Singlet−Singlet, Triplet−Triplet, and "Optically-Controlled" Energy Transfer in Polychromophores. Preliminary Models for a Molecular Scale Shift Register

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Received: May 8, 1998; In Final Form: June 23, 1998

The photophysics of two trichromophoric molecules have been studied by a combination of absorption, fluorescence, phosphorescence, and laser flash photolysis. TRI-1 consists of phenanthrene and naphthalene terminal chromophores joined to a central biphenyl group by methyl ester bridges. Intramolecular singlet−singlet energy transfer (SSET) between the biphenyl and terminal chromophores occurs efficiently with $k_{SSET} > 6 \times 10^{10}$ s^{-1}. Longer range SSET from the naphthalene moiety to the phenanthrene group takes place with a lower rate, $k \sim 2.5 \times 10^8$ s^{-1}. In TRI-2, the biphenyl moiety is replaced by a benzophenone group. SSET here occurs from the phenanthrene chromophore to the central benzophenone chromophore although with a significantly lower rate than the biphenyl → phenanthrene rate in TRI-1. This is likely due to the change in configuration ($\pi\pi^*$ to nπ^*) of the excited singlet states involved in the energy transfer. Triplet−triplet (TTET) energy transfer between biphenyl and the terminal chromophores is not observed as a result of a low biphenyl triplet population. That both the phenanthrene and naphthalene triplets are observed following laser photolysis and have different lifetimes and different excitation wavelength concentration ratios indicates that there is no significant TTET between these two groups on the time scale at which the triplets are decaying. This is attributed to the large interchromophore distance (∼12.5 Å) as indicated by modeling studies. In TRI-2, TTET from benzophenone to the terminal chromophores is indicated by both phosphorescence and laser flash photolysis results. Two-laser flash photolysis of the phenanthrene triplet in TRI-1 results in the production of the naphthalene triplet by the following suggested route: (i) production of the upper excited triplet state of the phenanthrene group, (ii) energy transfer to the central biphenyl moiety, and (iii) further energy transfer to the naphthalene chromophore. The utility of this two-laser behavior as the basis for the operation of an optically coupled molecular scale shift register is discussed.

Introduction

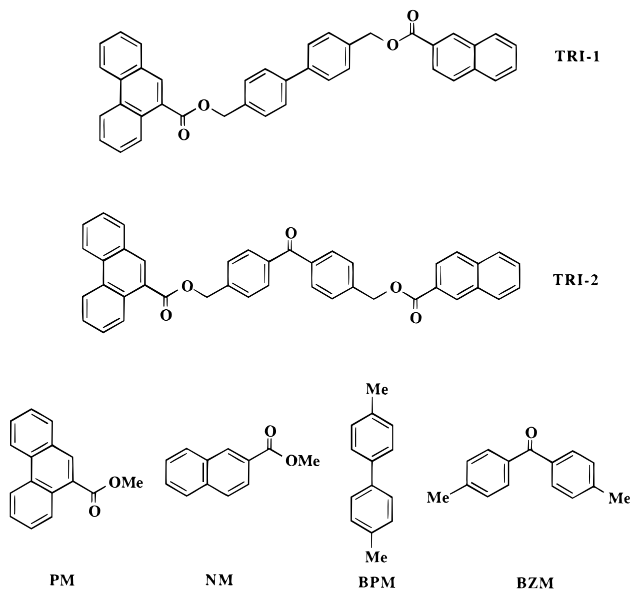
Intramolecular charge and energy transfer in bichromophores has been the subject of increasing interest in recent years.[1−4] Particular attention has been paid to the kinetics of transfer processes and how they are effected by molecular conformation, the rigidity or flexibility of the connecting bridges, and interchromophore distance. The observed relationships between the efficiency of transfer and these parameters have been used to suggest through-bond and through-solvent superexchange transfer mechanisms. In general, the through-bond mechanism seems to be favored for molecules in which the chromophores are joined by rigid saturated hydrocarbon bridges such as those synthesized and characterized by Closs,[1] Morrison,[2] Paddon-Row and Verhoeven,[3] Zimmerman,[4] and ourselves.[5] In these bridges, orbital overlap facilitating a superexchange interaction is provided by an "all-trans" arrangement of the σ bonds. Bichromophores containing flexible bridges, on the other hand, allow the chromophore−bridge−chromophore structure to sample a large number of rotational conformations, only a small number of which produce orbital overlap conducive to through-bond transfer. In these molecules, the transfer process has traditionally been regarded as a through-space interaction, with the effect of the solvent being largely ignored. However, recently Zimmt[6] has used "C-clamp" bichromophores to show the through-space mechanism is more accurately described as a solvent-mediated superexchange interaction.

More recently, larger molecules containing more than two chromophores have been studied. Morrison has incorporated singlet and triplet energy donors and acceptors on a steroidal backbone and has observed singlet−singlet and triplet−triplet energy-transfer processes occurring with reasonably large rate constants, via a through-bond mechanism.[2d−2g] Paddon Row observed rapid charge separation between the terminal chromophores in a trichromphore connected by fused norbornyl spacers,[3g] and Lindsey constructed a 9 nm long polychromophore from a series of tetraphenyl zinc porphyrin moieties connected by ethyne linkages.[7] The efficiency of singlet energy transfer through this molecule was 75%. These studies build upon recent literature that suggests large polychromophores could be used as molecular wires and devices.[8]

We report here our initial study of two trichromophoric molecules, TRI-1 and TRI-2, shown in Chart 1 along with related model compounds used in this study. We have chosen to study these molecules for several reasons including their relative ease of synthesis, the well-characterized photophysics of the individual chromophores, and the intriguing possibility that large molecules such as these compounds may eventually be used as molecular scale devices. As it turns out, these compounds exhibit an unexpectedly rich photophysics that includes singlet−singlet energy transfer between the central and terminal chromophores as well as between the terminal chromophores themselves. Triplet−triplet energy transfer from the central chromophore to the terminal chromophores in TRI-2 is

10.1021/jp9821782 CCC: $15.00

CHART 1



also observed. We also present preliminary evidence showing that re-excitation of the triplet state of the terminal phenanthrene chromophore in TRI-1 results in energy transfer to the naphthalene group. We discuss the relevance of this process to the operation of molecular scale devices such as a shift register.

Experimental Section

Materials and Methods. All solvents in spectroscopic and laser studies were Aldrich spectrophotometric grade and were used as received. Phenanthrene, 9-phenanthraldehye, biphenyl, 4,4′-dimethylbiphenyl, benzophenone, 4,4′-dimethylbenzophenone, naphthalene, and 2-naphthoic acid were obtained from Aldrich and recrystallized twice prior to use. All other reagents were used as received from Aldrich.

Synthesis. Flash chromatography was performed using "Baker" Silica Gel, 40 μm Flash Chromatography Packing. Melting points given are uncorrected and were measured with a capillary apparatus. ^{1}H and ^{13}C NMR spectra were obtained using a Bruker Avance 400 Digital NMR.

4,4′-Dibromodimethylbiphenyl. *N*-Bromosuccinimide[9] (1.0154 g, 5.64 mmol), 4,4′-dimethylbiphenyl (0.5173 g, 2.84 mmol), and benzoyl peroxide (26 mg, 0.3 mmol) were placed in a boiling flask fitted with a condenser and an anhydrous $CaCl_2$ hood. The solid mixture was suspended in 15.0 mL of CCl_4 and brought to a gentle reflux with stirring. The solution was refluxed overnight in order for the starting material to be completely consumed. The hot mixture was filtered through a fritted glass funnel, and the white insoluble solid was washed (2 × 5 mL) with hot CCl_4. The final yellowish solution was chilled in an ice−water bath, and the precipitate was filtered. This procedure gave 0.37 g of the pure product (38% yield). The mother liquor was reduced to a volume of 10 mL, and 5 mL of hexane was added in small portions. The precipitate formed was redissolved by heating, and the solution was allowed to reach room temperature. The crystals were filtered and washed with a few drops of cold CCl_4. This produced an additional 0.31 g of pure product (32% yield, total yield, 70%). In some cases the latter precipitate was purified by column chromatography using hexane as the starting solvent (to eliminate 4,4′-dimethylbiphenyl), and then a mixture of CH_2Cl_2/hexane. Mp: 145−146 °C. ^{1}H NMR ($CDCl_3$): 4.55 (s, 4H); 7.47 (d, 4H, 8.4 Hz); 7.56 (d, 4H, 8.4 Hz). ^{13}C NMR ($CDC1_3$): 33.68 (2C, CH_2); 127.92 (4C, $C_{3,3',5,5'}$); 129.98 (4C, $C_{2,2',6,6'}$); 137.51 (2C, $C_{4,4'}$); 140.96 (2C; $C_{1,1'}$).

(4′-Bromomethyl-4-methylnaphthoate)biphenyl. Potassium naphthoate was prepared by neutralization of 2-naphthoic acid with KOH (1 N) in ethanol, using phenolphthalein as an indicator. The solvent was evaporated, and the solid used without further purification. The salt (0.1006 g, 0.48 mmol) was suspended in 2.0 mL of HMPA in a boiling flask, and enough water was added to dissolve the acid.[10] Finally, a solution of 4,4′-dibromomethylbiphenyl (0.2060 g, 0.61 mmol) in 2.0 mL of HMPA was added drop by drop, over a 3 h period. After the addition was completed, the mixture was stirred at 25 °C for 24 h. The reaction was quenched by addition of 5% HCl (20 mL) producing a white precipitate. The suspension was extracted with ethyl ether (2 × 30 mL). The organic phases were combined, washed with 10% NaOH, H_2O, and brine, and then dried over magnesium sulfate. The solvent was eliminated to give 0.17 g of a mixture of unreacted halide and mono- and diester. The mixture was purified by flash chromatography (CH_2Cl_2/hexane) to give 77 mg (39% yield) of the pure bichromophore. Mp: 142−143 °C. ^{1}H NMR ($CDCl_3$): 4.52 (s, 2H); 5.51 (s, 2H); 7.62 (m, 7H); 7.80 (m, 7H); 8.66 (s, 1H). ^{13}C NMR($CDC1_3$): 33.77; 66.98; 125.72; 127.13; 127.79; 127.92; 127.97; 128.15; 128.65; 128.78; 129.25; 129.82; 130.00; 131.69; 137.412; 141.24; 167.08.

Potassium Phenanthrene-9-carboxylate. Phenanthrene-9-carboxaldehyde (0.1605 g, 0.78 mmol) and silver nitrate (0.4885 g, 2.8 mmol) were suspended in a mixture of 6 N NaOH (1.0 mL), water (3.0 mL), and ethanol (3.0 mL).[11] The suspension was protected from light and refluxed for 18 h. The hot solution was filtered, the solid was washed with NaOH, and the combined liquids were made acidic with HCl. The suspension formed was extracted with ethyl ether (2 × 30 mL), the organic phases were combined and dried over Na_2SO_4, and the solvent was evaporated. The product, phenanthrene-9-carboxylic acid (0.1636 g, 0.74 mmol, 95% yield), was neutralized with ethanolic KOH, as described for the naphthoate, and used without further purification.

[4′-(Phenanthrene-9-carboxylate) Methyl-4-methylnaphthoate]-biphenyl (TRI-1). In a boiling flask, (4′-bromomethyl-4-methylnaphthoate)biphenyl (0.080 g, 0.20 mmol) and potassium phenanthrene-9-carboxylate (0.0547 g, 0.21 mmol) were suspended in 4.0 mL of HMPA, and water was added drop by drop until the solid salt dissolved. The mixture was stirred at 25 °C for 24 h, and the final solution was treated as described for (4′-bromomethyl-4-methylnaphthoate)biphenyl. The crude product was purified by flash chromatography (CH_2Cl_2/hexane), yielding 44 mg (39% yield) of the diester. Mp: 138−139 °C. ^{1}H NMR ($CDCl_3$): 5.47 (s, 2H); 5.54 (s, 2H); 7.63 (m, 16H); 7.95 (m, 4H); 8.15 (d, 2H); 8.53 (s, 1H); 8.68 (m, 2H). ^{13}C NMR($CDCl_3$): 67.00; 67.08; 122.67; 123.08; 123.27; 125.72; 127.02; 127.11; 127.37; 127.46; 127.83; 127.87; 127.90; 128.63; 129.26; 129.34; 129.45; 129.81; 130.46; 131.08; 132.25; 135.74; 137.30; 137.62; 141.13; 167.08; 167.80.

4,4′-(Bis(bromomethyl))benzophenone. *N*-Bromosuccinimide (0.4967 g, 2.79 mmol), 4,4′-dimethylbenzophenone, (0.2931 g, 1.39 mmol) and benzoyl peroxide (5 mg) were placed in a boiling flask fitted with a condenser and an anhydrous $CaCl_2$ hood. The solid mixture was suspended in 15.0 mL of CCl_4 and brought to a gentle reflux, with stirring. The solution was refluxed overnight. Then the hot mixture was filtered through a fritted glass funnel, and the white insoluble solid was washed (2 × 5 mL) with hot CCl_4. The volume was reduced in half, and hexane was added, producing a precipitate. This solid was

TABLE 1: Ground-State Extinction Coefficients and Initial Excitation Distributions (ED Values) for TRI-1, TRI-2, and Model Compounds

	PM	NM	BPM	BZM	TRI-1	TRI-2
ϵ_{226}[a]	24 500	59 900	5 100	10 090	103 300	91 500
ϵ_{252}	47 800	3 600	45 100		107 500	
ϵ_{260}	34 700	4 500		42 200		84 100
ϵ_{308}	9 600	900	25	155	10 010	11 300
ϵ_{355}	400	<10		150		610
ED$_{226}$[b]						
(1) for TRI-1	27%	67%	6%	11%		
(2) for TRI-2	29%	60%				
ED$_{252}$						
(1) for TRI-1	50%	4%	46%			
(2) for TRI-2						
ED$_{260}$						
(1) for TRI-1						
(2) for TRI-2	43%	6%		51% (λ_{max})		
ED$_{308}$						
(1) for TRI-1	93%	7%	<0.5%			
(2) for TRI-2	90%	8%		2%		
ED$_{355}$						
(1) for TRI-1						
(2) for TRI-2	73%	1%		26%		

[a] Extinction coefficients have an estimated error of ±0.5% [b] Excitation distributions have an estimated error (based on composite spectra) of ±0.3%

recrystallized once more (CCl$_4$/hexane), producing 0.2251 g of product (0.61 mmol, 44% yield). There was also product in the mother liquour, which could be recovered by flash chromatography. Mp: 128−129 °C. ^{1}H NMR (CDCl$_3$): 4.54 (s, 4H); 7.51 (d, 4H, 8.3 Hz); 7.78 (d, 4H, 8.3 Hz). ^{13}C NMR (CDC1$_3$): 32.64 (2C, *C*H$_2$); 129.50 (4C, C$_{3,3',5,5'}$); 130.94 (4C, C$_{2,2',6,6''}$); 137.59 (2C; C$_{1,1'}$); 142.70 (2C, C$_{4,4'}$); 195.68 (1C, *C*═O).

(4′-Bromomethyl-4-methylnaphthoate)benzophenone. The procedure described for (4′-bromomethyl-4-methylnaphthoate)-biphenyl was followed. The monoester was purified by flash chromatography, producing 0.2479 g of pure product (26% yield). Mp: 83−84 °C. ^{1}H NMR (CDCl$_3$): 4.65 (s, 2H); 5.52 (s, 2H); 7.62 (m, 6H); 7.89 (m, 7H); 8.10 (d, 1H); 8.67 (s, 1H) ^{13}C NMR (CDC1$_3$): 33.68; 66.72; 125.18; 125.97; 126.17; 126.77; 127.35; 127.56; 127.94; 128.33; 128.77; 129.65; 130.33; 130.61; 131.09; 136.94; 137.54; 138.36; 141.10; 141.78; 166.00.

[4′-(Phenanthrene-9-carboxylate) Methyl-4-methylnaphthoate] Benzophenone (TRI-2). The procedure described for [4′-(phenanthrene-9-carboxylate) methyl-4-methylnaphthoate] biphenyl was followed. The asymmetric diester was purified by flash chromatography, producing 0.0300 g of pure product (17.3% yield). Mp: 135−136 °C ^{1}H NMR (CDCl$_3$): 5.52 (s, 2H); 5.58 (s, 2H); 7.66 (m, 9H); 7.87 (m, 9H); 8.10 (d, 1H); 8.56 (s, 1H); 8.69 (m, 3H); 8.98 (d,1H). ^{13}C NMR (CDC1$_3$): 66.06; 66.14; 122.67; 122.82; 125.19; 125.86; 126.50; 126.76; 127.02; 127.10; 127.53; 127.76; 127.79; 127.86; 128.30; 128.45; 129.38; 130.05; 130.43; 130.47; 132.47; 132.61; 132.78; 135.05; 135.54; 140.74; 166.47; 167.13; 195.76.

Absorption and Emission Spectroscopy. Ground-state absorption spectra and extinction coefficients were obtained with a Shimadzu 2100U absorption spectrometer. Fluorescence emission spectra and quantum yields were measured in nitrogen- and air-saturated acetonitrile and were found to be independent of saturating gas. Spectra were recorded with a Perkin-Elmer LS-50 spectrofluorimeter. Yields were measured using the parent aromatic molecules as standards.[12] Phosphorescence spectra were recorded with the same instrument. Samples were in 77 K 1:1 ethanol:methanol glasses.

Laser Flash Photolysis. The laser flash photolysis system has been described in detail elsewhere.[5,13] Briefly, for kinetic studies and transient absorption spectra, solutions were prepared at concentrations sufficiently large to give absorbances in the range 0.6−0.8 at the excitation wavelength. Unless otherwise noted, the solutions, contained in a reservoir, were continuously purged with a stream of nitrogen and were caused to flow through a specially constructed quartz cell (7 mm × 7 mm) by means of a peristaltic pump. This ensured that a fresh volume of solution was exposed to each laser pulse, thereby avoiding accumulation of any photoproducts. Samples were irradiated with the pulses of a Lumonics EX 510 excimer laser (308 nm; ~ 20 mJ/pulse; 8 ns pulse duration) or the frequency-tripled output of a Continuum Nd:YAG laser (355 nm, ~30 mJ/pulse, 5 ns). In two-laser studies, the 308 (or 355) nm pulse was followed, after a period of 1−2 μs, by the pulse from a flashlamp-pumped dye laser (output tuned to the particular T−T absorption maximum; ~120 mJ; 400 ns).

Calculations. To obtain minimum energy conformations of the trichromophores, conformational space was explored using ChemPlus 1.5 and the MM+ force field. The lowest energy conformations were further minimized using AM1 and PM3 parameters in the Hyperchem semiempirical option. These minimized conformations were used to obtain the spectroscopic energies with ZINDO/S parameters.

Results and Discussion

Absorption and Fluorescence Spectroscopy and Singlet−Singlet Energy Transfer (SSET). *(i) Absorption and Fluorescence Measurements.* Table 1 gives ground-state extinction coefficients for model compounds PM, NM, BPM, and BZM as well as for both trichromophores TRI-1 and TRI-2 at various wavelengths in the UV. The absorption spectra for the trichromophores are virtually identical to composite spectra constructed by adding proportional contributions from the model compounds, indicating that there is little interaction in the ground-state between the chromophores. Furthermore, ZINDO/S calculations indicate that the highest six occupied molecular orbitals and the lowest six unoccupied molecular orbitals are localized on individual chromophores. Therefore, it is likely that excitation of the localized ground state of one of the chromophores initially will result in the production of an excited state that is also localized on the same chromophore.

TABLE 2: Fluorescence Maxima, Quantum Yields, Singlet Energies and Lifetimes, and Triplet Energies for the TRI-1, TRI-2, and Model Compounds

	PM	NM	BPM	BZM	TRI-1	TRI-2
λ_{max} ($\lambda_{ex} = 226$ nm)	380, 370(sh)	344, 358.5	321	not obsd	380, 367, 346 (sh)	374 (br), 345 (sh)
λ_{max} ($\lambda_{ex} = 252$ nm)	380.5, 369 (sh)	345, 358	321.5	not obsd	381, 370 (sh) 345 (sh)	380.5, 369.5 (sh) 345 (sh)
λ_{max} ($\lambda_{ex} = 260$ nm)						381.5, 371 (sh) 344 (sh)
λ_{max} ($\lambda_{ex} = 308$ nm)	380.5, 369.5 (sh)	358.5, 345 (sh)	321.5	not obsd	381, 370.5, 346 (sh)	380.5, 370 (sh), 345 (sh)
λ_{max} ($\lambda_{ex} = 355$ nm)						381.5, 370.5 (sh)
$\Phi_{Fl}{}^{a}$	0.26	0.45	0.32			
τ_s	$10.3^{(14)b}$	$15.5^{(15)}$	$16.5^{(12)}$	$\sim 0.02^{(12)}$		
$E_s{}^{c}$ (kcal/mol)	80.0	84.0	100.1	78.4		
$E_t{}^{d}$ (kcal/mol)	58.4	59.4	65.8	68.8	58.4	58.4

[a] From refs 14, 15. [b] Extrapolated to concentration used in these experiments from published self-quenching data. [c] From fluorescence and absorption data. [d] From phosphorescence data. [e] Wavelengths quoted are ±1 nm. sh: shoulder. br: broad.

In addition, the *relative* energies predicted by ZINDO/S for the HOMO−LUMO transitions in the trichromophores are consistent with experimental absorption spectra of the models. As a result, the extinction coefficients of the model compounds at each wavelength can be used to estimate how the initial excitation is partitioned between each chromophore in TRI-1 and TRI-2. These "excitation distributions" (ED), expressed as percentages of the total excitation for each excitation wavelength, are also shown in Table 1. For example, we estimate that exposure of TRI-1 to $\lambda_{ex} = 226$ nm results in the ED values 27%, 6%, and 67% for phenanthrene, biphenyl, and naphthalene moieties, respectively. As is indicated by the ED values in Table 1, the wavelengths chosen correspond to quite different absorption conditions. Thus at 226 nm most of the incident light is absorbed by the naphthalene chromophore, while at 252 nm the phenanthrene and biphenyl chromophores have roughly the same absorbance and at 308 nm most of the excitation takes place in the phenanthrene chromophore. The effect of using these different excitation wavelengths is reflected in the results of fluorescence and phosphorescence emission measurements which, in turn, allow a detailed description of the photophysics of the trichromophores.

Table 2 shows the fluorescence maxima, quantum yields, singlet energies, and lifetimes for the trichromophores and model compounds. The quantum yields for the model compounds were independent of excitation wavelength within experimental error and agree closely with those published previously.[12,14,15] Figure 1 shows the emission spectrum ($\lambda_{ex} = 226$) of TRI-1 as well as the spectra of its associated model compounds, PM, NM, and BPM. It is apparent from these spectra that the emission of TRI-1 closely resembles that of PM, the phenanthrene model compound. An additional feature of the TRI-1 emission is a shoulder at 345 nm. The emission is quite similar at the other two excitation wavelengths although there are small, but important, differences. First, the magnitude of the 345 nm shoulder decreases with increasing λ_{ex}. Accompanying this change is a shift of the 367 nm peak to 370 nm and a decrease in the intensity of this peak relative to the other major peak at 380 nm. In effect, as λ_{ex} increases, the spectrum of TRI-1 becomes more similar to that of PM. These changes can be explained *partially* by the increase in the initial ED value for the phenanthrene chromophore with increasing wavelength. The decrease in the magnitude of the 345 nm shoulder, and the shift in the 367 nm peak as well as its decrease in magnitude with increasing λ_{ex} also correlates *roughly* with the decrease in the ED of the naphthalene group, indicating that there is a contribution to the emission of TRI-1 from this chromophore.

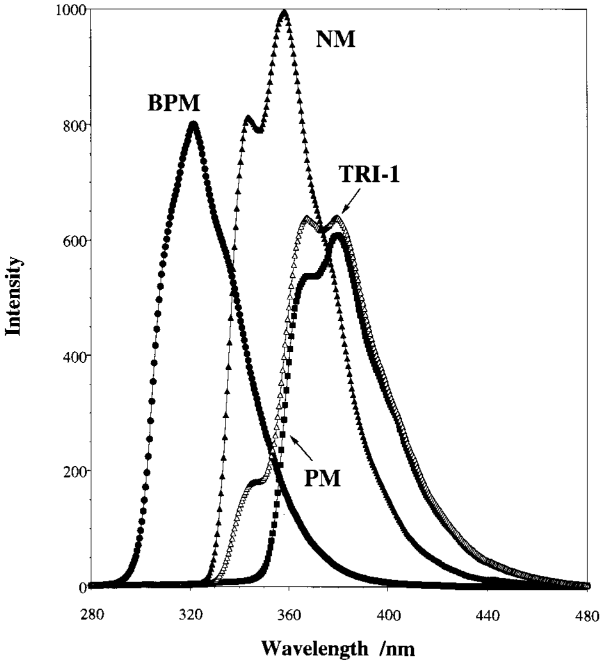


Figure 1. Fluorescence emission spectra of TRI-1 and the model compounds NM, PM, and BPM in N_2-saturated acetonitrile ($\lambda_{ex} = 226$ nm).

Figure 2 shows the emission spectrum of TRI-1 ($\lambda_{ex} = 226$ nm) along with a composite spectrum constructed by summing the emission spectra of all three chromophores in the proportion indicated by their initial ED values for this wavelength (i.e., 0.27(PM) + 0.06(BPM) + 0.67(NM)). The most striking features of the TRI-1 spectrum when compared to the composite are the absence of any emission associated with the biphenyl moiety and the weak naphthalene emission. The lack of strong naphthalene fluorescence is apparently at odds with the strong absorption of this chromophore at 226 nm. While it could be argued that the relatively small absorption expected for biphenyl at 226 nm is responsible for the lack of biphenyl emission, the same result was obtained at $\lambda_{ex} = 306$ nm, and at 252 nm where roughly half of the absorption is due to the biphenyl group.

It is clear from Figure 2 that the contribution due to naphthalene is considerably less than that expected from the ED for this chromophore (67%). To determine the actual contribution of the naphthalene emission to the TRI-1 spectrum, composite spectra were created in which no biphenyl emission was included and the relative contributions of naphthalene and

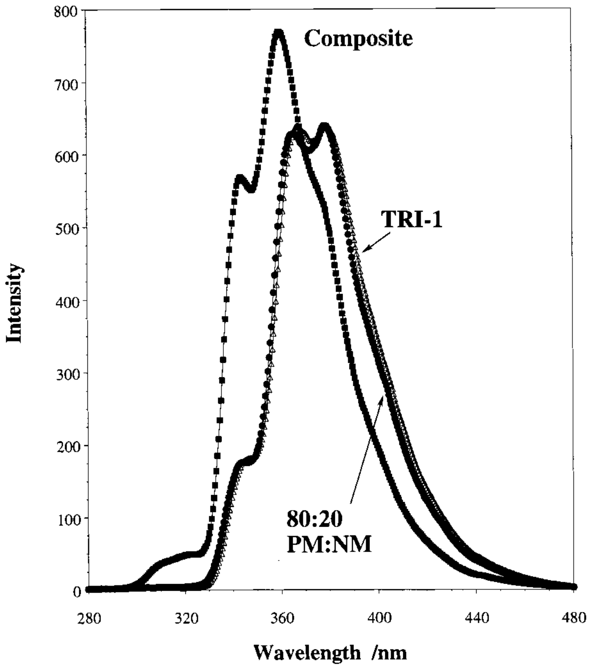


Figure 2. Fluorescence emission and composite spectra for TRI-1 in acetonitrile. Composite spectra were calculated based on: (i) (filled squares) the ED and emission spectra for the model compounds at $\lambda_{\mathrm{ex}} = 226$ nm; (ii) (filled circles) an 80:20 PM:NM ratio.

phenanthrene were varied. Figure 2 also shows a composite spectrum constructed by assuming a 80:20 ratio of emission intensities, i.e., 0.80(PM) + 0.20(NM). This particular ratio accurately reproduces the magnitude of the 345 nm shoulder. It also reproduces the blue-shifted position (relative to PM) of the 370 nm peak and the enhanced magnitude of the peak (again, relative to PM). Small changes in this ratio (more than a 0.5% change in the distribution of each chromophore) result in distinct changes in spectral shape in the composite spectrum, and for this reason we are confident that the ratio used is an accurate reflection of the relative contributions of the phenanthrene and naphthalene chromophores. This method was also used successfully to reproduce the TRI-1 spectra obtained at $\lambda_{\mathrm{ex}} = 252$ and 308 nm. For the latter wavelengths, the PM:NM ratios for the matching composite spectra were 95:5 and 98:2, respectively.

Generally, the emission behavior observed for TRI-2 paralleled that of TRI-1 in that at all wavelengths the fluorescence was similar to that of PM but also included a contribution due to the naphthalene chromophore, especially at 226 nm where naphthalene absorption is strongest. Construction of composite spectra was hampered for this compound owing to the fact that, unlike TRI-1, the emission intensities observed at all excitation wavelengths were smaller than expected from the model compound intensities and the ED values (vide infra). Therefore, it was necessary to normalize the spectra of TRI-2 to the composites in order to compare the band shapes. By following this procedure it was possible to demonstrate that the contribution to the emission due to the naphthalene group was less than expected from the ED. Thus, the PM:NM ratios were 75:25, 97:3, and 98:2 at 226, 260, and 306 nm, respectively. The extent to which the emission intensity of TRI-2 decreased relative to the model compounds was calculated by comparing the integrated area for the TRI-2 spectrum with that of the PM spectrum at 308 nm, i.e., at a wavelength where the majority of the excitation is into the phenanthrene chromophore. The ratio of the PM to TRI-2 areas was ∼7, indicating a reduction of about 7-fold in the phenanthrene emission in TRI-2.

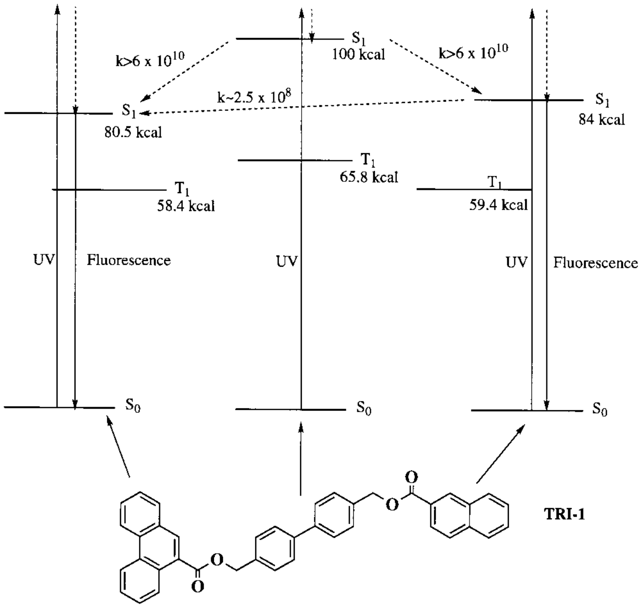


Figure 3. Energy diagram showing the intramolecular energy transfer processes in TRI-1.

(ii) Singlet−Singlet Energy Transfer (SSET). The results described above for TRI-1 are consistent with the energy transfer mechanism shown in Figure 3. The results support three intramolecular singlet−singlet energy transfer pathways: biphenyl → phenanthrene, biphenyl → naphthalene, and naphthalene → phenanthrene. Considering the singlet energies given in Table 1, it is clear that energy transfer from the biphenyl singlet to both the phenanthrene and naphthalene chromophores is thermodynamically possible as is further energy transfer from naphthalene to phenanthrene. That energy transfer occurs from the biphenyl chromophore is most distinctly illustrated by the lack of observed biphenyl emission, even at $\lambda_{\mathrm{ex}} = 252$ nm where the biphenyl group absorbs strongly. This indicates that there is an efficient quenching pathway for the biphenyl singlet state. To assign this quenching process as intramolecular energy transfer it was first necessary to rule out the possibility of photoinduced product formation. (Although CW UV irradiation of BPM in MeCN does not lead to chemical conversion, incorporation of this chromophore into TRI-1 could potentially open up new chemical decay pathways). Product studies carried out under steady-state lamp irradiation of TRI-1 failed to show any significant conversion of starting material, indicating that if there is a chemical deactivation route, it is inefficient. Intermolecular processes, including energy transfer, could also account for singlet quenching given sufficiently high concentrations of TRI-1. However, the maximum concentration of TRI-1 used in any of the fluorescence experiments was less than 10 μM. Since the singlet lifetime of BPM has been reported as ∼16 ns[12] (see Table 2), diffusion-controlled quenching could account for a maximum reduction in biphenyl emission intensity of only 0.16%, not the complete quenching observed. Of course, using the singlet lifetime for BPM in this calculation assumes that incorporation of the biphenyl group into the trichromophore does not significantly alter the rate of the intrachromophore photophysical decay pathways of the singlet state (i.e., those decay routes available to the model compound, BPM, such as ISC and internal conversion). While it is not possible to determine with complete certainty the effect of the neighboring chromophores on such processes, the lack of interaction between chromophores in the ground state argues against a large effect.

At this point, we are unable to determine exactly how the biphenyl singlet energy partitions between the naphthalene and phenanthrene chromophores, although evidence given below confirms that at least some of the energy is transferred to the naphthalene group. Modeling the conformation of TRI-1 (see Experimental Section for details) indicates that in the ground state the biphenyl−naphthalene and biphenyl−phenanthrene distances are similar (4.3 Å) as are the conformations of naphthalene and phenanthrene relative to the biphenyl group. Given previously reported results for bichromophores containing naphthalene or phenanthrene groups linked with methyl ester bridges in which singlet−singlet energy transfer was shown to proceed by a Förster-type (and therefore "through-space") mechanism,[15] it is reasonable to suggest that energy transfer from biphenyl in TRI-1 follows both possible pathways and that the relative efficiencies are roughly similar.

Evidence for energy transfer from the naphthalene moiety to the phenanthrene group can be found in the spectra generated at all three excitation wavelengths and a comparison of these spectra with the composite spectra constructed as described above. The spectrum at $\lambda_{ex} = 226$ nm provides the most direct indication of naphthalene−phenanthrene energy transfer. Clearly, the ratio of naphthalene to phenanthrene emission as indicated from the composite spectrum is considerably smaller than that expected from the initial ED. This indicates that some of the naphthalene singlet states initially produced are subsequently quenched. Since energy transfer to biphenyl is uphill energetically and there was no observed chemical conversion, this quenching must be due to either inter- or intramolecular energy transfer to the phenanthrene group. The reported singlet lifetime of the naphthalene model compound, NM, is also ~16 ns.[15] Therefore, the same argument used against intermolecular energy transfer for the biphenyl moiety can also be used here; i.e., the extent of naphthalene singlet quenching is much greater than the 0.16% quenching expected for intermolecular interaction. That at least some of the naphthalene emission was not quenched while that of biphenyl was completely quenched is consistent with the larger interchromophore distance for naphthalene−phenanthrene and the attendant smaller rate constant expected for energy transfer (vide infra). At $\lambda_{ex} = 308$ nm, similar behavior is observed. The contribution to the emission due to naphthalene as indicated by the composite spectrum is 2% whereas the ED is 8%. Thus, although when compared to 226 nm the naphthalene group absorbs considerably less, thereby producing a smaller contribution to the emission, there is even less contribution to the emission in the composite spectrum (again, we found the spectral shape of the composite to be quite sensitive to small changes in the emission ratio, and therefore we are confident that this represents a real difference).

The results obtained at 252 nm were somewhat different but can still be explained in the context of naphthalene−phenanthrene energy transfer. The absorption due to the naphthalene group in TRI-1 at 252 nm is minor (4%) compared to that of phenanthrene and biphenyl. The composite spectrum that most closely reproduces the actual emission spectrum indicates a 5% contribution due to naphthalene, i.e., an increase over the ED rather than a decrease as observed at 226 and 308 nm. This result would appear to be at odds with the energy transfer interpretation described above. However, if decay of the biphenyl singlet state partitions between naphthalene and phenanthrene, the actual concentration of naphthalene singlet states produced following 252 nm excitation will be considerably greater than 4%. Table 3 shows the ED, the distribution assuming equal partitioning of the biphenyl excitation to phenanthrene and naphthalene and the distribution of emitting chromophores as indicated by the matching composite spectra. The reduction in the naphthalene distribution from its value following biphenyl energy transfer to that indicated by the emission spectra reflects the actual efficiency of energy transfer quenching of the naphthalene singlet state.

TABLE 3: Initial, Intermediate, and Final Excitation Distributions for TRI-1

excitation wavelength (nm)	initial excitation distribution (ED)	distribution after energy transfer from biphenyl (equal partitioning)	final distribution
226	27:67:6	30:70:0	80:20:0
252	50:4:46	73:27:0	95:5:0
306	93:7:0	93:7:0	98:2:0

These fluorescence emission data also contain information on the rates of biphenyl−naphthalene−phenanthrene singlet−singlet energy transfer. In the case of energy transfer from biphenyl, the lack of any observable biphenyl emission is an indication that transfer is quite rapid. The sensitivity of our fluorimeter is such that we are able to observe emission intensities as low as 0.1% of the level that was recorded for the biphenyl model compound. Given that the singlet lifetime of the model is 16 ns ($k_s = 6.25 \times 10^7$ s^{-1}), we infer that the lower limit for the energy transfer rate constant is 6×10^{10} s^{-1} (i.e., a smaller rate constant would lead to the observation of biphenyl emission).

The extent of the reduction of naphthalene emission allows an estimate of the naphthalene−phenanthrene energy transfer rate constant. The data in Table 3 indicate that an average of 77% (admittedly with a large uncertainty) of the naphthalene emission is quenched in TRI-1. Since the singlet lifetime of the model NM is 16 ns, we estimate the naphthalene−phenanthrene energy transfer rate constant to be $\sim 2.5 \times 10^8$ s^{-1}, i.e., at least 50 times less than the biphenyl−phenanthrene (or naphthalene) energy transfer rate constant. The smaller rate constant is a reflection of the larger interchromophore distance between phenanthrene and naphthalene (12.5 Å). These two rate constants are consistent with an approximate R^{-6} distance dependence consistent with a Förster type energy transfer mechanism. We emphasize that these rate constants are estimates and therefore this conclusion must be regarded as speculative. However, as noted above, previously studied bichromophores incorporating two NM molecules and variable length spacers also showed an R^{-6} distance dependence.[15]

Figure 4 shows the energy transfer mechanisms proposed for TRI-2. Here, unlike in TRI-1, the singlet state of the central (benzophenone) group lies lower in energy than either of the terminal chromophores, making it a more likely energy acceptor than an energy donor. The fluorescence results give direct evidence for phenanthrene → benzophenone energy transfer. The noted 7-fold decrease in fluorescence intensity for TRI-2 compared to PM as measured at 308 nm indicates that a majority of the phenanthrene excited states are quenched. Since there is no observable photochemical products and as in the case of TRI-1 the concentration used is too small to allow appreciable intermolecular quenching, we attribute the quenching effect to SSET from phenanthrene to benzophenone.

In TRI-2, it is somewhat surprising that the phenanthrene fluorescence is observed at all. Since the benzophenone−phenanthrene separation in TRI-2 is approximately the same as the biphenyl−phenanthrene distance in TRI-1, one could expect comparable rates of SSET. As the biphenyl and phenanthrene model compound singlet lifetimes are comparable,

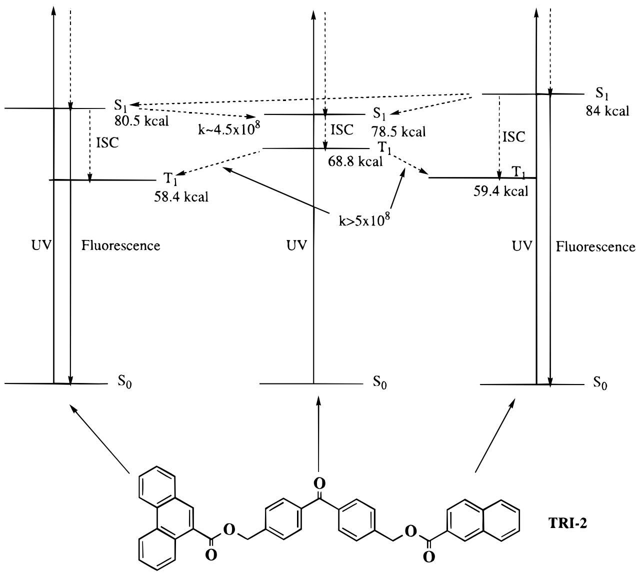


Figure 4. Energy diagram showing the intramolecular energy transfer processes in TRI-2.

this should result in no phenanthrene emission observed. There are two possible explanations for this observation. First, the proximity of the phenanthrene and benzophenone singlet energies ($\Delta E_S = 1.9$ kcal/mol) could result in a singlet−singlet equilibrium between the two chromophores. The viability of this equilibrium will depend on the magnitude of the energy transfer rate constants in both directions (which may or may not be equal) and how these compare with the ISC rate constant in the benzophenone chromophore ($k_{ISC} \sim 10^{11}$ s^{-1}). Assuming energy transfer rates that are comparable with that estimated in TRI-1 ($k > 6 \times 10^{10}$ s^{-1}) could result in an equilibrium and the observed phenanthrene emission intensity. On the other hand, $\pi\pi^* \rightarrow n\pi^*$ intramolecular SSET has been reported to be considerably slower than $\pi\pi^* \rightarrow \pi\pi^*$ SSET for similar distances of separation.[16] If this holds in TRI-2, the SSET rate constants would be too slow to support an equilibrium, and at the same time the reduced efficiency of energy transfer could account for the observation of phenanthrene emission. Preliminary studies of the effect of temperature on the observed TRI-2 emission intensity failed to show any effect on the emission intensity, arguing against an equilibrium and in favor of the second explanation. The rate constant for SSET from phenanthrene to benzophenone can be estimated from the observed fluorecence intensity and the PM singlet lifetime.[14] Thus $k \sim 4.5 \times 10^8$ s^{-1}.

Phosphorescence Spectroscopy and Triplet−Triplet Energy Transfer (TTET). *(i) Phosphorescence Measurements.* Phosphorescence spectra of the trichromophores and their model compounds measured in 77 K 1:1 ethanol:methanol glasses yield the triplet energies shown in Table 2. The spectra of the model compounds PM and NM were nearly identical indicating similar triplet energies for the two chromophores. The major feature of the spectra of TRI-1 obtained at a variety of excitation wavelengths was an emission that closely resembled that of PM and NM, although it was not possible to distinguish between the two. There was no evidence for biphenyl phosphorescence even at wavelengths where this chromophore absorbs strongly (the BPM model phosphoresces strongly[12]). For several reasons, composite spectra (analagous to the fluorescence composite spectra) could not be used to determine the relative contributions due to the phenanthrene and naphthalene chromophores. First, the combination of the small sample tube (2 mm i.d. quartz sample tubes were used) and the motion of the tube in the Dewar contributes to fairly large variations in the effective path length. In addition, solubility of the compounds vary in the low-temperature glasses contributing both to light scattering and differences in O.D. from sample to sample.

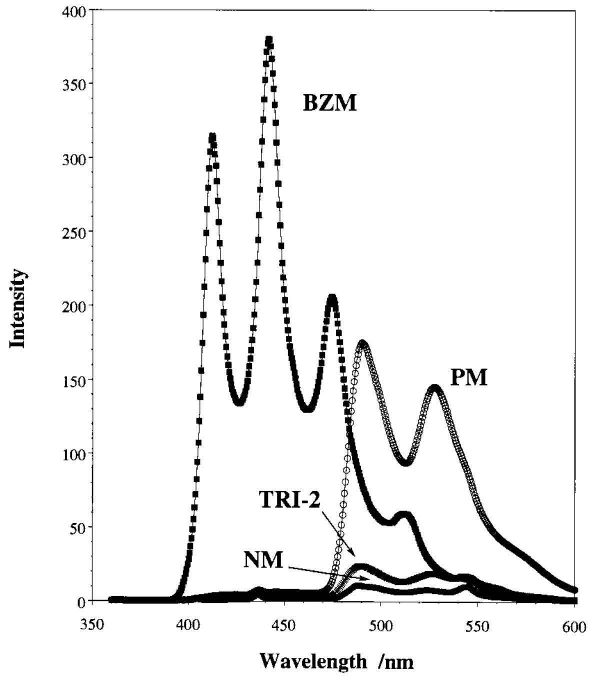


Figure 5. Phosphorescence emission spectra for TRI-2 and its model compounds obtained at 77 K in a N_2-saturated 1:1 ethanol:methanol glass. (For TRI-2, $\lambda_{ex} = 260$ nm.)

The phosphorescence spectra of TRI-2 and its model compounds are shown in Figure 5. As in the case of TRI-1, it is clear that the emission of TRI-2 is nearly identical to the spectra of the PM and NM model compounds. There was also no evidence for emission from the central benzophenone chromophore although the benzophenone model exhibits very strong phosphorescence under similar excitation conditions.

(ii) Triplet−Triplet Energy Transfer (TTET). The clearest indication of TTET from the phosphorescence measurements was found for TRI-2. In this spectrum the lack of phosphorescence emission from the benzophenone chromophore must be due to TTET to either or both of the terminal chromophores. From the triplet energies given in Table 2 and Figure 4 it is apparent that transfer to either phenanthrene or naphthalene is energetically feasible. The lack of benzophenone phosphorescence in TRI-2 is not surprising given that TTET over similar distances in benzophenone−naphthalene bichromophores has been shown to proceed efficiently with a large rate constant ($k \sim 10^{10}$ s^{-1}).[16,18] In the absence of quantitative emission intensity or lifetime data it is not possible to estimate the rate constant in TRI-2. However, from the phosphorescence lifetime for the benzophenone model, BZM ($\tau = 6$ ms),[12] a lower limit to the rate constant can be assigned on the basis of an assumed instrument sensitivity. Thus, $k_{TTET} > 1 \times 10^5$ s^{-1}. As discussed below, laser flash photolysis measurements indicate that this rate constant is actually considerably larger. Owing to the similarity of the phenanthrene and naphthalene emission spectra, it was not possible to speculate on the occurrence of TTET between these two chromophores. We are currently attempting to synthesize a trichromophore consisting of a phenanthrene−benzophenone−anthracene sequence. The triplet energy of anthracene is considerably lower than that of phenanthrene and

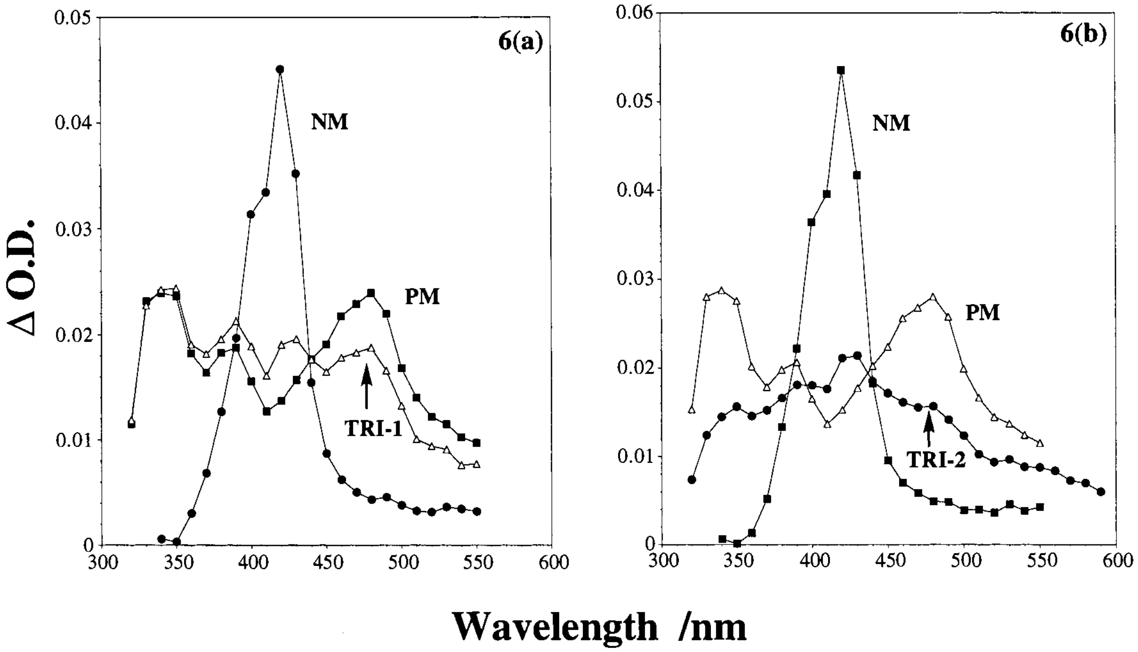


Figure 6. Transient absorption spectra obtained for TRI-1 (a) and TRI-2 (b) in N$_2$-saturated acetonitrile, 1 μs following 308 nm excimer laser photolysis.

should afford the opportunity to distinguish between the possible energy transfer pathways.

TTET in TRI-1 could not be confirmed from the phosphorescence spectra. Although there was no observed biphenyl emission, this is likely caused by the inefficiency of singlet → triplet ISC in the biphenyl chromophore relative to the efficient SSET already discussed. A comparison of the rate constants further supports this conclusion. The rate constant for ISC in the DBM model compound as indicated from yield data[12] is roughly 3 orders of magnitude less than the value of k_{SSET} estimated above.

Laser Flash Photolysis and Triplet−Triplet Energy Transfer (TTET). *(i) Laser Flash Photolysis.* Figure 6a shows the transient absorption spectra obtained following 308 nm excimer laser photolysis of TRI-1, PM, and NM in nitrogen-saturated acetonitrile. The spectrum for BPM was not included since the absorption due to the biphenyl chromophore at 308 nm was negligible compared to the other two model compounds. The spectrum was obtained ~1 μs after the laser pulse.

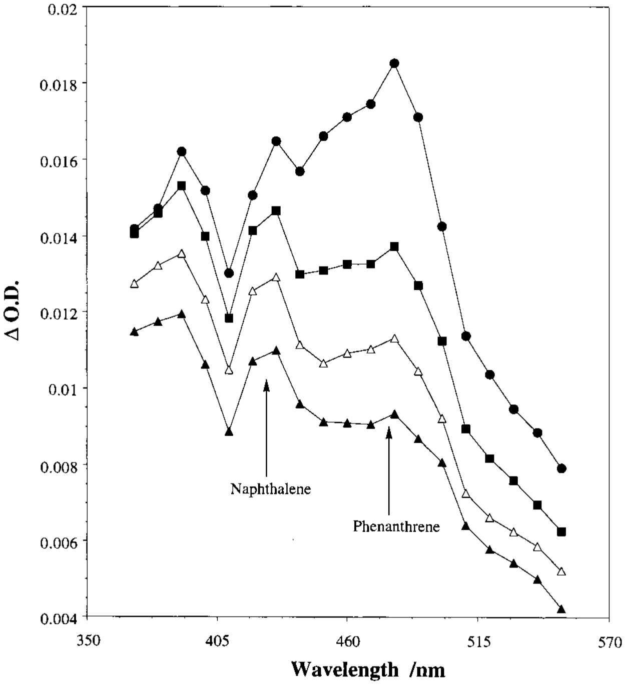


Figure 7. Transient absorption spectra of TRI-1 in N$_2$-saturated acetonitrile obtained 0.4 (filled circles), 0.8 (filled squares), 2.0 (open triangles), and 5.0 μs (filled triangles) following 308 nm excimer laser photolysis.

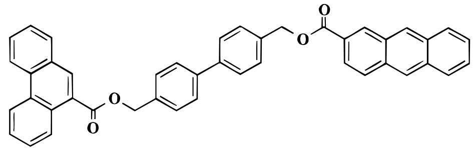
The transient spectra obtained for PM and NM were sensitive to air, similar to the T−T absorption spectra of the parent aromatic compounds, and had absorption maxima similar to those reported previously for NM and a variety of compounds similar in structure to PM.[17] Thus, they are assigned to the triplet states. The observed low wavelength maximum for PM (350 nm) does not necessarily coincide with an actual absorption maximum. Rather, strong fluorescence (as described above) in the 360−390 nm region may interfere with the T−T absorption. The spectrum obtained for TRI-1 was also air sensitive and, on the basis of the maxima, we conclude that it is a combination of the phenanthrene and naphthalene chromophore T−T absorptions. Supporting this conclusion is the observation of similar but not identical decay kinetics at 490 and 430 nm, the wavelengths associated with the model compound triplets, indicating that there are two transients present. This fact is demonstrated more clearly in Figure 7. which shows the transient spectra for TRI-1 at four different times after the laser pulse. It is clear from this figure that the 490 nm phenanthrene and 425 nm naphthalene absorptions are decaying at different rates. For further confirmation, a composite spectrum was constructed in which the spectra of NM and PM were combined in a ratio reflecting the ED. Larger errors are associated with these laser measurements than with the emission expermiments described above, and therefore, an exact match between the composite and the measured spectra was difficult to obtain. Nevertheless, there was a reasonable correspondence between the composite and measured spectra using the ED values. However, as we have discussed above, incorporating the naphthalene chromophore into TRI-1 causes a 4-fold decrease in the observed fluorescence for this moiety as a result of energy transfer to the phenanthrene chromophore. Since the fluorescence and ISC quantum yields in NM are comparable,[15,19] we also would expect a 4-fold decrease in triplet yield, leading to considerably less observed naphthalene triplet in the transient spectrum of TRI-1 than indicated from the composite spectrum. Notwithstanding the greater uncertainty in these laser measurements, such a decrease should be discernible. Possible reasons for this discrepancy are offered below.

Figure 6b shows the transient absorption spectrum obtained following 308 nm photolysis of TRI-2 in nitrogen-saturated acetonitrile. As with TRI-1, the absorption is air-sensitive and is therefore assigned to triplet states. In this case the features in the spectrum are clearly identifiable as phenanthrene and naphthalene triplets with relatively more naphthalene triplet present than in the case of TRI-1. There was no absorption observed due to the benzophenone triplet. Excitation at 355 nm also failed to yield a benzophenone triplet absorption although ∼30% of the excitation at 355 nm is absorbed by this chromophore. A composite spectrum indicated approximately 35−40% contribution due to the naphthalene chromophore, again considerably more than the ED values. This is also discussed below.

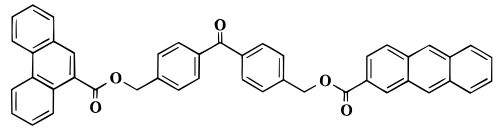
(ii) Triplet−Triplet Energy Transfer (TTET). Missing from the transient spectrum of TRI-2 is the T−T absorption due to the benzophenone chromophore, which, judging from the spectrum of BZM, should be found in the 500−600 nm region ($\lambda_{\max} \sim 545$ nm). From the ED values at 308 and 355 nm and from the emission studies performed at these wavelengths, it is clear that significant population of the benzophenone excited singlet (and therefore, also, triplet) state should occur. The absence of this T−T absorption is the clearest transient evidence for TTET in the trichromophores studied and reinforces the results obtained from the phosphorescence measurements on TRI-2. The inability to detect the benzophenone triplet even at short time scales confirms the efficiency of this process in solution and allows an estimate of a lower limit for the rate constant of TTET, $k > 5 \times 10^8$ s^{-1} (based on the time resolution of the detection system and the laser pulse duration). Further confirmation of TTET is given by the observation of the phenanthrene and naphthalene T−T absorptions, even with 355 nm excitation where the naphthalene ground-state absorption is negligible. TTET from benzophenone to the naphthalene and/or phenanthrene chromophores is expected to be rapid on the basis of previous studies of benzophenone−naphthalene bichromophores incorporating a variety of linking groups.[16,18]

While both the phenanthrene and naphthalene triplet absorptions were observed in the spectrum of TRI-2, they were not in a proportion consistent with the ED values (35−40% naphthalene triplet absorption observed for an initial excitation of 8%). However, given the SSET processes that occur upon excitation, this is not surprising. Following excitation, the majority of the excitation energy should be transferred to the benzophenone singlet state from where it efficiently forms the triplet (recall the significantly attenuated phenanthrene and naphthalene fluorescence emission intensities). Therefore, we suggest that to a large extent the amount of phenanthrene and naphthalene triplets found in the transient spectrum is a reflection of how the triplet benzophenone partitions to each of the other chromophores and actually depends little on which chromophore was originally excited. In fact, the proportion of naphthalene triplet determined from the composite spectrum indicates that the benzophenone triplet partitions roughly equally between naphthalene and phenanthrene. Assuming that the ISC efficiency in the phenanthrene group is attenuated to the same extent—a 7-fold decrease—as the fluorescence emission (i.e., the quantum yield of ISC and fluorescence in PM are comparable), equal partitioning of benzophenone triplet to phenanthrene and naphthalene would yield a 55:45 phenanthrene triplet: naphthalene triplet ratio, similar to the ratio obtained from the composite spectrum.

CHART 2



TRI-3



TRI-4

In reaching the conclusion above we have chosen to discount the potential of a TTET equilibrium between the phenanthrene and naphthalene chromophores that could be established owing to the similarity of their triplet energies. An equilibrium could contribute to a ratio of triplets dissimilar to that expected from the ED values. We rule out the possibility of an equilibrium primarily on the basis of (i) the expected large distance between the two groups and (ii) the results we have obtained for two analogous trichromophores (TRI-3 and TRI-4) shown in Chart 2.

(i) TTET follows an exchange mechanism requiring either good through-bond orbital overlap or small donor−acceptor separations for efficient transfer. Modeling studies indicate that, in the ground state, there is a 14 Å separation in TRI-2. In previous studies, the TTET rate constants in bichromophores with large interchromophore distances (14−15 Å) were 3 orders of magnitude smaller ($k < 10^2$ s^{-1}) than the triplet decay rate constants measured for TRI-2. Admittedly in these systems the linking groups were rigid and thereby ensured a large separation. In TRI-2, the methyl ester links are flexible and will allow a certain degree of conformational freedom to the chromophores. However, with the intervening benzophenone group, a relatively large separation is still assured even if significant geometry changes occur upon excitation. Furthermore, the flexible ester bridges should greatly reduce the efficiency of through-bond transfer, ensuring that the transfer follows a through-space (through-solvent) path that is more directly distance-dependent. Additional evidence against an equilibrium is provided by the transient spectrum obtained for 355 nm excitation, which shows a smaller phenanthrene:naphthalene ratio than for 308 nm photolysis. Equilibrium concentrations of the two chromophores should be independent of excitation wavelength. The relative increase in naphthalene triplet can be explained by a smaller ED for phenanthrene at 355 nm and a larger benzophenone distribution.

(ii) TRI-3 and TRI-4 are similar to TRI-1 and TRI-2 with the exception that the naphthalene group has been replaced by an anthracene group. The triplet energies of anthracene and phenanthrene are dramatically different removing the possibility of TTET between them and ruling out an equilibrium. Since the anthracene triplet lies lower in energy than the phenanthrene, intramolecular energy transfer would result in quenching of the phenanthrene triplet and production of the anthracene triplet. In fact this is what occurs. However, the decay/growth kinetics are slow and are correlated with the concentration of the trichromophore, indicating that the interaction here is intermolecular, not intramolecular.

In the case of TRI-1, the efficiency of TTET from the biphenyl chromophore could not be probed owing to the negligible absorption of this chromophore at 308 nm. In any case, the fluorescence results indicated that SSET probably depopulates the biphenyl singlet before it can undergo appreciable ISC. The poor correlation between the phenanthrene: naphthalene triplet ratio (as indicated from the composite spectrum) and the expected ratio given the SSET processes discussed above is puzzling. Certainly, if a triplet−triplet equilibrium exists, the amount of naphthalene triplet produced could be larger. However, the interchromophore distance in TRI-1 is 12 Å, nearly as large as in TRI-2, arguing against an equilibrium. Furthermore, excitation at 355 nm resulted in a transient absorption spectrum different from that at 308 nm. Also the different lifetimes for the phenanthrene and naphthalene triplets at 490 aand 430 nm, respectively, were clearly evident from spectra taken at different times after the pulse.

Preliminary Evidence for Optically Controlled Energy Transfer. Polychromophoric molecules that have demonstrated long-range charge and energy transfer capabilities have been suggested as molecular scale electronic and photonic devices such as wires, switches, diodes, shift registers, and charge coupled devices.[7,8] We have designed TRI-1 and TRI-2 so as to demonstrate the feasibility of a molecular scale shift register such as that described below.

In our view, the operation of a device such as a molecular scale shift register based on energy transfer will rely on the ability to control the flow of excitation energy within the molecule. Some of our recent work on polychromophores has focused on demonstrating that the intramolecular flow of triplet excitation energy can be controlled by the application of additional photons.[5] We visualize a molecular scale shift register somewhat analogous to that described previously,[8c] but one that is entirely optically coupled to the macroscopic regime and operates on the basis of triplet energy transfer rather than charge transfer. In such a device, a data bit is written to and read from the shift register with photons, and photons are used to shift the bit within the register. A single memory location consists of three covalently linked chromophores (A−B−C triads) having triplet energies that decrease sequentially, A > B > C. Identical triads linked together covalently in serial fashion form the shift register ((A−B−C)−(A−B−C)$_n$−...). A unique chromophore, L, is attached to the A chromophore at the end of the chromophore chain, absorbs in a region of the spectrum where the other chromophores are transparent, has a large ISC yield, and has a triplet energy greater than that of A. A "1" bit is written to the chromophore chain by (i) photoexcitation of L, (ii) population of the triplet state of L, and (iii) efficient TTET along the first triad to form the triplet of C. (Writing a "0" bit is the "null" case and involves no excitation.) Further TTET to the A chromophore of the next triad is uphill energetically, and therefore, with the exception of decay processes normally associated with triplet C alone, the excitation energy ("1" bit) is stored at this location for a finite period of time.

Shifting this triplet energy ("1" bit) into the next triad (memory location) can be achieved by re-excitation of triplet C to an upper triplet level having an energy greater than that of triplet A. The re-excitation step can be achieved with a second laser pulse firing a short time after the first pulse. The wavelength for the re-excitation is different from the original excitation wavelength and corresponds to the maximum of the T−T absorption band of C. Since the upper triplet of C is higher in energy than triplet A, re-excitation allows TTET to continue into the next triad. Each time photons of the appropriate wavelength are supplied, this "data" shift step operates resulting in the controlled flow of triplet energy from one triad to the next. By coupling each shift step with a "write" operation (writing a "1" bit or a "0" bit), an entire data string can be stored.

Finally, reading the shift register can also be optically controlled. At the opposite end of the chromophore chain from L another unique chromophore (E) is attached. E has a triplet energy lower than that of C and a unique T−T absorption spectrum. A sequence of shift steps moves the "1" and "0" bits along the chain from one location to the next until they reach E. Shifting a "1" bit to E causes excitation to its triplet state. Photoexcitation of triplet E with a photon of the appropriate wavelength results in population of the upper triplet state. Since E is also chosen for its large reverse ISC and fluorescence yields, this re-excitation step can result in strong fluorescence emission. This means that fluorescence from E coupled with the excitation of triplet E indicates that a "1" bit has been read. No emission indicates a "0" bit.

Our previous work with rigidly linked bichromophores has clearly demonstrated that intramolecular triplet energy transfer from an upper triplet state to an energy acceptor can occur efficiently.[5] In effect, these systems represent the C−A chromophore pair that connects the triads in the shift register and are directly involved in the data shift operation described above. Although upper state energy transfer was observed in these systems, they were not ideal models for demonstrating the efficiency of the proposed data shift operation because there was no "B" chromophore available to accept the triplet energy once it had been transferred to A. This means that back-transfer from the triplet of A to the lowest triplet of C can occur without any competition from a forward-transfer step. Indeed, this back-transfer step was observed in the systems studied. Molecules TRI-1 and TRI-2 are more realistic models of the triad connection since their triplet energies have the same order as the C−A−B chromophore sequence; i.e., the lowest triplet states of the terminal chromophores lie lower in energy than that of the central chromophore, but the upper triplets are higher in energy. Also, an alternative destination for the energy of triplet A is provided in chromophore C.

To demonstrate that triplet energy transfer can be optically controlled, the following experiment was performed. As already described, pulsed UV irradiation of TRI-1 results in production of both the naphthalene and phenanthrene triplet states. The triplet state of phenanthrene was re-excited approximately 1.5 μs after the initial pulse with the output of a flashlamp pumped dye laser tuned to the phenanthrene T−T absorption band (488 nm). At this wavelength, the majority of the absorption is due to the phenanthrene triplet with a minor component due to the naphthalene triplet (T−T extinction coefficients at 490 nm determined by benzophenone sensitization:[12,20] NM, 1070 ± 200; PM, 7100 ± 1400 M^{-1} cm^{-1}). The results of this two-laser excitation are shown in Figure 8. At 490 nm, the second laser pulse causes permanent depletion of the phenanthrene triplet absorption indicating that the upper triplets produced by the second pulse do not repopulate the lowest phenanthrene triplet. The fate of the upper triplets can be determined from the two-laser kinetics observed at 425 nm, the maximum of the absorption for the naphthalene triplet. Here, little or no depletion was observed. The T−T extinction coefficients for

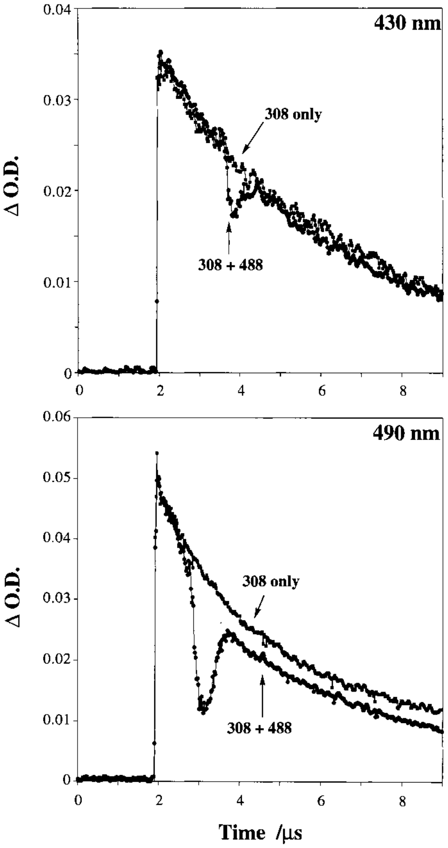


Figure 8. Kinetic profiles generated following one- (308 nm) and two-laser (308 + 488 nm) photolysis of TRI-1 in N_2-saturated acetonitrile monitored at 430 and 490 nm. The downward spike concurrent with the second laser pulse is a result of scattered light.

PM and NM were almost identical at this wavelength (extinction coefficients at 425 nm: NM, 5075 ± 800, PM, 5400 ± 900 M^{-1} cm^{-1}). This suggests that the depletion observed at 490 nm should also be observed at 425 nm unless another transient absorption is being produced concurrently with the second laser pulse. We previously have observed a similar transient effect in the two-laser photolysis of 2-acetylnaphthalene in CCl_4 and benzene.[21] That the extinction coefficients are nearly equal for the two chromophores at 425 nm strongly suggests that the loss of phenanthrene T−T absorption is being balanced by the production of naphthalene T−T absorption. In other words, the upper triplet of phenanthrene decays to form the naphthalene T_1 state. We have already concluded that there was little direct interaction between the lowest triplet states of these two chromophores on the time scale of their observed decay owing to the large distance between them. We also expect no direct interaction between the phenanthrene upper triplet state and naphthalene owing to the much shorter lifetime of the phenanthrene upper triplet state. It is therefore likely that the energy transfer process involves an initial transfer step to the much closer biphenyl chromophore and a subsequent step in which transfer proceeds from biphenyl to naphthalene. This, then, represents preliminary evidence for optically controlled energy transfer in a chromophore chain and supports the suggestion of using such molecules in a molecular scale shift register. We are currently attempting to optimize the efficiency of this process by investigating different chromophore sequences and a variety of bridging structures.

Acknowledgment. This work was supported in part by National Science Foundation Grant CHE-9617830. The authors thank the donors of the Petroleum Research Fund administered by the American Chemical Society, for partial support of this work. The authors also thank Professor S. J. Weininger for helpful discussions.

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