_2 (10.44 ± 0.23), and pK_3 (1.55 ±0.11). However, there is considerable variability in the values determined for the pK_4 (0.94−2.41) of cyclam. The benzonitrile aza group of DMABN-Cyclam will have the lowest pK_a value due to the strong, electron-withdrawing nature of this group. By comparison to the pK_a's recorded for aniline (pK_a = 4.63) and diethylamine (pK_a = 10.5), we can expect that the pK_a for this aza group will be as much as 4 orders of magnitude lower than that found in cyclam, particularly since the nitrile functionality makes this group an even stronger acceptor. As the acidity drops below pH 2, DMABN-Cyclam will likely be triply protonated, causing intramolecular exciplex formation to decrease dramatically due to the inability of the protonated aza groups to donate charge to the phenyl acceptor group. As the pH increases above pH 3, the intramolecular exciplex emission band steadily decreases. This appears to be

---

[16] Petrov, N. Kh.; Borisenko, V. N.; Alfimov, M. V.; Fiebig, T.; Staerk, H. *J. Phys. Chem.* **1996**, *100*, 6368−6370.

[17] Van der Auweraer, M.; Vannerem, A.; de Schryver, F. C. *J. Mol. Struct.* **1982**, *84*, 343−351.

[18] Lewis, F. D.; Cohen, B. E. *J. Phys. Chem.* **1994**, *98*, 10591−10597.

[19] Swinnen, A. M.; Van der Auweraer, M.; De Schryver, F. C.; Nakatani, K.; Okada, T.; Mataga, N. *J. Am. Chem. Soc.* **1987**, *109*, 321−330.

[20] Knibbe, H.; Röllig, K.; Schäfer, F. P.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1184−1185.

[21] Okada, T.; Karaki, I.; Matsuzawa, E.; Mataga, N.; Sakata, Y.; Misumi, S. *J. Phys. Chem.* **1981**, *85*, 3957−3960.

[22] Collins, G. E.; Choi, L.-S. *J. Chem. Soc., Chem. Commun.* 1997, *12*, 1135−1136.

[23] Bianchi, A.; Micheloni, M.; Paoletti, P. *Coord. Chem. Rev.* **1991**, *110*, 17−113.

Table 1. Relative Change in LE, E, and TICT Emission Observed for the Addition of 12 μM of Each Metal Salt to a 25 μM Solution of DMABN-Cyclam in Buffered Water (pH = 7)

metal ion	LE	E	TICT
none	0.54	1.2	1.4
Zn(II)	2.2	1.0	1.2
Cd(II)	0.68	1.1	1.4
Cu(II)	0.42	0.90	1.2
Ni(II)	0.43	0.94	1.2
Pb(II)	0.51	1.1	1.4
Hg(II)	0.51	0.93	1.2

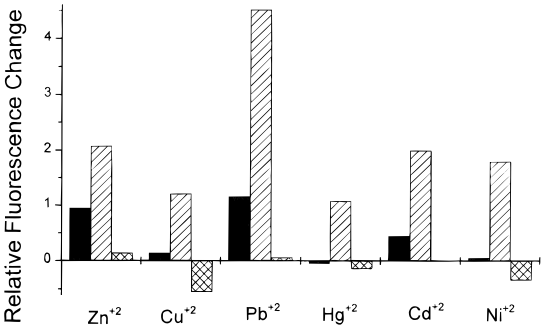


Figure 5. Relative change in LE (solid), E (diagonal lines), and TICT (hatched lines) emission summarized for addition of 12 μM of each metal salt to a 25 μM solution of DMABN-Cyclam in acetonitrile.

due to a shift in the equilibrium from the exciplex to the TICT state as the pH is increased. We can see evidence for this shift in a plot of the change in TICT/E vs pH (open squares, Figure 4). In general, the TICT emission band slowly dominates the emission spectra as the pH increases, perhaps due to the fact that unlike the exciplex state, the charge-transfer step for the TICT state formation requires no structural rearrangement.

The TICT emission band (closed triangles, Figure 4), in a fashion similar to the exciplex emission band, passes through a maximum at pH 3. However, the emission band for TICT is nearly level from pH 3−8, before steadily declining as the alkalinity is increased from pH 8−13. The decrease in TICT emission seen above pH 8 is attributed to an increase in quenching by the exciplex aza groups. The quenching of DMABN's TICT fluorescence has been reported by Wang in the examination of a series of tertiary amines.[24] At pH values less than 2, DMABN-Cyclam will be triply protonated, and TICT state formation will decrease due to the decrease in charge transfer resulting from electrostatic repulsion with the three protonated nitrogens closely linked to the benzonitrile aza group.

The LE emission intensity (solid circles, Figure 4) reported a steady decrease in intensity with increasing pH, ultimately leveling off at pH 8 and above. As DMABN-Cyclam is deprotonated and charge transfer facilitated, the equilibrium will shift toward the formation of the two charge-transfer states, E and TICT.

Effect of Metal Complexation on Triple Fluorescence of DMABN-Cyclam. Because the aza groups responsible for metal cation binding are also directly involved with the formation of the two charge-transfer excited-state complexes (E and TICT), metal binding by DMABN-Cyclam should have a dramatic influence upon the fluorescence intensity of the triple fluorescence. A series of different metal cations were investigated in both protic (water, pH = 7, Table 1) and aprotic solvents (acetonitrile, Figure 5). To simplify the discussion, the metal ions have been classified as follows: (1) diamagnetic metal cations—Zn^{2+} and Cd^{2+}; (2) paramagnetic metal cations—Cu^{2+} and Ni^{2+}; and (3) diamagnetic, heavy metal cations— Hg^{2+} and Pb^{2+}.

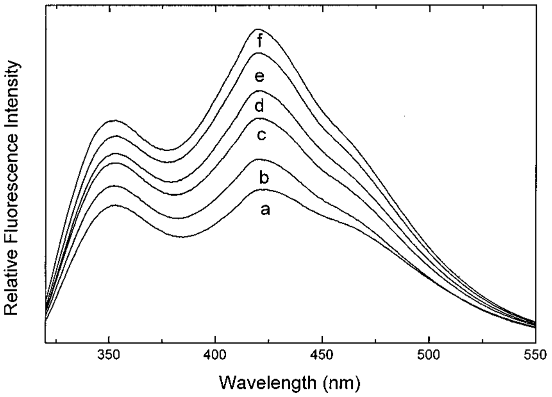


Figure 6. Influence of Zn^{2+} addition on the triple fluorescence of a 25 μM solution of DMABN-Cyclam in acetonitrile: (a) 0 μM, (b) 6.2 μM, (c) 12 μM, (d) 18 μM, (e) 25 μM, and (f) 37 μM.

Consider first the situation evident for DMABN-Cyclam dissolved in water. As was mentioned earlier, DMABN-Cyclam likely conforms to an open geometry in this strongly polar solvent, a conformation lowering the extent of exciplex and LE emission, while favoring TICT state formation. Complexation of metal cations by DMABN-Cyclam in water (Table 1) causes a net decrease in the TICT and E state emission. Complexation of the cyclam aza groups by metal cations lowers the extent of charge transfer possible with the benzonitrile acceptor group, and hence, diminishes each of these charge-transfer emission bands. In conjunction with the equilibrium shown in Figure 2, as the TICT and E concentrations decrease, the LE emission increases. This was, in fact, observed for the diamagnetic metal cations, Zn^{2+} and Cd^{2+}; however, the paramagnetic and heavy metal cations caused a decrease in the LE emission following complexation. Paramagnetic[25] and large or easily reducible cations[26] are recognized for their intracomplex, quenching behavior, and, apparently, are responsible for the decrease observed in LE emission.

A completely different set of results are obtained when the aprotic solvent, acetonitrile, is used for the metal complexation studies. Summarized in Figure 5 are the relative changes seen for LE (solid), E (diagonal lines), and TICT (hatched lines) emission following the addition of 12 μM of each metal salt to a 25 μM solution of DMABN-Cyclam in acetonitrile. Shown in Figure 6 is an example set of emission spectra, indicating the influence of Zn^{2+} addition on the triple fluorescence of DMABN-Cyclam in acetonitrile. The most dramatic difference realized from the situation observed in water, is that in all cases, complexation of metal cations by DMABN-Cyclam caused an increase in the exciplex emission. This result is surprising, considering that complexation of the exciplex aza group would normally be expected to reduce the extent of charge transfer and, hence, lower the exciplex emission intensity. Because the intramolecular exciplex emission does not decrease, we can conclude that in acetonitrile, the nitrogen involved in exciplex formation is no longer complexed with the metal cation. This contention is also supported by the absence of any blue shifting seen in the exciplex emission. As was concluded previously from the study of DMABN-Cyclam in solvents of varying

---

(24) Wang, Y. *J. Chem. Soc., Faraday Trans. 2* **1988**, *84* (11), 1809−1823.

(25) Varnes, A. W.; Dodson, R. B.; Wehry, W. L. *J. Am. Chem. Soc.* **1972**, *94*, 946−950.

(26) Akkaya, E. U.; Huston, M. E.; Czarnik, A. W. *J. Am. Chem. Soc.* **1990**, *112*, 3590−3593.

polarity, DMABN-Cyclam forms a more compact, folded geometry in acetonitrile wherein the exciplex aza group apparently does not participate in the complexation of the metal cation. Apparently, complexation of a metal cation by the three remaining nitrogens provides enough shielding to slow electron transfer from the benzonitrile radical anion moiety. The dominating influence on the exciplex emission band arises from the elimination of quenching amines due to the interaction of the remaining three aza groups with the complexed metal cation. Additionally, binding of the metal cation may result in a new, metal/ligand, complex geometry that further favors exciplex formation.

Reduction in the charge-transfer character of the TICT aza group due to binding of a metal cation in the ground state will result in at least three effects: (1) providing that the exciplex aza group is not partaking in metal cation complexation, the exciplex emission will increase when quenching from the TICT aza group is reduced; (2) TICT emission will decrease along with the reduced capability for the complexed aza group to donate charge to the benzonitrile acceptor group; and, (3) the LE emission band will increase with the shift in equilibrium from TICT to LE. The only exception to the expected increase in LE emission was found for the metal cation, Hg^{2+}. We attribute this reduction in emission intensity to the quenching behavior of this large and easily reducible metal cation. For higher concentrations of paramagnetic metal ions, such as Cu^{2+}, we have the additional impact of uncomplexed metal ions causing diffusional quenching of the [DMABN-Cyclam:Metal ion] complex. This is shown in Figure 7, which plots the change in triple fluorescence seen for the sequential addition of Cu^{2+} to DMABN-Cyclam in acetonitrile. As the concentration of copper cations becomes greater than the equimolar concentration of DMABN-Cyclam (25 μm), the overall triple emission intensity can be observed to decrease in intensity due to quenching. The paramagnetic effect is weak enough for this system that it is not observed until the addition of greater than a stoichiometric amount of Cu^{2+}. This effect is perhaps related to a small coefficient of the benzonitrile LUMO on the amino nitrogen complexed with the Cu^{2+}.

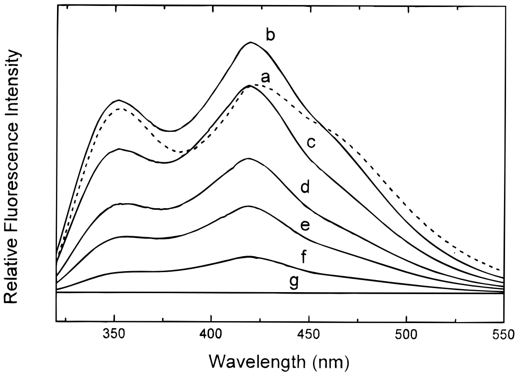


Figure 7. Influence of Cu^{2+} addition on the triple fluorescence of a 25 μM solution of DMABN-Cyclam in ethanol: (a) 0 μM, (b) 12 μM, (c) 74 μM, (d) 149 μM, (e) 223 μM, (f) 372 μM, and (g) 1880 μM.

Conclusions

In conclusion, DMABN-Cyclam is a unique molecule which exhibits triple fluorescence arising from the LE state and two excited-state complexes, a TICT state and an intramolecular exciplex (E). All three emission bands are strongly perturbed by solvent polarity, pH, and metal complexation. The unique perturbation of the three excited-state species by different metal cations suggests the possibility of utilizing DMABN-Cyclam in the selective detection of metal cations.

Acknowledgment. The authors gratefully acknowledge the Office of Naval Research for funding support of this study.

JA972169R