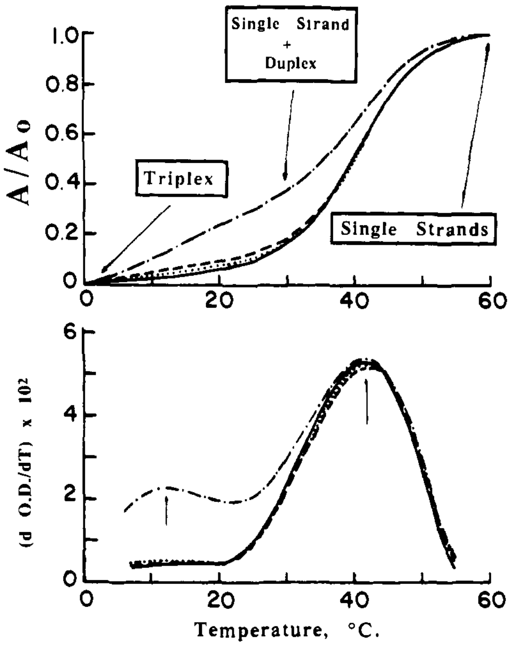

Figure 2. Upper panel: Relative absorbance, $A/A_0 = [A(T\,°\text{C}) - (A(0\,°\text{C})]/[A(60\,°\text{C}) - A(0\,°\text{C})]$, vs temperature at 260 nm. Lower panel: Absorbance change $[\Delta A(260\,\text{nm})/\Delta T]$ vs temperature; (—) duplex d alone, (-·-) mixture of a and d, (···) mixture of b and d, (- - -) mixture of c and d. All solutions contain each oligomer (3 μM), 1.0 M NaCl, 20 mM $MgCl_2$, and 0.01 M sodium cacodylate, pH 7.0. T_m's are indicated by arrows.

(Figure 2, lower panel). One transition (T_m = 42 °C) was identical with the melting of **d** and the second transition (T_m = 12 °C) was surmised to be the dissociation of the third strand **a** from the duplex **d** as illustrated in the upper panel of Figure 2. This mixture of **a** and **d** showed similar transition profiles between pH 7 and pH 8.7 (data not shown).

Also, we studied the circular dichroism (CD) spectra of mixtures of oligomers. Spectra of a mixture of **a** and the duplex **d** at both 3 °C (dotted line) and 30 °C (solid line) in neutral condition are shown in Figure 3A. As a control, the sum of a spectrum of **a** and a spectrum of **d** in the same buffer at 3 °C is shown in the same figure (broken line). The control spectrum and the spectrum of the mixture at 30 °C showed similar patterns. In contrast, the spectrum of the mixture at 3 °C showed a different pattern, especially in the shorter wavelength region. A positive band at 215 nm in the control spectrum changed to a negative band in the spectrum of the mixture at 3 °C. This difference indicated the association of the third strand with the duplex.[23-26] Furthermore, a CD mixing study showed that the association has a 1:1 stoichiometry. These results indicated the triplex formation of **a** with **d**.

It has been reported recently that the substitution of 2′-deoxycytidine by 2′-deoxy-5-methylcytidine (^{m}C) and the substitution of thymidine by 2′-deoxy-5-bromouridine in an oligomer can cause triplex formation above neutral pH.[27] In such a situation, the substitution at position 5 of pyrimidines was able to add a stabilizing factor (nature unknown) for the triplex. Our approach is different. A triplex can be formed without the requirement of protonation if one designs an oligonucleotide containing **1**, a 2′-deoxycytidine analogue, which contains a hydrogen at the N-3 (or N-1) position, and which can form a pair of hydrogen bonding with 2′-deoxyguanosine in the Hoogsteen scheme through this very hydrogen. With this innovative approach, it is anticipated that the possibility of triplex formation of an oligonucleotide analogue with genomic DNA in mammalian cells can be tested.

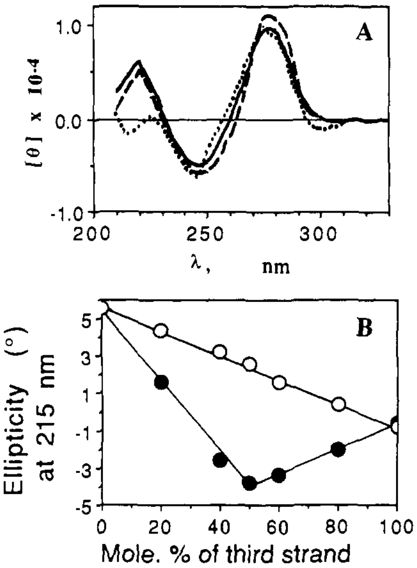

Figure 3. (A) CD spectra of mixtures of a and d at 3 °C (dotted line) and 30 °C (solid line) and the sum of a spectrum of a and a spectrum of the duplex d in the same buffer at 3 °C (broken line) with 3 μM a and d, respectively, in 1.0 M NaCl, 20 mM $MgCl_2$, 0.01 M sodium phosphate, pH 7.5. Molar ellipticity, [θ], is given per base residue. (B) CD mixing curves of a and d (filled circles) as well as b and d in 1.0 M NaCl, 20 mM $MgCl_2$, 0.01 M sodium phosphate, pH 7.5 at 3 °C (open circles).

Acknowledgment. CD spectra were obtained by using a JASCO 500A CD spectrometer (in Dr. S. K. Yang's laboratory) at Uniformed Services University of Health Sciences. The work was supported in part by Department of Energy Grant DE-FG02-88 ER60636 and in part by National Cancer Institute Grant CA-42762-04A1. Finally, we thank Ms. T. Trapane for her helpful discussion.

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Excited-State Properties in Supramolecular Systems. Luminescence and Intercomponent Interactions in a 3-Catenand and Some 3-Catenates

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Supramolecular species obtained by assembling molecular components are currently the object of extensive photochemical

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Chart I

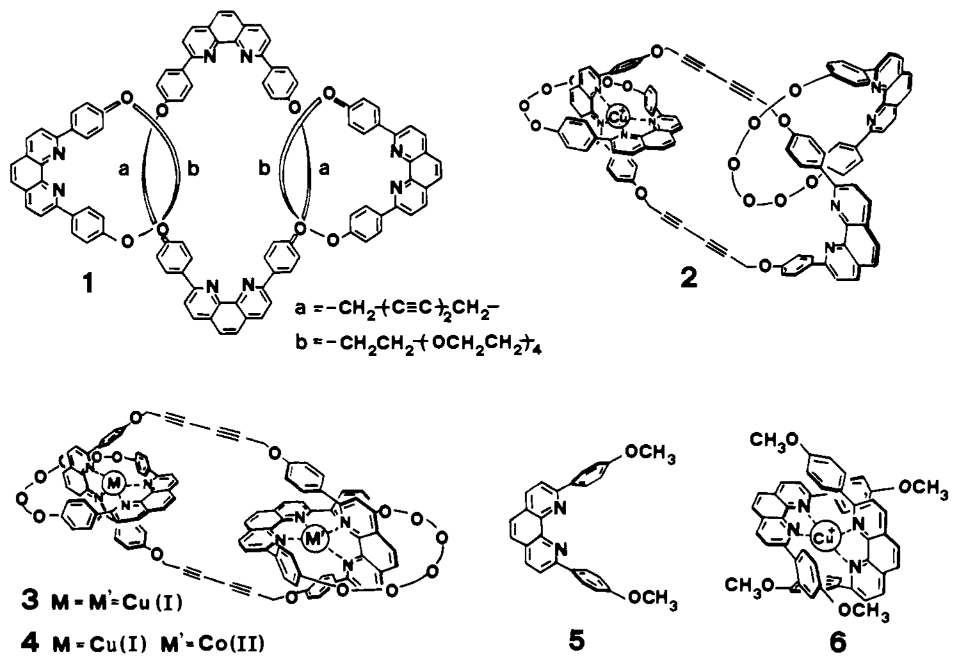

Table I. Luminescence Properties[a]

	LC ($^1\pi\pi^*$)		LC ($^3\pi\pi^*$)[b]		^{3}MLCT[c]	
	λ, nm	τ, ns	λ, nm	τ, s	λ, nm	τ, ns
3-catenand **1**	401	2.4	500	1.5		
Cu(3-catenand)$^+$ **2**	395	2.4	501	1.5	695	115
Cu_2(3-catenand)$^{2+}$ **3**					700	118
CuCo(3-catenand)$^{3+}$ **4**						
DAP **5**	398	2.0	502	1.8		
Cu(DAP)$_2^+$ **6**[d]					710	260

[a] Air-equilibrated 10^{-5} M CH_2Cl_2 solution at 300 K, unless otherwise noted; LC = ligand-centered; MLCT = metal-to-ligand charge-transfer. [b] EtOH/MeOH/CH_2Cl_2, 4:1:1 v/v, at 77 K. [c] Concentration: 10^{-4} M. [d] From ref 6.

investigations because of promising applications in the fields of solar energy conversion and signal processing.[2] Interlocked macrocyclic molecules (catenanes)[3-5] are fascinating supramolecular species where the interaction between the various subunits may lead to interesting photochemical and photophysical properties.[6-9] Several catenanes that exhibit coordination ability (*catenands*) and their metal complexes (*catenates*) have been recently synthesized.[4,9-13] We report here the results of an investigation on the luminescence properties of the 3-catenand **1**, the mononuclear Cu(3-catenand)$^+$ **2**, and the binuclear Cu_2(3-catenand)$^{2+}$ **3** and CuCo(3-catenand)$^{3+}$ **4** (Chart I).

The syntheses and characterizations of compounds **1**–**4** have already been reported.[12,13] The equipment used to obtain luminescence spectra and lifetimes has also been described.[14] Experiments were carried out in CH_2Cl_2 solution at 300 K and in a rigid matrix (EtOH/MeOH/CH_2Cl_2, 4:1:1 v/v) at 77 K. Some of the results obtained are summarized in Table I, where data concerning the parent dianisylphenanthroline ligand, DAP **5**, and its Cu$^+$ complex, Cu(DAP)$_2^+$ **6**, are also shown.

The absorption spectrum of **1** shows intense bands in the near-UV region, as does the parent component **5**, that can be assigned to spin-allowed $\pi \rightarrow \pi^*$ transitions. The lowest energy band of **1** has its maximum at 326 nm with $\epsilon = 67\,000$ M^{-1} cm^{-1}. Such ligand-centered (LC) bands are present (more or less perturbed) in the catenates **2**–**4**, which in addition exhibit a broad, less intense absorption band in the visible spectrum (λ_{max} = 440 nm, ϵ_{max} of the order of 10^3 M^{-1} cm^{-1}). This visible absorption band is also present in **6** and can be assigned to spin-allowed metal-to-ligand charge-transfer (MLCT) transitions.

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Excitation of **1** in CH_2Cl_2 solution generates a very strong emission centered at 401 nm (τ = 2.4 ns). This emission strongly resembles that observed for **5** (Table I) and can be assigned as a LC $^1\pi\pi^*$ fluorescence. For both **1** and **5** a $^3\pi\pi^*$ phosphorescence in a rigid matrix at 77 K ($\tau \approx 1.5$ s) is also observed.

The emission spectrum of the monometallic Cu(3-catenand)$^+$ shows a band at 695 nm (τ = 115 ns at 300 K, 2.16 μs at 77 K) besides the ligand-centered $^1\pi\pi^*$ fluorescence and $^3\pi\pi^*$ phosphorescence shown by **1** (Table I). The 695-nm band can be assigned to a ^{3}MLCT (triplet MLCT) transition by analogy with the luminescence behavior of **6** and of other Cu(I) polypyridine complexes.[6,15,16] The luminescence spectrum of **2** is therefore that expected for a "catenand" and a "catenate" moiety, each one showing its own emission spectrum. The intensity of the ($^1\pi\pi^*$) LC fluorescence of **2**, however, is about 50 times lower than that of **1**. This indicates that the catenand fluorescence is quenched efficiently by the catenate moiety. Calculations based on the Förster type[17] energy transfer mechanism show that a consistent energy transfer rate constant (2.5×10^{10} s^{-1}) is obtained for a center-to-center distance of 14 Å.

For the dimetallic Cu_2(3-catenand)$^{2+}$ **3**, only a ^{3}MLCT band (λ_{max} = 700 nm, τ = 118 ns) can be observed. Its intensity is half that of the ^{3}MLCT band of **2**. Since the excited-state lifetime is practically the same in the two cases, the different emission intensities must be related to different values of the radiative rate constant k_r. This suggests that the metal coordination geometry is somewhat different in the catenate units of **2** and **3**. Significantly different geometries have been found in the solid state for the Cu(I) coordination sphere in **3**[18] and in **6**.[19]

The heterobimetallic CuCo(3-catenand)$^{3+}$ **4** does not show any luminescence. The lack of luminescence from the Co catenate moiety was expected because Co(II) complexes possess nonluminescent metal-centered (MC) excited states at very low energies,[20] which also facilitate the radiationless decay of the upper lying LC and MLCT levels. The lack of luminescence from the Cu catenate moiety indicates that an efficient quenching mechanism is operative. The most likely quenching mechanisms are (i) electron transfer from the ^{3}MLCT level of the Cu catenate moiety to the ground state of the Co catenate moiety ($\Delta G°$ about -0.6 eV) and (ii) exchange energy transfer from the ^{3}MLCT level of the Cu catenate moiety ($\sim$1.8 eV) to a MC level of the Co catenate moiety that lies below 1.2 eV.[21] It should be noticed that the metal-to-metal distance in **4** can be much smaller than it would appear from its schematic formula. Actually, for **3** a Cu–Cu distance of 8 Å was found in the solid state.[18]

In conclusion, the luminescence behavior of the supramolecular species **1–4** can be rationalized on the basis of the luminescence behavior of their components and of intercomponent interactions.

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Registry No. 1, 109748-90-5; **2**, 133166-44-6; **3**, 109333-85-9; **4**, 132943-27-2.

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Excited-State Intramolecular Proton Transfer in 1-(Acylamino)anthraquinones

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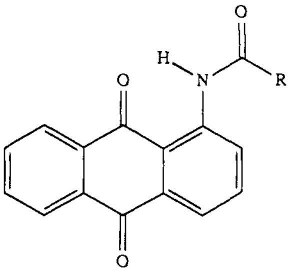
Excited-state intramolecular proton transfer (ESIPT) is currently of considerable experimental and theoretical interest.[1] The vast majority of ESIPT systems involve transfer of a proton from an oxygen donor. 1,5-Dihydroxyanthraquinone is typical, with ESIPT leading to dual fluorescence emission.[2] The emission is conveniently discussed in terms of a four-state diagram (Scheme I), where S_0(N), S_1(N), S_0(T), and S_1(T) correspond to the normal 9,10-keto ground state, the normal 9,10-keto excited state, the 1,9-keto ground tautomeric state, and the 1,9-keto excited tautomeric state, respectively. The short-wavelength emission has been assigned to the normal excited state and the long to the excited tautomer.

ESIPT with nitrogen as the proton donor is rare and is often complicated by dimerization.[3,4] Previous studies of 1-aminoanthraquinone[5] and 1-(acetylamino)anthraquinone[6,7] have found no evidence for ESIPT. We now report compelling evidence for ESIPT in 1-(acylamino)anthraquinones (**1a–d**).[8] As expected,[9] the absorption of **1** shows a blue shift with increasing solvent polarity and with increasingly electron withdrawing substituents. This is consistent with a charge-transfer transition leading to an excited state of reduced polarity. There is no evidence of specific solvent–dye equilibria.



	R
1a	n-C_6H_{13}
1b	CH_2Cl
1c	$CHCl_2$
1d	CF_3

The absorption and corrected emission spectra for **1a** and **1d** in cyclohexane solution at room temperature are shown in Figure

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