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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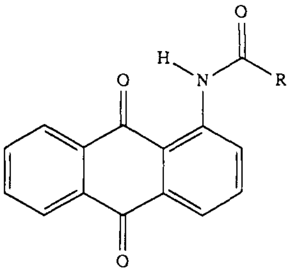
Excited-state intramolecular proton transfer (ESIPT) is currently of considerable experimental and theoretical interest.[1] The vast majority of ESIPT systems involve transfer of a proton from an oxygen donor. 1,5-Dihydroxyanthraquinone is typical, with ESIPT leading to dual fluorescence emission.[2] 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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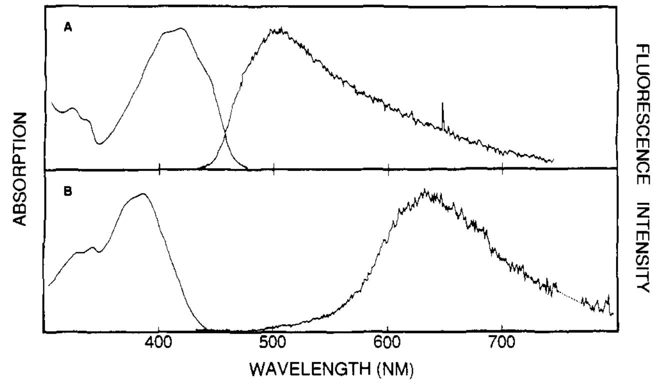
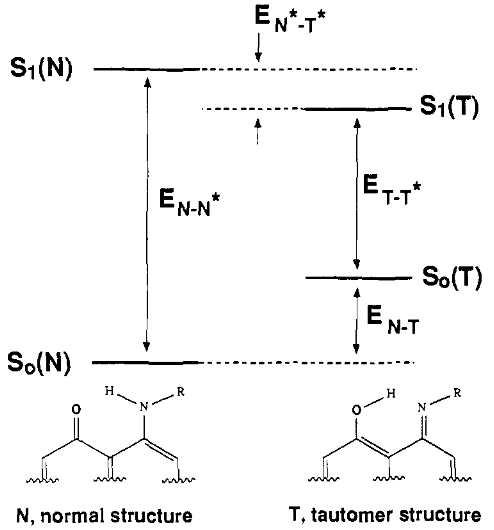


Figure 1. Absorption and emission spectra for dilute solutions in cyclohexane of **1a** (A) and **1d** (B). An artifact due to scattered second-order excitation light has been replaced by a dashed line in panel B.

Scheme I



1. **1a** has a broad short-wavelength emission (SWE), peaking at 509 nm, with a distinct tail to the red. The Stokes shift is substantial, but the large overlap with the lowest absorption and the near mirror image relationship to it provide strong evidence for an emission chiefly to the normal $S_0(N)$ isomer. **1d** shows predominantly a long-wavelength emission (LWE) at ca. 635 nm, with a weak feature at ca. 510 nm. The absorption and emission are clearly not mirror images, and the Stokes shift is very large. The emission spectra of **1b** and **1c** in cyclohexane solution are intermediate between those of **1a** and **1d**.

Excitation spectra, monitoring the SWE and the LWE, are virtually identical with each other and with the absorption spectrum. The two emission features are, therefore, derived from a common, initially prepared excited state, and a stoichiometric solvent–dye complex is not responsible for dual peaks.

The fluorescence spectra are solvent dependent, particularly for **1b** and **1c**. The LWE/SWE ratio increases drastically with decreasing solvent polarity or donicity (Figure 2). This solvent dependence is clearly inconsistent with a LWE from a twisted intramolecular charge-transfer emission. Emission from an anthraquinone anion can also be ruled out since the LWE can be observed in the solid state, and the emission of authentic anion is more solvent sensitive than the LWE.

The ratio LWE/SWE in cyclohexane can be related to the pK_a of the anilide corresponding to **1** by $\ln(\mathrm{LWE/SWE}) = 10.8\ (\pm 0.9) - 0.77\ (\pm 0.08)pK_a$ ($r = 0.996$, $n = 4$). This relationship predicts the lack of observable ESIPT in 1-aminoanthraquinone[5] and is consistent with the known ESIPT of 1-hydroxyanthraquinone.[10]

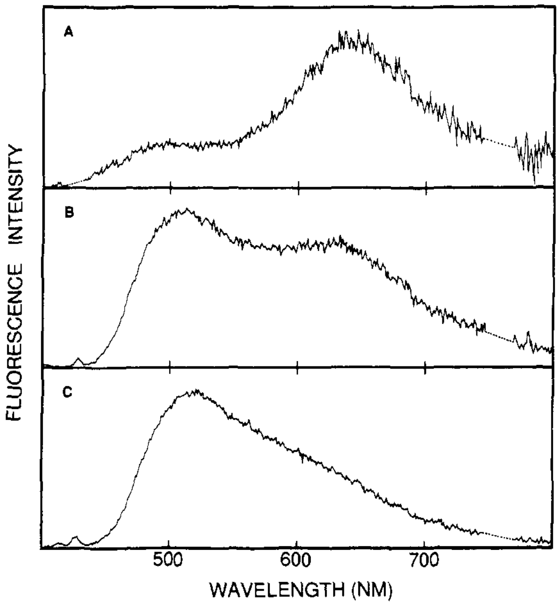


Figure 2. Corrected emission spectra for **1b** in cyclohexane (A), dichloromethane (B), and acetonitrile (C). Artifacts due to solvent Raman lines and second-order scattered excitation light have been replaced by dashed lines.

In the absence of ESIPT or intersystem crossing, **1a–d** are expected to have fluorescence lifetimes of 300–1000 ps in aprotic solvents.[7] Instead, lifetimes of about 100 ps are observed along with fluorescence efficiencies of ca. 3×10^{-3}. **1a** in polar aprotic solvents is different. Here, lifetimes are around 400–700 ps and are associated with a reduced LWE/SWE ratio, coupled with a roughly 10-fold higher fluorescence efficiency. The shortened lifetimes thus correspond to emission to the tautomeric $S_0(T)$ state, for which radiationless deactivation is more efficient.

The fluorescence dynamics of **1c** were examined at 533 and 595 nm in acetone by the fluorescence up-conversion technique.[11] The fluorescence transients both show rapid rise times (<300 fs) and ca. 83-ps decays, implying an ESIPT equilibrium established in <300 fs. The rapidity of the process indicates ultrafast proton tunneling. In fact, for certain cases, such as **1c** in 2-methylpentane, dual emission is even observed at 77 K. This suggests that non thermally assisted proton delocalization due to proton tunneling is at least partly responsible for the dual emission, as in the case of 1,5-dihydroxyanthraquinone[5] (i.e., $S_1(N)$ and $S_1(T)$ in Scheme I are the same state). It is interesting that the ESIPT time scale is much shorter than that for polar solvation relaxation of medium-size polar molecules in acetone, i.e., 1 ps.[12] This suggests that solvation dynamics in the usual sense are not rate-limiting and that quite subtle effects are responsible for the dramatic solvent dependence of the static emission.

The results described provide evidence of a new example of ESIPT, where nitrogen acts as the proton donor. The electron density on the nitrogen can be adjusted by appropriate substitution of the acyl group. The ground-state pK_a of the amino hydrogen is related to the ratio of tautomer emissions. The solvent also has a significant influence on this ratio; in some cases, the effects are comparable to those observed for changes in substitution. The use of acylamino groups as proton donors allows for fine-tuning of the driving force and adds a new dimension for studying ESIPT reactions.

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