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Excimer Formation in the Interlayer Region of Arene-Derivatized Zirconium Phosphonates

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Metal phosphonate systems comprise a fruitful area of research applications in many fields of solid-state inorganic chemistry.[1] The interlayer region of zirconium phosphonates provides an ideal environment for the investigation of the photochemistry and photophysics of molecular species because of the physical constraints and the two-dimensional nature of the environment it provides. A number of studies to date have been focused on the behavior of species interacting with the layered solid.[2−10] Photophysical behavior of the pendant groups themselves, as part of a zirconium phosph(on)ate system (see graphic in Table of Contents), is a more unusual phenomenon.[11−14] Because of the long-term impact of these materials in the area of photochemistry and spectroscopy, we have embarked on an exploration of excimer formation in an interlayer environment.

Structural features of zirconium phosphonates, and specifically the interlayer *d* spacing as a consequence of conformational degrees of freedom of pendant groups, have recently been explored in our laboratory.[15,16] Knowledge of these structural details provoked the belief that the arrangement of aromatic rings may force excimer formation within the interlayer of these solids. Furthermore, it was thought that the size, conformational degrees of freedom, and electronic properties of the pendant groups may direct excimer formation to different extents. Presently, we would like to report the initial results of this project: the bis(2-anthracene) and bis(2-naphthalene) compounds. As will be shown, these two prototypical systems exhibit excimer formation to a strikingly different degree.

For a first-order investigation of such properties, the relatively simple techniques of absorbance and emission spectroscopy proved powerful in demonstrating the interesting photophysical behavior. The absorbance and emission spectra of the precursor phosphonic acids were also measured, in solution, for the purpose of comparison of aggregates with their corresponding isolated chromophores. To establish that the arene chromophores do not form ground-state dimers, the electronic absorption spectra of the solid must not show new, red-shifted bands as compared to its phosphonic acid (monomeric) chromophore.

Figure 1 shows the UV−vis absorption spectra of zirconium bis(2-anthracenylphosphonate) [Zr(anth)$_2$], acquired as a suspension of the powdered solid in glycerol, as well as its precursor, 2-anthracenylphosphonic acid [2-APA], obtained using a solution of concentration on the order of 10^{-5} M.

The latter spectrum is virtually indistinguishable from the absorption spectrum of anthracene. As can be seen, the solid retains its overall profile, with only a minor red-shift induced by the altered environment of the solid state, and an expected concomitant broadening.

The direct comparison establishes that there is no electronic communication, due to physical aggregation, between the arene rings in their ground electronic states. Similar results were obtained for the naphthalene-based systems: zirconium bis(2-naphthylphosphonate) [Zr(naph)$_2$] and 2-naphthylphosphonic acid [2-NPA]. To summarize, within the zirconium phosphonate interlayer the pendant aromatic rings are behaving as independent, isolated chromophores, analogous in behavior to that of the arene-phosphonic acids in solution.

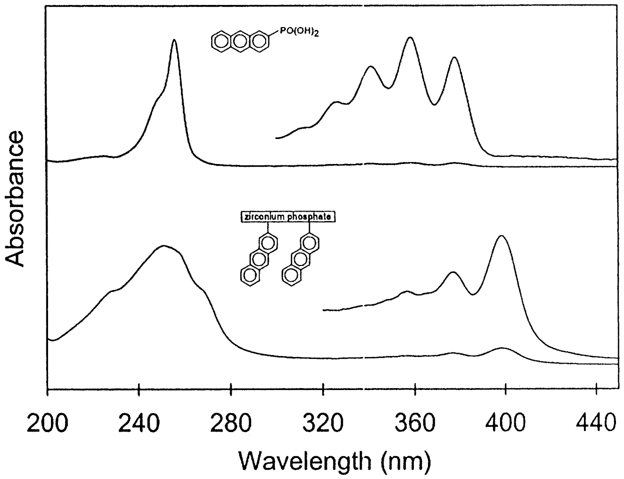

Figure 1. UV−vis absorption spectra of 2-anthracenyl phosphonic acid in methanol solution (upper) and of Zr(anth)$_2$ as a solid suspension in glycerol (lower).

As mentioned earlier, it was believed that the confining and ordered arrangement of the aromatic moieties in the zirconium phosphonate interlayer region would be conducive to the creation of excimers between the aromatic chromophores. Förster showed in the seminal work on pyrene[17] (later elaborated by Stevens and Ban[18]) that excimer formation is accompanied by the appearance of a fluorescence that is broad, unresolved, and red-shifted with respect to the emission band of the isolated chromophores.

It was found that the fluorescence spectra of the two arene-phosphonic acids in dilute solution (labeled (a) in Figures 2 and 3) generally resemble those of the unsubstituted, parent aromatic hydrocarbons. Only minor differences in the relative intensities and resolution of the vibronic transitions were observed for each of the two cases.

The fluorescence spectra of the zirconium bis(arene-phosphonate) solids were measured as suspensions in glycerol. For Zr(naph)$_2$ and its precursor phosphonic acid, Figure 2 clearly shows the addition of a new emission band in the solid. As can be seen by a comparison of these spectra, the peaks at 329, 343, and 361 nm in the spectrum of Zr(naph)$_2$ can be assigned to emission from the isolated or monomer naphthalene chromophore. The observed peak positions for the monomer emission in Zr(naph)$_2$ are red-shifted slightly (6−10 nm) with respect to the peak positions of 2-NPA; this is believed to be due to the effect of the chromophore being within the solid, crystalline, inorganic matrix environment, analogous to the shifting

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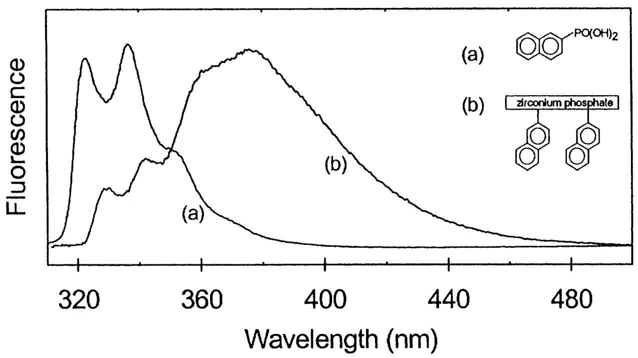

Figure 2. Fluorescence spectra of 2-naphthyl phosphonic acid in methanol (a) and of Zr(naph)$_2$ as a solid suspension in glycerol (b).

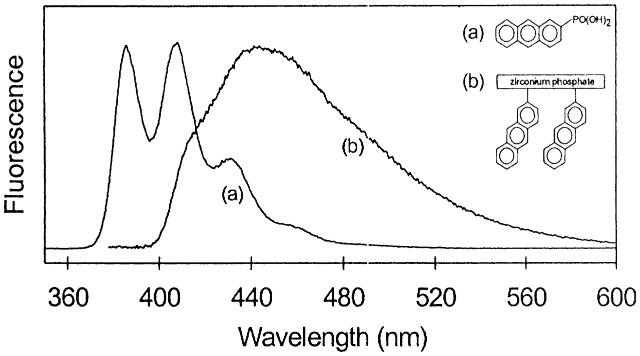

Figure 3. Fluorescence spectra of 2-anthracenyl phosphonic acid in methanol (a) and of Zr(anth)$_2$ as a solid suspension in glycerol (b).

of peaks often observed for the same molecule in different solvents. The peak at 378 nm, however, can only be attributed to emission from a naphthalene excimer in Zr(naph)$_2$. A confirmation was obtained by finding that the fluorescence excitation spectra using any of the emission peaks as the monitoring wavelength were identical to each other and resembled the absorption spectrum of 2-NPA. No new, red-shifted excitation bands were observed, which would have indicated aggregation of the chromophores in the ground electronic state. It should also be noted that the intensity of the excimer emission band appears to be larger than that of the monomer emission bands, suggesting that the quantum yield for the excimer is considerably larger than the quantum yield for monomer emission.

The fluorescence spectrum of Zr(anth)$_2$, displayed in Figure 3, trace (b), consists of a broad, structureless emission band, with a maximum at 448 nm and a minor shoulder at higher energy.

The major component of the emission band is clearly due to an anthracene excimer, because the fluorescence excitation spectra and the absorbance spectrum both exhibit the expected, monomeric behavior. Moreover, Figure 3 clearly establishes that the shoulder cannot be assigned to monomer species as it does not coincide with the 0−0 band in the emission spectrum observed for 2-APA. The emission profile indicates that the quantum yield for monomer emission is extremely small, resulting in its lack of observable emission.

Finally, the overall line shape and peak width of the Zr(anth)$_2$ excimer emission band strongly resembles that of the Zr(naph)$_2$ excimer emission band, which can be obtained via spectral subtraction of the trace (a) from the trace (b) of Figure 2, suggesting that the breadth of the excimer potential energy wells[19] are similar for the two systems.

In solution, anthracene itself is believed to form excimers, but does not display excimer fluorescence at room temperature due to very efficient photodimerization to dianthracene (covalent bonds formed between the C_9 and C_{10} positions of two anthracene molecules) for which the excimer is an intermediate. Chandross and Ferguson,[20] however, discovered that irradiation (254 nm) of frozen solutions (77 K) of dianthracene in methylcyclohexane produced closely spaced pairs of anthracene molecules which did exhibit a broad, structureless excimer emission ($\lambda_{\max} = 469$ nm). The observation that Zr(anth)$_2$ does display excimer emission at room temperature and did not show a time-dependent quenching of this excimer emission (as is observed with photodimerization), suggests that the photodimerization reaction of anthracene to dianthracene is not occurring within the solid. This is understandable considering that the bond lengths between the C_9 and C_{10} atoms of the two rings in dianthracene[20] is 1.6 Å, while the distance between adjacent anthracene rings[1] in Zr(anth)$_2$ is approximately 5 Å. The dramatic difference in the quantum yields of excimer formation for naphthalene versus anthracene is undoubtedly a result of the degree of π-overlap that is larger for the anthracene moieties than it is for the naphthalene pendant groups. Molecular modeling of these systems will shed light on the structural details that determine such overlap and are currently in progress.

We have shown that excimer formation is a readily occurring phenomenon in zirconium phosphonate compounds. While interlayer excimer formation has been observed earlier in vanadium systems,[14] the zirconium phosphonate matrix has been shown to be especially useful in its ability to tune the extent of excimer formation based on the nature of the pendant group. Experiments to discern the parameters controlling this phenomenon are currently underway in our laboratory.

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Note Added after ASAP Posting. Figure 2 was incorrectly cited as Figure 3 in the last paragraph of column one of the second page in the version posted on November 6, 2003; the corrected version posted on November 7, 2003.

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