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Effect of Pressure on the Emission Efficiencies of a Series of Phenylacetylene Dendrimers

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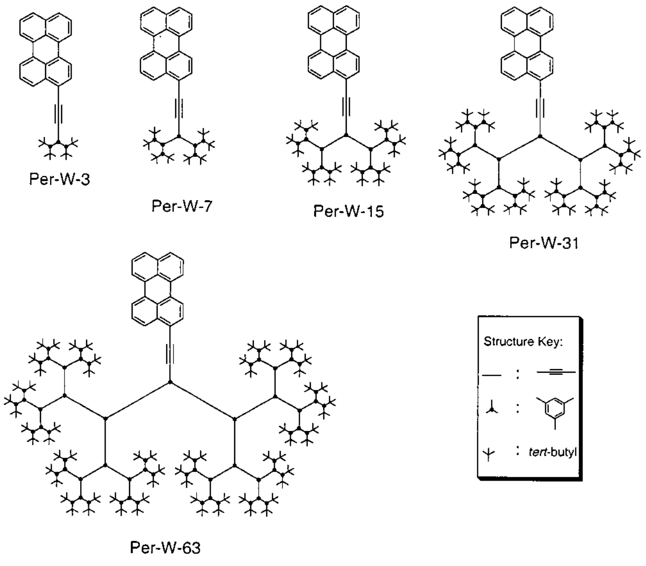
ABSTRACT: The effect of pressure to 60 kbar has been measured on the emission intensity of five dendritic macromolecules. The emission efficiency decreases with increasing pressure in all cases, but to a greater extent for the larger dendrimers. An explanation is given in terms of changing efficiency of Förster energy transfer. The efficiency is expressed in terms of an effective “Förster distance” R_0, a parameter that depends on the overlap between the donor emission and acceptor absorption. From the peak shifts, it appears that R_0 decreases significantly with pressure, and an argument is given to explain why this decrease is more important for the larger dendrimers.

Introduction

Dendrimers are highly branched macromolecules that have attracted considerable attention during the past two decades for their unique molecular architecture, novel properties, and well-defined structure.[1,2] An important feature of these highly branched polymers is that they can be site-specifically functionalized to create new materials such as light harvesting molecules or organic materials for electroluminescent devices with molecular level control.[3,4] By careful selection of the terminal groups, internal branching units, and the core, these molecules can be tailored to transfer energy along specific pathways. The transfer of energy over long distances by a multistep process demands extremely high efficiencies for the individual steps. The ability to efficiently control the flow of excitons in materials has applications in the area of sensors, electroluminescent materials for use as light-emitting diodes, and photovolatics.

In recent years, light-harvesting dendrimers have been reported from our laboratory[5] and by others.[6−9] For example, Fréchet has utilized dye-labeled poly(aryl ether) dendrimers[7a] to achieve efficient energy transfer by the Förster mechanism. Aida et al. reported large aryl ether azobenzene dendrimers that are claimed to trap infrared photons, causing cis-to-trans isomerization of the azo focal unit by transferring the excitation energy to the core.[8a]

From our laboratory a series of phenylacetylene dendrimers and their perylene-substituted derivatives have been studied with respect to their energetic absorption and funneling characteristics.[5] The intramolecular energy transfer has been quantified using steady-state as well as time-resolved fluorescence spectroscopy. The light-harvesting ability of these compounds was found to increase with increasing generation because light absorption grows faster than exciton decay by nonradiative processes. To better understand and to probe the limits of this phenomenon, we describe here the effects of hydrostatic pressure on energy transfer in a homologous series of dendritic macromolecules. Until now, the energy-transfer measurements of dendritic molecules have been investigated in liquid solutions and in self-assembled monolayers.[7b] Here the energy transfer efficiency is studied in solid polymer matrices (PMMA and PVCl). In addition to the intrinsic interest in solid polymeric media, practical electronic and optoelecronic devices involving organic molecules almost universally utilize solid polymer matrices.



Perylene-terminated phenylacetylene monodendrons.

Figure 1. Structures of the dendrimers studied.

Experimental Section

The structures of the dendrimers are shown in Figure 1. We use the notation Per-W-*X* to designate perylene-terminated monodendrons containing *X* phenylene ethynylene units. Poly(methyl methacrylate) (PMMA, medium molecular weight, $M_n \sim 55\,000$) and poly(vinyl chloride) (PVCl, high molecular weight, $M_n \sim 99\,000$) were purchased from Aldrich. The polymers were used without further purification, because neither of them gave any emission when irradiated at the excitation wavelengths.

The dendrimer and polymer were dissolved in spectral grade chloroform, and then the transparent solution was poured into a glass dish to form a blended film. After the solvent evaporated at room temperature, the film was then put in a vacuum oven for several days. The films were stored under vacuum.

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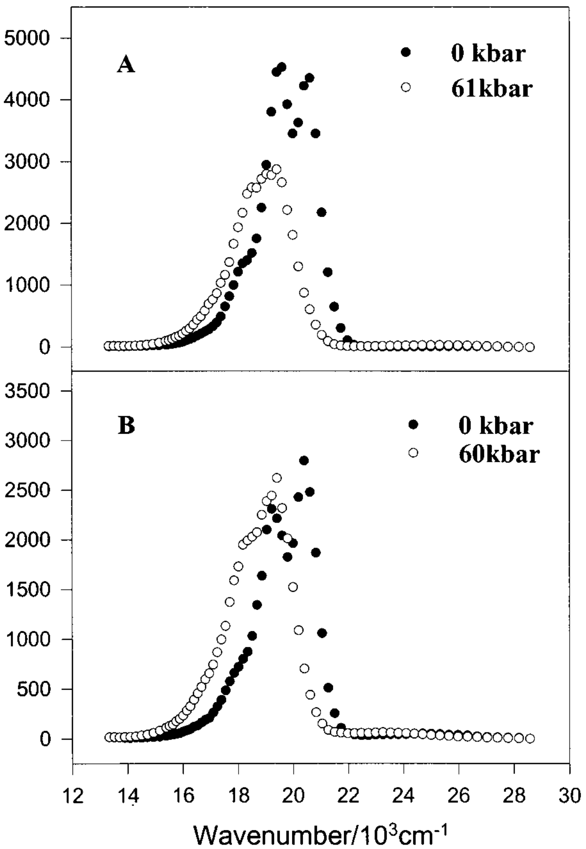

Figure 2. Spectra of Per-W-3 (A) in PMMA 0.05% and (B) in PVCl 0.025% at 1 atm (0 kbar) and at ~60 kbar.

The concentrations of dendrimer were 0.05 wt % for PMMA and 0.025 wt % for PVCl.

The high-pressure studies utilize a Merrill-Bassett diamond anvil cell (DAC). The high-pressure absorption and emission techniques have been described in detail elsewhere[10] and need not be repeated here in any detail. The steady-state emission excitation involves the 325 nm line of a He–Cd laser, which excites the tail of the dendrimer's absorption band.

Results

Figures 2–4 present typical spectra for dendrimers Per-W-3, -15, and -63 at 1 atm and at 60 kbar in solid PMMA (A) and PVCl (B). Dendrimers Per-W-7 and Per-W-31 exhibit intermediate behavior. In all cases the intensities are corrected for the change of absorption intensity with pressure at the exciting wavelength (325 nm). In the lower dendrimers (Per-W-3 and -7) there is a measurable decrease in intensity accompanied by a shift to lower energy (red shift) of −1000 to −1200 cm^{-1}, somewhat larger in PMMA than in PVCl. The spectra for perylene dissolved in the two polymers (not shown here) exhibit a peak location, structure, and red shift very similar to, but not identical with, the results for Per-W-3. The absorption spectra for perylene in the region 24 000–26 000 cm^{-1} shifted essentially identically to the emission.

The high dendrimers show a significantly larger decrease in intensity in the region 15 000–21 000 cm^{-1}, where perylene emits. This is accompanied by some growth in intensity in the region of the donor emission (24 000–26 000 cm^{-1}), distinctly more noticeable in PMMA than in PVCl.

Discussion

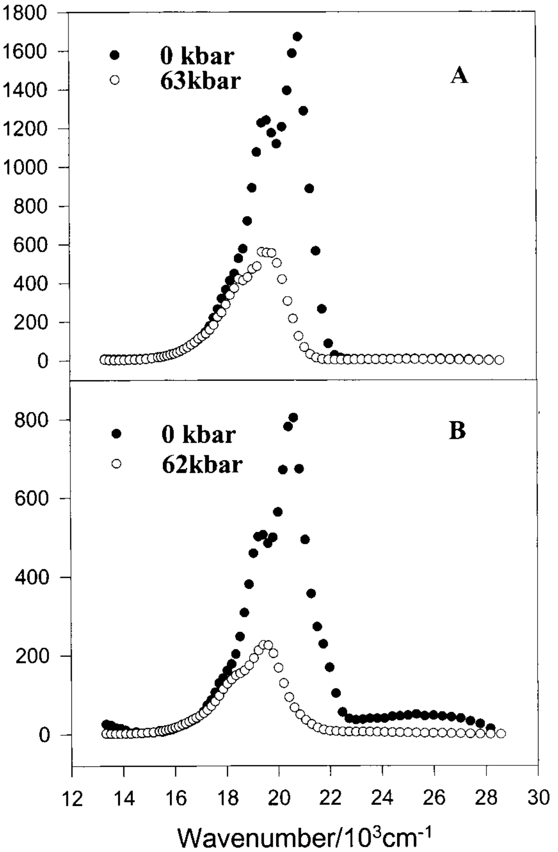

Figure 3. Spectra of Per-W-15 (A) in PMMA 0.025% and (B) in PVCl 0.025% at 1 atm (0 kbar) and at ~60 kbar.

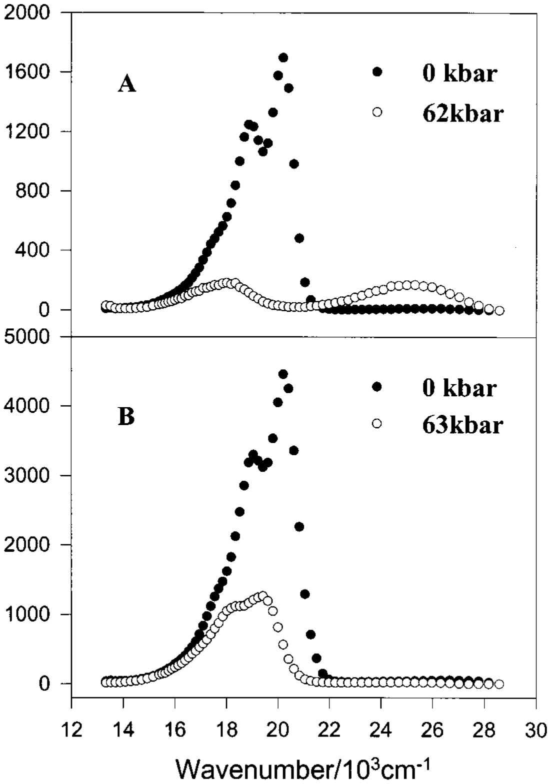

Figure 4. Spectra of Per-W-63 (A) in PMMA 0.025% and (B) in PVCl 0.025% at 1 atm (0 kbar) and at ~60 kbar.

For excitation in the region 290–330 nm (30 000–35 000 cm^{-1}), the emission from the perylene element is presumed to be excited primarily by Förster energy transfer from the absorbing phenyl rings. Since there are a series of steps with the donors having different distances from the perylene and, quite possibly, different orientation of the emitting dipoles, it is not surprising that it has not been possible to apply the equations for Förster energy transfer quantitatively to the 1 atm data[5] using the time dependence. Förster also gives a relationship for the efficiency that can be evaluated in terms of the parameter γ extracted either from the time dependence or from steady-state data.[11]

The relationship is of the following form:

$$E = \frac{{R_0}^6}{r^6 + {R_0}^6} = \frac{1}{1 + \left(\frac{r}{R_0}\right)^6} \tag{1}$$

The parameter r is some mean donor–acceptor distance, and R_0 (the Förster distance) is a parameter which establishes a 50% efficiency when $r = R_0$. While the transfer process in dendrimers is complex, involving intramolecular Förster transfer from phenyl rings at various distances from the emitter as well as possible exciton hopping, one can give a first-order treatment in terms of steady-state Förster energy-transfer theory. Although other factors may contribute to the observed behavior, the interpretation provided below is consistent with both our results and the simplest explanation of the data.

Using only steady-state data, one obtains the following equation for ${R_0}^6$:[11]

$${R_0}^6 = \frac{9000 \ln 10 \Phi_D k^2}{128\pi^5 n^4 N} \int_0^\infty \frac{f_D(\nu)\, \epsilon_A(\nu)}{\nu^4}\, d\nu \tag{2}$$

where Φ_D is the absolute fluorescence quantum yield of the donor in the absence of an acceptor and quencher, n is the refractive index of the medium, N is Avogadro's number, $f_D(\nu)$ is the emission spectrum of the donor with the area (intensity) normalized to unity, $\epsilon_A(\nu)$ is the absorption spectra of the acceptor in M^{-1} cm^{-1}, ν is the wavenumber in cm^{-1}, and k^2 depends on the orientation of donor and acceptor dipoles.

As mentioned above, trends can be extracted using changes in R_0 implied in this formulation. The donor quantum yield Φ_D may change with pressure. Where it has been measured[12] this is not a major effect. k^2 depends on the relative orientation of donor and acceptor dipoles, which may change with pressure but in an unknown manner. The change in refractive index with density is given quite accurately by the Lorenz–Lorentz equation:

$$\frac{n^2 - 1}{n^2 + 2} = \alpha\rho \tag{3}$$

where ρ is the density and α is a constant. $p-v$ data for a series of typical polymers indicate that the term n^{-4} decreases by a factor of ~0.6 in 60 kbar.

Distinctly the most important factor is the change in the overlap integral. A rigorous evaluation of the overlap integral involves measuring the emission spectrum of the donor in the absence of the acceptor and the absorption spectrum of the acceptor with no donor present.[12] In the complex case of intramolecular energy transfer involved here these measurements are not possible. The donor absorption shifts by ~-500 cm^{-1} in either medium. It can be assumed that the donor emission band shows a similar shift. The absorption and emission bands of the acceptor shift about -1000 cm^{-1} in PVCl and -1200 cm^{-1} in PMMA. Thus, a very large decrease in the overlap results as pressure is applied. The structure of the emission band at 15 000–21 000 cm^{-1} is complex, but we approximate the change in area with pressure by using the height of the smoothed band times the full width at half-maximum (fwhm). The results are given in Table 1.

Table 1. Intensity Changes and Calculated Initial Efficiency for $R^1 = 10^a$

polymer	dendrimer	int(60)/int(0) uncor	int(60)/int(0) cor^b	E_0 (calc)	E_0 (in CH_2Cl_2)
PVCl	3	0.90	1.00	1.00	0.95
	7	0.76	0.94	0.99	0.91
	15	0.35	0.47	0.87	0.95
	31	0.19	0.28	0.74	0.90
	63	0.32	0.32	0.78	0.85
PMMA	3	0.83	0.94	0.99	0.95
	7	0.73	0.90	0.98	0.91
	15	0.37	0.50	0.89	0.95
	31	0.22	0.32	0.80	0.90
	63	0.21	0.35	0.80	0.85

[a] $R^1 = R_0$(60 kbar)/R_0 (1 atm). [b] Corrected for loss in intensity due to the red shift, as described in the text.

The loss of intensity with increasing pressure has two sources: the increase in the nonradiative rate of energy dissipation due to the red shift—the energy gap law[13]—and the decrease in Förster energy-transfer efficiency. The spectrum of the perylene dissolved in PMMA and PVCl can be used to approximate the former effect. The red shift is measured and the area change estimated from the half-width and height changes as described above. This correlation of red shift and intensity change for perylene is then applied to the dendrimer data. The corrected values also appear in Table 1.

The shifts are essentially identical in all the dendrimers so the change in R_0 with pressure should be the same. However, the resulting change in efficiency is quite different depending on the initial conditions. In CH_2Cl_2 the 1 atm efficiency for Per-W-3 is estimated to be ~95% while for Per-W-63 it is ~85%.[5] As can be seen from eq 1, a large decrease in ${R_0}^6$ will have a much stronger effect on the efficiency for Per-W-63 than for Per-W-3.

Since r is an intramolecular distance, it is reasonable to assume the change with pressure is negligible. For a series of assumed values for the efficiency E at 1 atm we made calculations of $E(60)/E(0)$ for values of $R^1 = {R_0}^6(0)/{R_0}^6(60)$ ranging from 2 to 12. Using the corrected efficiency change with pressure from Table 1, we extract the initial efficiencies necessary to fit the data. These are shown for $R^1 = 10$ in Table 1. Given the approximations involved, they correspond very well with estimates for these dendrimers in CH_2Cl_2.[5] $R^1 = 8$ gives too large a spread of efficiencies, and $R^1 = 12$ gives too small a spread. Apparently, a decrease in R_0 by a factor of 1.47 ± 0.03 corresponds accurately to the data. Given the decrease in n^{-4} and the large decrease in the overlap, this is not unreasonable. The calculated 1 atm efficiencies compare quite closely with those obtained at 1 atm in liquid solution.[5]

Summary

The luminescence efficiency from a series of phenylacetylene dendrimers decreases with increasing pressure to a higher degree in the larger dendrimers. The Förster energy transfer from the phenyl rings to the emitting perylene is complex. However, an analysis indicates that the major factor is a decrease in the overlap of the donor emission with the acceptor absorption corresponding to a decrease in the "Förster distance" R_0.

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