

Figure 3. Variations of occupation numbers of natural reaction orbitals during dissociation of lowest two  ${}^1A_g$  states of ethylene.

to ethylene *under appropriate conditions*, in particular excluding competing processes.

The first excited state of the same symmetry corresponds to the coupling of two  ${}^1A_1$  methylenes to the lowest excited  ${}^1A_g^*$  state of ethylene and has the rough orbital characterization

$$(\sigma_L^2 \text{ singlet})(\sigma_R^2 \text{ singlet}) = (\sigma^2 \sigma^{*2} \text{ singlet}) \rightarrow (\sigma^2 \pi^{*2} \text{ singlet})$$

Here orbital symmetry is *not* conserved and Woodward-Hoffman rules apply. An *ab initio* MCSCF calculation of the same quality as that described for the ground state was carried out for this state as well. The variation of the optimal HCH angle, the variation of the energy along this reaction path, as well as the variation of orbital occupation numbers are also shown in Figures 1, 2, and 3, respectively. It is seen that, in spite of the replacement  $\sigma^{*2} \rightarrow \pi^{*2}$ , and in spite of rather dramatic changes in occupation numbers, *no* barrier exists if the HCH angles vary appropriately. This is so because the antibonding character of the  $\pi^*$  orbital lifts the ethylene state substantially above the dissociated species and because, in addition, a substantial  $\pi$ -orbital occupation occurs in the transition region. This latter contribution cannot be predicted from a knowledge of the reactant and product structures alone and illustrates the value of a full MCSCF approach.

The details of this work will be described in a forthcoming publication.<sup>3</sup>

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## Exciton Collection from an Antenna System into Accessible Traps

Sir:

Photosynthetic systems are known to maintain a simplicity in design by collecting light over a large set of antenna chromophores and subsequently channeling the energy into a few reaction centers, where apparatus for utilizing the photogenerated carriers is localized.<sup>1-3</sup> We have been able to mimic this effect in assemblies of thin films. Such systems open some new avenues for experimentation with the collection and utilization of photonic energy.

Figure 1a shows a typical device. The antenna chromophore is fluoroanthene (singlet energy,  $E_s = 3.14$  eV), which is distributed within a polystyrene (PS) phase that is spin coated onto a glass substrate. The trapping center is perylene ( $E_s = 2.85$  eV) at submonolayer coverage on the surface of the polystyrene. Amounts are assayed by dissolving the assemblies in xylene and performing fluorometric analysis on solutions. Fluoroanthene was contained at  $6.5 \times 10^{-9}$  mol/cm<sup>2</sup>, which represents 4.6% of the film's mass and implies an 18-Å mean spacing between molecules.

The film system was monitored by its fluorescence. The excitation beam was normal to the substrate and passed through it to the film. Emission was observed along virtually the same line by front-face optics. The absorbance was small enough that excitation was uniform. Emission spectra of fluoroanthene and perylene are shown in Figures 2a and 2b.

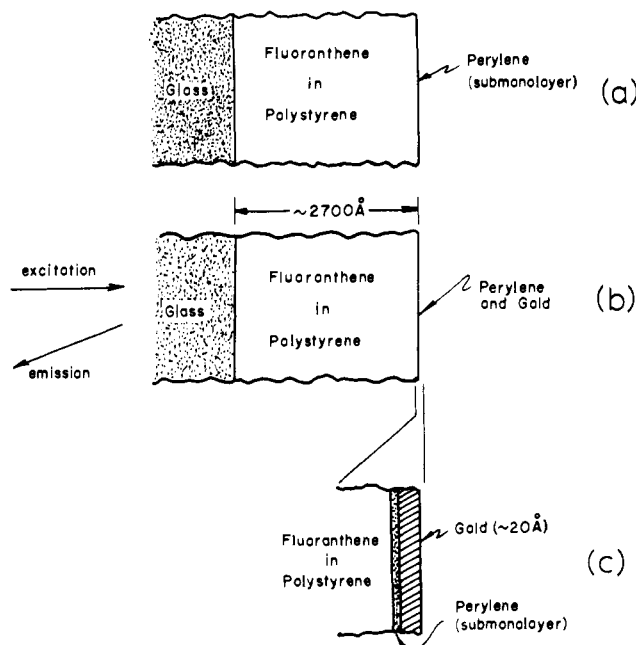
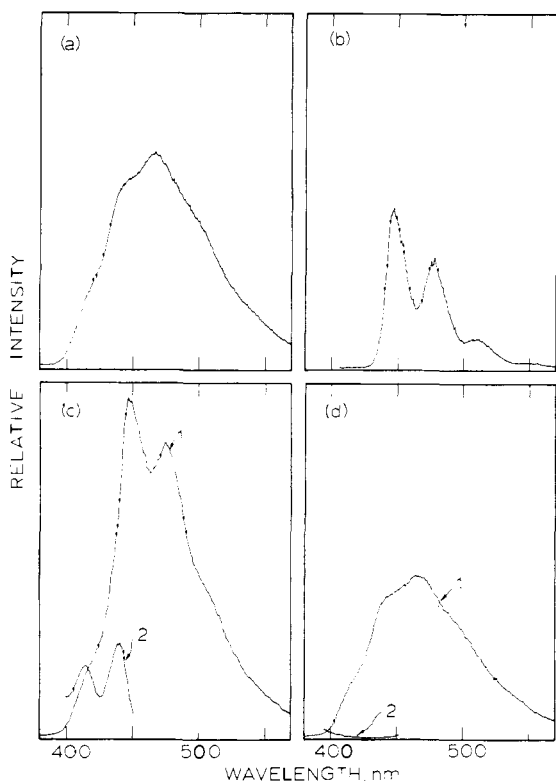


Figure 1. Schematic diagrams of structures of film assemblies: (a) two-layer system, (b) three-layer system, (c) enlarged representation of interfacial region of b.



**Figure 2.** Fluorescence emission spectra: (a) fluoranthene in polystyrene film (excitation at 337 nm); (b) perylene deposited in vacuo from a cold vapor on polystyrene (coverage, 1.6 ng/cm<sup>2</sup>; excitation at 390 nm); (c) fluoranthene in polystyrene with perylene overlay at 9.1 ng/cm<sup>2</sup> (curve 1 is emission excited at 337 nm; curve 2 shows direct excitation of perylene surface layer which emits 478 nm); (d) system in c with 20-Å gold overlay added (intensity scale is the same as c; curves 1 and 2 correspond to those in c).

Both are virtually identical with the spectra for isolated molecules in xylene solution. In particular, there is no evidence for crystalline association of perylene molecules.

Figure 2c shows the effect of the overlayer. When perylene is present, it dominates the emission spectrum, despite its being outnumbered in the example by 180:1 and despite the fact that the sample is excited in a region where perylene receives only 1% of the total excitation. The excitation spectrum for emission at 478 nm matches that of fluoranthene from 300 to 380 nm.

The intensities of the fluoranthene and perylene emission components were evaluated individually from digitized spectra. A least-squares method yielded the optimal linear combination of the pure component spectra. Perylene always quenched the fluoranthene component. For PS thicknesses of 2700 Å, the effect ranged from 9 to 30%, depending on the perylene load, which lay in the range of 1–9 ng/cm<sup>2</sup>.

These observations imply that the surface layer is being fed by energy absorbed in the fluoranthene/PS zone, and the degree of quenching by the perylene suggests that absorbers possibly as far as ~500 Å from the outer surface serve as antennas for the perylene sites. The readiest explanation involves energy migration by exciton diffusion among fluoranthene chromophores<sup>6–8</sup> until the exciton approaches the perylene plane sufficiently closely to be harvested, presumably by Förster's transfer,<sup>8,9</sup> into a perylene trap. Surface trapping effects like these have been used to evaluate exciton diffusion lengths in single molecular crystals,<sup>10,11</sup> but we are not aware of other studies involving thin films of any type.

At least two complications could apply to our results: (1) diffusion of perylene molecules into the bulk PS to produce homogeneous trapping centers, and (2) the presence of a sur-

face excess of fluoranthene so that ~20% quenching could be effected within a short range of the traps.

The first issue was explored in experiments involving overlays of gold deposited by evaporation at nominal thicknesses of 20 Å. One such system is shown in Figure 1b. Figure 2d shows that the placement of the gold selectively removed the perylene components from the luminescence spectra of the assembly. Analysis revealed that about half of the perylene molecules were lost during the deposition of the gold. Apparently they were etched by the hot impinging gold atoms. Selective total quenching of the remaining perylene indicates that it is adjacent to the gold, and not homogeneously distributed in the polystyrene. Ageing of the system over an 8-day period did not cause a reappearance of the perylene luminescence components. These experiments suggest that the structural integrity of the device is preserved over our experimental time scale, and that the perylene is indeed a surface trapping center.

A surface excess is more difficult to detect, and we are presently unable to comment further about this possibility. Experiments bearing on the issue are now underway.

The results presented here have two particularly noteworthy aspects. The first is the possible range over which energy may be harvested. A collection distance of several hundred ångströms is surprisingly large for a system of dispersed, randomly oriented chromophores. Its magnitude, if verified by additional experimentation, suggests that effective antenna systems might be created without special alignments or extremely high concentrations of the chromophores.<sup>7</sup> A second notable point concerns access to the traps. The real contribution of thin-film techniques to this problem is in the creation of trapping centers that are accessible in a way which permits the assembly of additional apparatus for utilization of the trapped energy.

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## [2 + 2] Cycloadditions of Tetraalkoxyethylenes with Ketenes: a General Route to 2-Substituted 1-Hydroxycyclobut-1-ene-3,4-diones<sup>1</sup>

Sir:

The parent acid **9** (X = H), 1-hydroxycyclobut-1-ene-3,4-dione (semisquaric acid), was reported several years ago.<sup>2</sup> Interest in **9** has increased since the discovery by Cole et al.<sup>3</sup> of potassium and sodium salts of **9** as fungal metabolites with plant growth regulating properties. These salts were named