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'Remote' Adiabatic Photoinduced Deprotonation and Aggregate Formation of Amphiphilic *N*-Alkyl-*N*-methyl-3-(pyren-1-yl)propan-1-ammonium Chloride Salts

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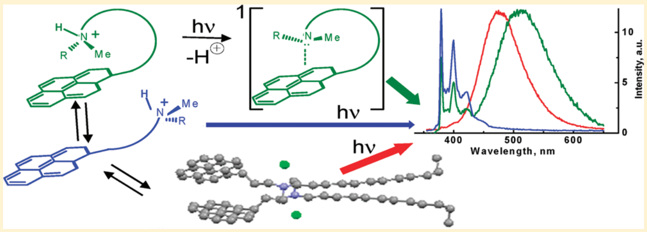
Supporting Information



ABSTRACT: The absorption and emission properties of a series of amphiphilic *N*-alkyl-*N*-methyl-3-(pyren-1-yl)propan-1-ammonium chloride salts were investigated in solvents of different polarities and over a wide concentration range. For example, at 10^{-5} M concentrations in tetrahydrofuran (THF), salts with at least one N−H bond exhibited broad, structureless emissions even though time-correlated single photon counting (TCSPC) experiments indicated negligible static or dynamic intermolecular interactions. Salts with a butylene spacer or lacking an N−H bond showed no discernible structureless emission; their emission spectra were dominated by the normal monomeric fluorescence of a pyrenyl group and the TCSPC histograms could be interpreted on the basis of intramolecular photophysics. The broad, structureless emission is attributed to an unprecedented, rapid, adiabatic proton-transfer to the medium, followed by the formation of an intramolecular *exciplex* consisting of amine and pyrenyl groups. The proposed mechanism involves excitation of a ground-state conformer of the salts in which the ammonium group sits over the pyrenyl ring due to electrostatic stabilization. At higher concentrations, with longer *N*-alkyl groups, or in selected solvents, electronic excitation of the salts led to dynamic and static *excimeric* emissions. For example, whereas the emission spectrum of 10^{-3} M *N*-hexyl-*N*-methyl-3-(pyren-1-yl)propan-1-ammonium chloride in THF consisted of comparable amounts of monomeric and excimeric emission, the emission from 10^{-5} M *N*-dodecyl-*N*-methyl-3-(pyren-1-yl)propan-1-ammonium chloride in 1:9 (v:v) ethanol/water solutions was dominated by excimeric emission, and discrete particles near micrometer size were discernible from confocal microscopy and dynamic light scattering experiments. Comparison of the static and dynamic emission characteristics of the particles and of the neat solid of *N*-dodecyl-*N*-methyl-3-(pyren-1-yl)propan-1-ammonium chloride indicate that molecular packing in the microparticles and in the single crystal are very similar if not the same. It is suggested that other examples of the adiabatic proton transfer found in the dilute concentration regime with the pyrenyl salts may be occurring in very different systems, such as in proteins where conformational constraints hold ammonium groups over aromatic rings of peptide units.

INTRODUCTION

The balance of interaction forces, both stabilizing and destabilizing, among amphiphilic molecules and between the solvent and the amphiphiles determines the degree and type of their aggregation.[1] Crudely, the amphiphile−amphiphile interactions can be separated into those affecting the hydrophilic and hydrophobic parts of each molecule, and they can lead to distinct ordering within the aggregates; even in the absence of aggregation, solvent−amphiphile interactions can affect the preferred conformations of the amphiphiles. Spectroscopic and electron microscopy techniques have been shown to be effective tools to probe both the conformational and aggregate interactions at the molecular level.[2,3]

When the amphiphile contains a luminescing group, emission spectroscopy (and especially fluorescence) can be a very sensitive tool to probe the conformational preferences and the nature of the aggregates. Here, we have attached the lipophilic lumophore, pyrene, to ammonium cationic head groups through α,ω-substitution of alkane linkers (Chart 1). Conformational preferences and aggregation in these *N*-alkyl-*N*-methyl-3-(pyren-1-yl)propan-1-ammonium chloride salts (PNn, where n is the length of the *N*-alkyl group) are driven by hydrogen-bonding, London dispersion, and electrostatic interactions, as well as by packing constraints imposed by molecular shape and solvent polarity.[4] Additionally, electronically excited pyrene derivatives may interact with ground-state molecules to form excimers and exciplexes which can be detected easily by static and dynamic fluorescence measurements.[5] Thus, when pyrenyl and amino groups are linked by short, saturated spacers, such as ethylene or propylene chains, in α-(pyren-1-yl)alkan-ω-amines, intramolecular exciplexes can be formed; virtually no exciplex fluorescence is observed when the linkers are butylene or longer spacers,[6] although excimers and intermolecular exciplexes can be formed with spacers of virtually any length.[7]

Here, we have used the static and dynamic fluorescence properties of the salts in Chart 1 to probe the dependence of molecular conformation and aggregation on salt concentration and

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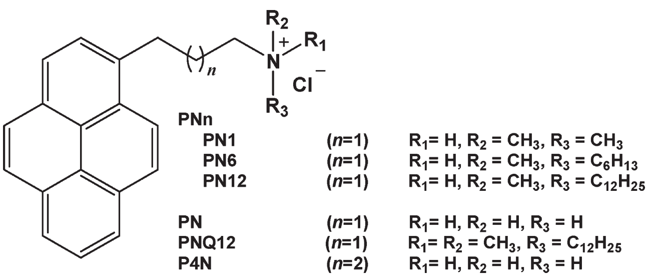
Chart 1. Structures of Amphiphilic Pyrenyl Ammonium Salts Investigated



structure (N.B., length of the spacer and the length of the *N*-alkyl group), the polarity of the solvent, and the ability of the solvent to act as a proton acceptor. With regard to the latter, at very low concentrations, where no ground-state aggregation is evident, we find that those salts with a propylene spacer and at least one N—H bond can undergo a very efficient and fast, unprecedented (to our knowledge)[8] adiabatic, proton-transfer within their excited singlet states, leading to intramolecular exciplex emissions characteristic of the corresponding *N*-alkyl-*N*-methyl-3-(pyren-1-yl)propan-1-amines.[9] Such 'remote' proton transfers are dependent on the ground-state conformations of the molecules. They compete with 'normal' pyrenyl emission from isolated molecules and excimer-like emission from excitation of ground-state aggregates and dynamically formed excited state pairs.

■ EXPERIMENTAL SECTION

Syntheses and characterization details for the molecules in Chart 1 are included in the Supporting Information file. UV—vis absorption spectra were recorded on a Perkin-Elmer Lambda-6 spectrophotometer. Steady-state excitation and emission spectra were obtained on a Photon Technology International Fluorimeter (SYS 2459); all emission spectra were normalized at the I_1 band (380 nm). Confocal images were recorded on a Zeiss LSM510META microscope with 364 nm excitation. One or two drops of each solution were placed on a Petri dish and covered with a lid immediately before measurement.

Solutions of the pyrenyl derivatives in organic solvents for single-photon counting were flame-sealed after degassing at least 5 times at $<10^{-5}$ Torr by freeze (liquid nitrogen)-pump-thaw cycles in flattened glass capillaries (0.4, 3, or 8 mm thickness; Vitro Dynamics). Before photophysical measurements were made, nitrogen was bubbled for 10 min through solutions containing water and KBr pellets were purged with nitrogen for 15 min. Fluorescence rise and decay histograms were collected on an Edinburgh Analytical Instruments FL900 single-photon counting system using H_2 as the lamp gas. An "instrument response function" was determined using Ludox as scatterer. Data were collected in 1023 channels. Deconvolution was performed by nonlinear least-squares routines that minimize χ^2 using software supplied by Edinburgh. Fits were considered acceptable when $\chi^2 \leq 1.3$ and residual plots exhibited no systematic deviations from zero. Single-crystal X-ray studies were carried out using a Siemens SMART 1000 diffractometer with an APEXII CCD detector (Bruker-AXS) and Mo Kα (0.71073 Å) radiation. The crystal structures were solved by methods using SHELX-97 and XSEED software.[10,11] The program Mercury (version 2.3) was used to open the CIF file and generate the figures.

■ RESULTS AND DISCUSSION

Syntheses of the ammonium salts were accomplished by continuous bubbling of anhydrous hydrogen chloride through solutions of the corresponding amines, followed by repeated washing with a solvent in which the amine was soluble but the salt was not (see Supporting Information). Complete transformation of the amines to their ammonium salts was confirmed by elemental analyses, mass spectra, and NMR spectroscopy. The NMR peaks of the methylene protons in the spacers and carbon atoms near the ammonium centers of the salts were shifted downfield with respect to those of the amines. An example using PN6 is shown in Figure 1. In addition, HCl gas was bubbled for 30 min into a solution of PN1 in tetrahydrofuran (THF). The THF was removed on a rotary evaporator and the residue was washed with water and dried under vacuum for 24 h. Within the limits of experimental error, the photophysical properties of the dried residue were the same as those of the original PN1.

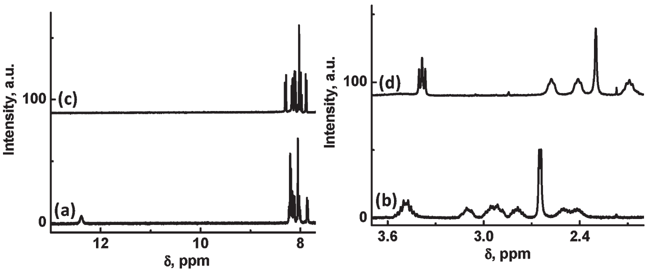


Figure 1. Aromatic (a and c) and aliphatic (b and d) regions of NMR spectra of PN6 and its precursor amine, respectively, in $CDCl_3$ at 25 °C.

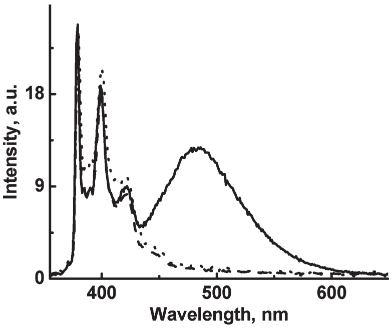


Figure 2. Normalized (at 380 nm) emission spectra of PN6 (λ_{ex} 345 nm) at 20 °C: 1×10^{-3} M (solid line) and 3×10^{-5} M (dashed line) in acetonitrile; 2×10^{-5} M in CH_2Cl_2 (dotted line).

At 10^{-5} M concentrations, solutions of the ammonium salts exhibited structured pyrenyl UV—vis absorption spectra. For example, PN6 showed a vibronic progression of peaks at 342, 326, and 312 nm in acetonitrile, CH_2Cl_2, or ethanol that is characteristic of $\pi-\pi^*$ transitions for unaggregated pyrenyl groups.[5a] Additional evidence for the isolated nature of the molecules in very dilute solutions of these solvents is found in the fluorescence spectra which give no indication of an excimeric emission (a broad, unstructured band centered ~485 nm in concentrated solutions of the salts; vide infra); only the classic, structured emission of a pyrenyl group, with peaks at 379, 400, and 422 nm, could be detected (Figure 2).

However, the emission spectra of the PNn at concentrations near 10^{-5} M in THF consisted of a broad emission band centered at 510 nm (Figure 3), *like the emission observed for the intramolecular exciplexes of the precursors of the PNn (Figure S1), the N-alkyl-N-methyl-3-(pyren-1-yl)propan-1-amines*! No such emission was observed at comparable concentrations in ethanol, CH_2Cl_2, or acetonitrile. The possibility that the 510 nm emissions

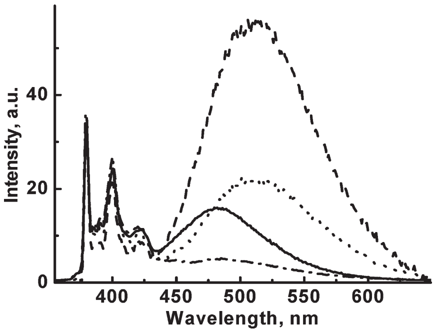


Figure 3. Normalized (at 379 nm) emission spectra (λ_{ex} 345 nm) at 20 °C of PN6 in THF at 1×10^{-3} M (solid line), 3.8×10^{-4} M (dotted line), 3.8×10^{-5} M (dash-dotted line), and 2×10^{-5} M (dashed line).

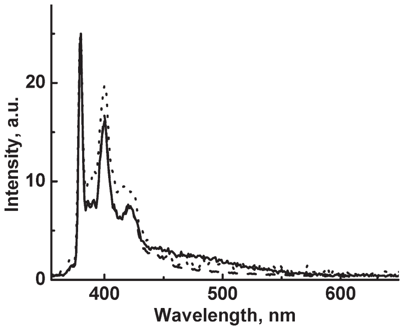


Figure 4. Emission spectra (λ_{ex} 345 nm) of 4×10^{-6} M PN (solid line), 4×10^{-5} M PNQ12 (dashed line), and 4×10^{-5} M P4N (dotted line) in THF at 20 °C.

are from ground-state dissociation of the salt is extremely unlikely because the known pK_a of triethylammonium perchlorate in THF is 14.07 (and $K_a = 2.2 \times 10^{-14}$).[12] If (as is reasonable) the PNn salts have pK_a values near that of triethylammonium perchlorate, the amount of free amine would be $<10^{-19}$ M at 10^{-5} M PNn concentrations; ground-state dissociation is negligible and the amount of amine present in THF is far too small to be detected by our fluorimeter. Thus, the 510 nm band is attributed to emission from an intramolecular exciplex.

The aggregation of other amphiphilic pyrenyl molecules has been investigated[13] and analogous behavior is expected for the pyrenyl salts in Chart 1. For example, as the concentration of PN6 in THF was increased, the relative intensity of the 510 nm peak (with respect to the monomeric emission) decreased and blue-shifted to ~485 nm (Figure 3). However, the very low intensity of the broad emission peak at the intermediate concentration, 3.8×10^{-5} M, indicates that at least one other distinct species besides the excimeric and exciplex precursors must be present as the PN6 begin to aggregate.[14]

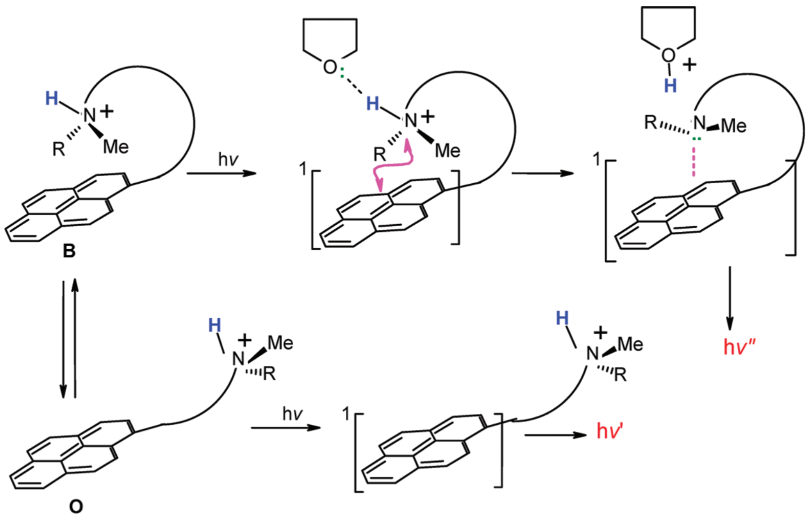
The 'Low Concentration' Regime. The origin of the exciplex-like emissions from the PNn at very low concentrations was investigated in several additional ways. The fluorescence from very dilute solutions of P4N, a salt with a butylene spacer between the pyrenyl and dimethylammonium groups, was found to contain almost no exciplex-like emission (Figure 4). This result was anticipated based upon the known dependence of fluorescence spectra from alkanes with α-aryl and ω-dimethylamino substituents on spacer length.[6,15] Also, exciplex emission from very dilute solutions of PN, a salt with a propylene spacer whose ammonium substituent has 3 hydrogen atoms on nitrogen, was discernible (but weak) while no exciplex emission could be detected from PNQ12, another salt with a propylene spacer whose ammonium substituent is quaternary (i.e., lacking a hydrogen atom on nitrogen) (Figure 4).

The first vibronic emission band (I_1 at ~378−380 nm) of the pyrenyl salts in THF was strong and sharp, and the third vibronic band (I_3 at ~390 nm) was very weak as well as poorly resolved in several cases. Although the I_1/I_3 peak-height ratio of unsubstituted pyrene is very sensitive to solvent polarity, those of alkylated pyrenes are much less so.[16] Regardless, the magnitudes of the I_1/I_3 ratios of PN1, PN4, and PNQ12 (Figure 4), 2−3, and those of the PNn (Figure 3 and Figure S1), 3−4, indicate that the local pyrenyl environments experienced by the PNn in THF are more polar than those of PN1, PN4, and PNQ12, suggesting that the two sets of salts may exist in different average conformations (vide infra).

A mechanism which is proposed to explain the role of solvent polarity on the photoinduced exciplex formation from the PNn at low concentrations is shown in Scheme 1. Density functional theory calculations at the M06/6-31G* level identified two different families of energy-minimized conformers for the PN1 cation, corresponding to the ammonium and pyrenyl groups being near (**B**, i.e., with a bent propylene linker) or far (**O**, i.e., with an extended propylene linker) (Scheme 1).[17] Although our discussion in this part will focus on the fate of the **B** conformers upon photoexcitation, a complete understanding of the role of the **B** and **O** conformers on the optical properties of ammonium salts requires studies at different concentrations and in different solvents. Salts such as the PNn exist preferentially in extended conformations (**O**) in high polarity solvents which can stabilize the charged centers of both the ammonium cation and chloride anion;[18] in lower polarity solvents, the positively charged center of nitrogen must rely more heavily on the π-electrons of the pyrenyl moiety for added stabilization,[19] and this requires that the propylene chains be bent (into an exciplex-like geometry, conformation **B**) when the interactions are intramolecular. If the electrostatic stabilizations of the ammonium cationic center by lone pairs of electrons on oxygen in THF (and related solvents) and by the π-electrons of the pyrenyl ring in the ground state are competitive, a significant fraction of the PNn molecules will exist in the bent conformation **B**. The experimental data indicate that this is the case. Furthermore, the presence of exciplex emission from salts with 1 or 3 hydrogen atoms attached to the ammonium nitrogen and its absence from the salt with no hydrogen atoms on nitrogen, PNQ12, is a clear indication that deprotonation of the ammonium group (leading to an amine group) during the excited singlet-state lifetime of the pyrenyl moiety is responsible for the exciplex emission. For deprotonation to occur on a short time scale, both the thermodynamic driving force for proton transfer must be favorable and the energy barrier to it must be very low.[8]

When completely dissolved in organic solvents such as CH_2Cl_2, acetonitrile, or ethanol at $\leq 10^{-5}$ M concentrations, these salts fluoresce with decay times ~200 ns, indicative of emission from isolated excited singlets in their **O** conformations.[20] Excitation of the isolated molecules can lead to dynamic and static (i.e., from ground-state aggregates) excimer emission with decay times typically <100 ns[21] at higher concentrations. As mentioned, at concentrations up to 10^{-3} M in these solvents, the shapes of the absorption spectra from PN6 were unaltered. However, the emission spectra contained a new, broad band with a maximum at 485 nm that is characteristic of an excimer (Figure 2).[5] Data from

Scheme 1. Proposed Mechanism for Excited-State Deprotonation of Isolated PNn Molecules in THF and Other Solvents in Which Exciplex-Like Emission Was Found



time-correlated single-photon counting (TCSPC) experiments show that excimer formation at this concentration is almost exclusively dynamic: when monitored at 380 nm (i.e., isolated emitting pyrenyl singlets), a decay time of 89 ns (98%) was found; the excimer emission monitored at 510 nm exhibited a delayed growth with a 48 ns rise time (and negative pre-exponential term) and a decay component of 89 ns, matching the monomeric emission (Figure S2); the ratio of the pre-exponential terms for the two time constants of the excimer emission was −1. Thus, in these more polar solvents, ground-state aggregation is virtually absent at PN6 concentrations up to 10^{-3} M.

The emission spectra of the PN1, PN6, and PN12 salts in THF at ∼10^{-3} M concentrations were similar to those observed in acetonitrile or ethanol; they consisted of monomer peaks and a broad excimer band with a maximum at ca. 485 nm. The decay time of the monomer emission of 3.8×10^{-4} M PN6 in THF monitored at 380 nm was 169 ns (98%), and two additional components with 50−60 and 2−3 ns rise times (i.e., negative pre-exponentials) were observed in histograms collected at 510 nm (Table S1). In the 510 nm histograms, the importance of the long-lived decay component decreased and a new component, having a 21−32 ns decay time, appeared with decreasing concentration; note data at 10^{-5} M. These data suggest that the environment experienced by excited singlets of some of the PN6 molecules changes drastically between 3.8×10^{-4} and 10^{-5} M concentrations despite the fact that the shape of the emission spectra do not. The decrease in the decay time and in the importance of the longer-lived decay component supports our hypothesis that the PNn prefer to adopt the more constrained **B** conformation at lower concentrations in solvents like THF. The emission spectra of PN1 and PN12 (Figure S3 and Table S2) at very low concentrations in THF also exhibit a broad emission band at 510 nm and a 3−4 ns short-lived decay components that are similar to the exciplex emission observed for the amine. The multiexponential fits, with more than one short-lived component, suggest that the exciplex emission involves more than two species in THF.

In P4N and PNQ12, salts with no exciplex-like emission, no negative pre-exponential component was observed in THF when emission was monitored at 450 nm (Table S3). These dynamic studies also support our attribution of the 510 nm emissions from the PNn salts to exciplexes of the corresponding *N*-alkyl-*N*-methyl-3-(pyren-1-yl)propan-1-amines.[6] The absence of a protracted rise time for the 510 nm emissions suggests that deprotonation of the ammonium salts within the excited singlet states of the pyrenyl moieties is an adiabatic process, leading directly to the excited singlet-state of the amines in their intramolecular exciplex geometry (i.e., deprotonation occurs from conformer **B**).

In general, conjugated aromatic amines and phenols are more acidic in their S_1 states than in their ground states, while aromatic heterocyclic compounds are more basic,[22] and electronic excitation is known to decrease the pK_a of ammonium salts which are conjugated with aromatic groups.[23] However, because the aromatic and ammonium parts of the PNn are *not* conjugated, a different source of the enhanced acidity of the excited singlet-states of the PNn in conformer **B**, the greater polarizability of the aromatic π-electrons, must be responsible.

This explanation can account for only a part of how and why the excited singlet-states of the amine exciplexes can be formed adiabatically. The transformation of ammonium salts to amines can be envisioned to occur by more than one pathway. An excited aromatic group has been suggested to transfer an electron intramolecularly to an antibonding orbital of an ammonium group in tryptamine, creating a putative aromatic cation-radical and a neutral, radical-centered nitrogen.[24] Dissociation of these species, leading to loss of a hydrogen atom from nitrogen, is proposed to occur via π,σ^* states.[24a,b] No exciplex emission has been detected during this process. Because excitation of the PNn in THF does produce a great deal of exciplex emission and there is no indication of chemical loss of PNn upon irradiation (which would be expected if free radicals were involved), this mechanism does not seem viable here.

An alternative pathway, involving loss of a proton from the ammonium group to the medium or chloride,[25] is proposed instead. Starting with excitation of the pyrenyl moiety in conformation **B**, a state analogous to (but not the same as) the π,σ^* singlets could be formed. The proximity of the pyrenyl and ammonium groups would facilitate orbital mixing and electron exchange, allowing the rapid[26] adiabatic formation of the pyrenyl-amine exciplexes (and proton loss). Note that the dipole moment between the pyrenyl and ammonium groups is predicted to change direction along the reaction pathway leading to proton loss. In highly polar media, where conformer **O** is favored in both the ground and excited states, the intramolecular interactions necessary for strong orbital mixing between the two groups are absent and proton loss from the ammonium group does not occur. Even if the conversion of the **O** to **B** conformer is favored thermodynamically, it is unlikely that the necessary movement of solvent molecules (which may include their translational diffusion along with the ammonium center in addition to their very fast relaxation about the excited state) and chain bending of the propylene spacer could occur within the excited singlet lifetime of the pyrenyl moieties; exciplex emission is not observed in highly polar solvents.[16]

The 'High Concentration' Regime. Although the appearances of the absorption spectra of 10^{-5} M PN1 and PN6 were unaltered when various amounts of water were added to the miscible organic solvents, the absorption spectra of PN12 were red-shifted and broadened (Figure S4A), indicating aggregation. In the PNn, the onset of aggregation depended on the length of the *N*-alkyl chain and the polarity of the solvent (vide ante). Consistent with the attribution of the red-shift to aggregation of PN12 molecules, the emission spectrum at 10^{-4} M in 1/9 (v/v) ethanol/water was dominated by a broad band centered at 485 nm (i.e., very little monomer emission was evident; Figure 5A). From confocal microscopy, the diameters of the aggregates are calculated to be ~0.8−1.1 μm (Figure 5B).[27]

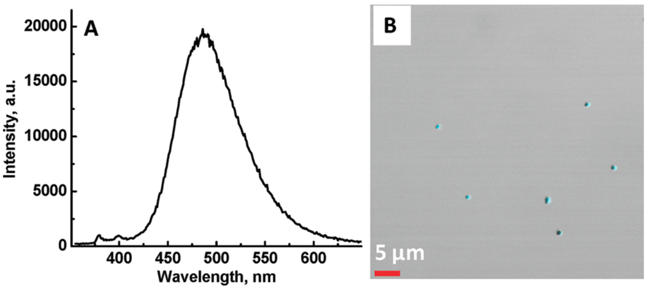


Figure 5. (A) Emission spectrum (λ_{ex} 345 nm) of 10^{-4} M PN12 in 1/9 (v/v) ethanol/water and (B) its confocal microscopic image.

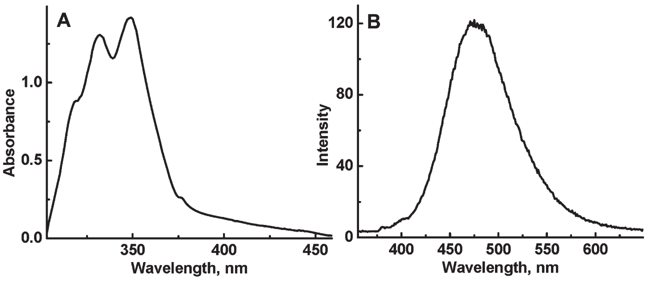


Figure 6. (A) Absorption and (B) emission (λ_{ex} 345 nm) spectra of 0.01 mol % PN12 in a KBr pellet.

Clearly, solvent polarity plays an important role in the critical concentration at which aggregation (as indicated experimentally by the excimeric emission at ~485 nm) commences. Also, as the length of the alkyl substituent on the ammonium nitrogen of the PNn increases, the ability of high polarity media to solvate effectively the salts and keep them separated decreases. This leads to the aggregation of 10^{-4} M PN12 noted in 1:9 (v/v) ethanol/water. Even at 10^{-5} M concentrations in the same solvent mixture, PN12 still exhibited a red-shifted absorption spectrum and a broad emission band centered at 485 nm that is characteristic of aggregation. The histograms from this sample could be fitted well to two decays (Table S4) with 53 ns as the major component (92−93%) and 13−19 ns as the minor one (7−8%). The absence of a growing-in component indicates ground-state aggregation rather than dynamic excimer formation. The sizes of the particles in this sample were smaller, ~0.4 μm (Figures S5 and S6B from dynamic light scattering and confocal microscopy, respectively), than those found at 10^{-4} M. We estimate the number of PN12 molecules in the average-sized particles at 10^{-5} and 10^{-4} M PN12 to be ca. 10^6 and 10^7, respectively (see Supporting Information).

When the concentrations were increased to ~6×10^{-4} M, the shapes of the absorption and emission spectra of PN12 in freshly prepared samples were unchanged, as were the absorption (Figure S4B) and emission spectra of PN1 and PN6. However, the PNn appeared to precipitate slowly: the intensities of the absorbances and emissions decreased with time although their shapes remained the same; at $\geq 10^{-3}$ M PNn, the presence of precipitated material was visible to the eye. The effects of employing smaller amounts of water to ethanol solutions of 10^{-4} M PNn were not investigated.

For comparison purposes, the absorption and emission spectra of PN12 were measured in the solid state as finely dispersed particles in a KBr pellet. The absorption spectrum was much broader and red-shifted (peak maxima at 349, 332, and 318 nm) in the pellet compared to that in solution (Figure 6A). The excitation spectrum was also broad and red-shifted, with a maximum at 350 nm (Figure S7). The emission spectrum was almost exclusively excimeric; it consisted of a broad band

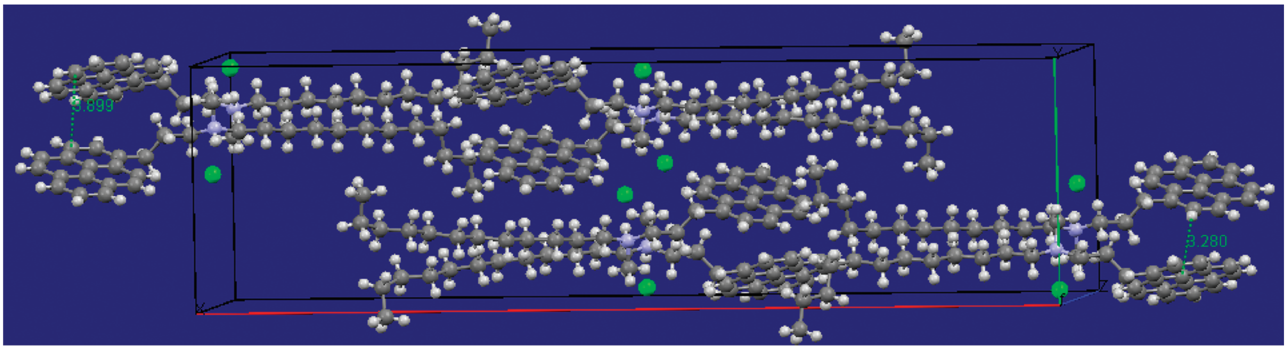


Figure 7. Crystal packing arrangement of PN12 molecules in two adjacent layers.

centered at ~480 nm (Figure 6B) which is very similar to the emission for the 1/9 (v/v) ethanol/water solution in Figure 5A. The decay constants from the solid (Table S4), 51−52 ns (38−40%) and 16−18 ns (40−44%), and the lack of a growth component, are remarkably similar to the fit in the solution as well.

Insights into the basis for the absorption and emission data in the pellet (and, by extrapolation, in the solution aggregates) were achieved when the molecular packing arrangement of PN12 was determined from a single-crystal X-ray analysis (Table S5 and Figures S8−S10). The extended molecular packing diagram shows extensive hydrogen-bonding interactions among ammonium head groups which lead to a head-to-tail orientation of the two PN12 molecules in a unit cell and close contacts among pairs of pyrenyl groups (Figure 7). Although pyrenyl groups of molecules in adjacent layers are tilted with respect to each other, small motions initiated by electronic excitation can bring them into geometries amenable to excimer formation. The closest contact between pyrenyl groups is ~3 Å (Figure 7 and Figure S10). In addition, a hydrogen atom on the central methylene of one molecule is within 2.84 Å of a carbon atom of the pyrenyl moiety in a neighboring molecule. Small changes in the orientation of these two parts upon electronic excitation may aid the movement of the pyrenyl groups into an excimeric geometry as well. Regardless, the packing arrangement of the pyrenyl groups in the aggregates detected by confocal microscopy and dynamic light scattering and that found in the crystal must be very similar.

CONCLUSIONS

The absorption and emission spectra have provided evidence for the nature of inter/intra-molecular interactions of the pyrenyl amphiphiles in Chart 1. At relatively high concentrations of the PNn and in poor Lewis base solvents, only characteristic monomeric and excimeric emissions of pyrenyl excited singlet states are detected. However, in better Lewis base solvents, such as THF, photoexcitation of the PNn leads to rapid, adiabatic proton transfer and exciplex emission from the corresponding *N*-alkyl-*N*-methyl-3-(pyren-1-yl)propan-1-amine (i.e., the PNn from which a proton has been lost). The data indicate that the ability of the adiabatic process to occur depends on the ability of the solvent (or chloride anion) to accept a proton as well as its ability to promote the formation of a ground-state conformer of the PNn which places the ammonium cation center over the pyrenyl π-electron cloud. We conjecture that excitation of PNn conformers in which the ammonium center is held far from the pyrenyl π-electron cloud does not lead to proton transfer and exciplex emission by the corresponding amines because emission from the isolated pyrenyl excited singlet states is faster than the rate at which the molecules can adopt an appropriately bent conformation. Although exciplex emission from excitation of similar ammonium salts has been not reported, we suggest that analogous processes involving 'remote' proton transfers may occur in some proteins and other conformationally constrained systems.[28]

The length of the *N*-alkyl group of the PNn and solvent polarity are important as well in determining the balance between monomeric and aggregates. For example, aggregates of PN12 (i.e., the PNn with the longest *N*-alkyl chain and, therefore, the most hydrophobic PNn) are formed even at 10^{-5} M concentrations in a very polar solvent such as 1/9 (v/v) ethanol/water. Comparison of the static and dynamic excimeric emission characteristics of PN12 in the micrometer-range particles in the polar solvent and in the solid (neat) state suggests similar molecular packing arrangements. From a single-crystal X-ray analysis of the latter, pyrenyl groups are within ~3 Å in adjacent layers. Thus, small motions, perhaps facilitated by excitation, can lead to excimeric species.

Although the research here identifies the gross nature of the excited state processes that occur in the individual PNn and their aggregates, how the balance between them can be altered by structural modifications of the PNn or changes in solvent and concentration, many very important details concerning these processes remain to be revealed. We believe that a large range of other aromatic amphiphiles with other types of 'remote' groups capable of donating a proton also undergo analogous adiabatic proton losses in their excited states. In the future, we intend to investigate the rate of proton loss from the PNn and rate of exciplex formation of the corresponding amines, the influences of temperature[29] and different anions and anion concentrations (added as inorganic salts) on these processes. Also, we will better calibrate the conformational changes between **B** and **O** and the excimer/exciplex interplay by 'titrating' the emission carefully as a function of PNn concentration, *N*-alkyl chain length, and solvent polarity.[30]

ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Synthesis and instrumentation details; additional spectra and images; details of PN12 single crystals and fluorescence lifetime data. This material is available free of charge via the Internet at http://pubs.acs.org.

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