the absorption spectra of **2** and **3a**.[10] This indicates the absence of any ground-state electronic interaction between the electron donor (porphyrin) and electron acceptor (viologen) subunits. The UV–vis spectra of **1** and **2** are each unchanged at concentrations ranging from 2×10^{-7} M (10-mm cell) to 6×10^{-3} M (0.1-mm cell), suggesting the absence of aggregation in this concentration range. Electrochemical reduction of **1** (1.46×10^{-3} M, 0.1 M $[n\text{-Bu}_4\text{N}]\text{ClO}_4/\text{CH}_3\text{CN}$, Pt wire electrode) in a solution containing an equimolar concentration of ferrocene (as an internal standard) shows a reversible, one-electron process ($E^{0\prime} = -0.32$ V versus Ag/AgCl), which is essentially the same as observed for **3a**.[11] Electrochemical reduction of **1** results in a decrease in the 260-nm UV absorption (due to the Bz_2V^{2+} moiety) and appearance of a visible absorption (~600 nm) due to the $\text{Bz}_2\text{V}^{\cdot+}$ moiety. The 390-nm absorption of $\text{Bz}_2\text{V}^{\cdot+}$ is masked by the Soret absorption of the porphyrin. All spectral and electrochemical data for **1** are thus consistent with the conclusion that **1** represents a simple admixture of porphyrin and viologen.

A Stern–Volmer analysis shows that **3a** can effectively quench the fluorescence of **2**.[12] Quenching presumably occurs by electron transfer with a value for $k_q\tau$ of 46 M^{-1}. **1** exhibits diminished fluorescence ($\Phi_{\text{rel}} = 0.74$) compared with **2** ($\Phi_{\text{rel}} = 1.0$).[13] The decay of the fluorescence of **1** and **2** was monitored following pulsed-laser excitation at 337 nm.[14] This experiment directly gives lifetimes of 5.3 ± 1.0 ns for **1** and 9.0 ± 1.0 ns for **2**. The lifetimes are independent of concentration in the range 2.9×10^{-6}–2.9×10^{-4} M, thereby ruling out static quenching due to aggregation. Given that the shorter lifetime of **1** relative to **2** is due to electron transfer (vide infra), we calculate a rate constant for electron transfer $k_{\text{et}} = 1/\tau_{\text{P-V}} - 1/\tau_{\text{P}} = {\sim}8 \times 10^7\ \text{s}^{-1}$. This relatively small value of k_{et} is consistent with the low driving force ($\Delta G^0 \sim -0.4$ eV)[15] and the large distance of the electron transfer.[2d,5,16]

For the RR studies, we employed the pulsed Raman spectrometer described previously.[6b,c] A single 10-ns pulse serves to both photoexcite the sample and perform the Raman scattering experiment. If electron transfer occurs within the pulsewidth, the charge separated intermediate can be observed by RR spectroscopy. Pulsed-laser excitation (354 nm, 10 ns pulse, 3 mJ per pulse at the sample, 10 Hz repetititon rate) of a 2.91×10^{-4} M solution of **1** in CH_3CN yields a RR spectrum which contains all of the bands appearing in the RR spectrum of porphyrin **2**, plus an additional strong band at 1664 cm^{-1}, Figure 1. The new band corresponds precisely to the most intense band in the RR spectrum of an authentic sample of $\text{Bz}_2\text{V}^{\cdot+}$ (prepared either chemically with Zn dust or electrochemically). However, the band at 1664 cm^{-1} is also very close to the most intense band (1656 cm^{-1}) in the weakly resonance-enhanced Raman spectrum of the nonreduced viologen, Bz_2V^{2+} (**3a**). Two additional experiments remove any ambiguity regarding the assignment of the 1664-cm^{-1} band. First, the RR spectrum of a sample of **1** reduced by one electron, prepared by bulk electrolysis of **1** (1.46×10^{-4} M, 0.1 M $[n\text{-Bu}_4\text{N}]\text{ClO}_4/\text{CH}_3\text{CN}$; -0.5 V versus Ag/AgCl, Pt foil electrode), displays a band at precisely 1664 cm^{-1}, characteristic of $\text{Bz}_2\text{V}^{\cdot+}$. Second, a solution containing a mixture of **2** (3.02×10^{-4} M) and **3a** (2.87×10^{-3} M) gives a RR spectrum containing both Bz_2V^{2+} (1656 cm^{-1}) and $\text{Bz}_2\text{V}^{\cdot+}$ (1664 cm^{-1}). We thus conclude with certainty that the feature at 1664 cm^{-1} in the RR spectrum of **1** is due to $\text{Bz}_2\text{V}^{\cdot+}$. Moreover, this experiment shows the fluorescence quenching of **2** by **3a** to occur via excited-state electron transfer. Since the UV–vis spectra and fluorescence lifetime measurements rule out aggregation and since bimolecular processes in homogeneous solution cannot account for either the steady-state (Φ_0/Φ) or dynamic (τ_0/τ) quenching values of **1** compared to **2**, we conclude that the excited-state electron transfer in **1** to give $\text{Bz}_2\text{V}^{\cdot+}$ is an *intra*molecular process. We have not yet characterized spectral features attributed to the oxidized porphyrin center.

In summary, excitation of porphyrin–viologen **1** leads to intramolecular electron-transfer quenching of the porphyrin singlet excited state. For related porphyrin–viologen molecules it has already been established that the triplet excited state does yield electron transfer to the linked viologen.[2c] These findings are necessary first steps in designing photosensitive interfaces for optical energy conversion. Derivatives of **1** have been prepared to orient the molecules on a surface and to explore interfacial excited-state electron transfer.[17]

Acknowledgment. We thank the United States Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences for support of this research. We also thank Dr. Nicholas Leventis for helpful discussions.

Registry No. **1**·3Br^-, 113508-95-5; **1**·3PF_6^-, 113508-99-9; **1**·3PF_6^- ($\text{Bz}_2\text{V}^{\cdot+}$), 113509-04-9; **2**·$\text{PF}_6^-$, 113509-01-6; **3a**·$2\text{PF}_6^-$, 68136-91-4; **3b**·$2\text{Br}^-$, 113508-97-7; pyridyltritolylporphyrin, 113508-96-6; α,α'-dibromo-p-xylene, 623-24-5; 4,4′-bipyridine, 553-26-4.

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(11) The second reduction of the viologen moiety of **1** overlaps the ring reduction of the free-base porphyrin moiety near -0.8 V versus Ag/AgCl. Irreversible porphyrin oxidation of **1** occurs at $+1.2$ V versus Ag/AgCl.

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(13) Optical densities of dilute solutions (ca. 2×10^{-7} M) of **1** and **2** in CH_3CN were matched at the excitation wavelength (420 nm). Samples were degassed with three freeze–pump–thaw cycles and were sealed under vacuum. Emission maxima occur at 655 and 715 nm at room temperature.

(14) The excitation source is a pulsed N_2 laser with a nominal pulse width of 12 ns. The emission signal is observed at 90° with an ISA Model H-20 monochromator and detected with an RCA IP28 PMT wired for fast pulse response. The PMT signal is processed by a PAR 162/165 boxcar averager and displayed on an X-Y recorder and passed to an IBM XT-compatible computer. Iterative least-squares reconvolution assuming single-exponential decay was used to determine the lifetime.

(15) Calculated from $\Delta G^0 = E_{1/2}\,(\text{P}^{0/+}) - E_{h\nu} - E_{1/2}(\text{Bz}_2\text{V}^{2+/+}) = +1.2\ \text{V} - 1.9\ \text{V} + 0.3\ \text{V} = -0.4$ V. $E_{h\nu}$ is the singlet excitation energy (650 nm).

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A New Class of Stable Head-to-Tail (Z-Type) Langmuir Blodgett Films. A Second Harmonic Generation Study

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The fabrication of polar multilayers currently attracts much interest due to their potential application in microelectronics and optics.[1] Polar assemblies are required in pyro- or piezo-electricity and nonlinear optics to assure constructive summation of dipoles and hyperpolarizability tensors. Multilayers produced by the Langmuir–Blodgett technique are usually of the Y-type, where the layers are deposited in a head-to-head, tail-to-tail fashion.[2]

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‡ Department of Isotope Research.

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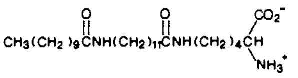
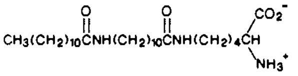
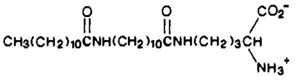
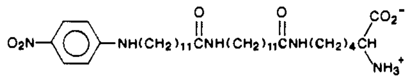
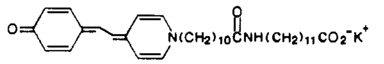
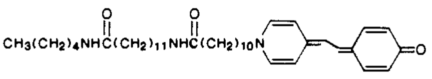
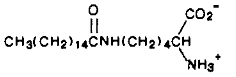
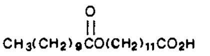
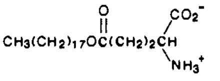
Table I

	compound[c]	mode of transfer[a]	advancing contact angle[b] (deg)	receding contact angle[b] (deg)
(1)	 $CH_3(CH_2)_9\overset{O}{\overset{\Vert}{C}}NH(CH_2)_{11}\overset{O}{\overset{\Vert}{C}}NH(CH_2)_4\overset{CO_2^-}{\underset{NH_3^+}{CH}}$	Z	75	15
(2)	 $CH_3(CH_2)_{10}\overset{O}{\overset{\Vert}{C}}NH(CH_2)_{10}\overset{O}{\overset{\Vert}{C}}NH(CH_2)_4\overset{CO_2^-}{\underset{NH_3^+}{CH}}$	Z	82	28
(3)	 $CH_3(CH_2)_{10}\overset{O}{\overset{\Vert}{C}}NH(CH_2)_{10}\overset{O}{\overset{\Vert}{C}}NH(CH_2)_3\overset{CO_2^-}{\underset{NH_3^+}{CH}}$	Z	80	25
(4)		Z	70	40
(5)		Z	68	45
(6)		Z	75	30
(7)	 $CH_3(CH_2)_{14}\overset{O}{\overset{\Vert}{C}}NH(CH_2)_4\overset{CO_2^-}{\underset{NH_3^+}{CH}}$	Z	80	24
(8)	 $CH_3(CH_2)_9\overset{O}{\overset{\Vert}{C}}O(CH_2)_{11}CO_2H$	Y	88	35
(9)	 $CH_3(CH_2)_{17}O\overset{O}{\overset{\Vert}{C}}(CH_2)_2\overset{CO_2^-}{\underset{NH_3^+}{CH}}$	Y	95	40

[a] Transfers were performed at 20 °C and at a dipping rate of 1 cm/min. [b] Static angles were measured with pure water by the sessile drop method at ambient atmosphere.[20] [c] The synthetic method for preparation of compound **7** is described in ref 21. **1**–**3** were prepared by transferring undecanoic or dodecanoic acid to the corresponding succinimidyl ester and reacting with 12-aminododecanoic or 11-aminoundecanoic acid, respectively. The resulting carboxylic acids were coupled with lysine or ornithine as for **7**. **4** was synthesized by reaction of 12-aminododecanoic acid with 1-fluoro-4-nitrobenzene. The resulting acid was "elongated" as in **1**–**3**. **5** and **6** were synthesized according to the method described in ref 22. **8** was prepared by activation of undecanoic acid with *N,N'*-carbonyldiimidazole and reaction with 12-hydroxydodecanoic acid. **9** was described in ref 23. All compounds were characterized by NMR, IR, and elemental analysis.

Polar mixed multilayer films comprising the ABAB...type arrangement[3] can be prepared by an alternating deposition of A and B, by using special troughs.[4] A few examples of the polar, head-to-tail Z-type films[5] have been reported,[6-10] but no correlation between molecular structure and deposition behavior has been provided. The type of monolayer transfer is primarily determined by the shape of the water meniscus during deposition (advancing and receding contact angles).[11] These contact angles depend on the polarity of exposed surface groups and roughness and heterogeneity of the surface[12-18] as well as on water penetration into the film.[19] A necessary requisite for the formation of Z-type films is an advancing contact angle with the floating monolayer lower than 90° and a receding one close to 0°.[20] In general, such a

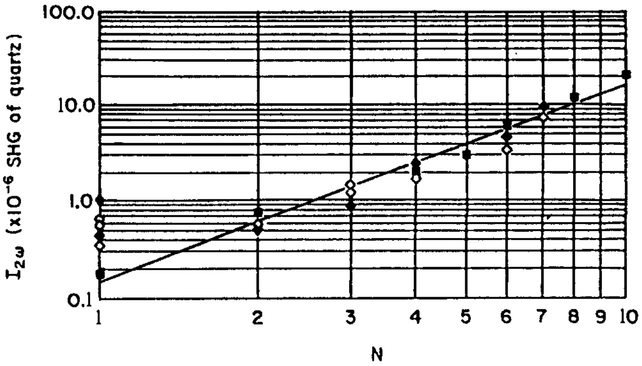


Figure 1. Intensity of second harmonic light ($I_{2\omega}$) produced by LB films of **4** as a function of layer number (*N*). Different symbols indicate films deposited at different times and/or troughs. The line is the best line of slope 2 according to the least-squares criterion.[26]

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situation is not achievable with amphiphiles exposing hydrophobic end groups.

Here we report that amphiphiles having a polar head group such as an α-amino or carboxylic acid and two amide groups along the chain invariably form Z-type multilayers. A list of representative molecules and their behaviors is given in Table I. The remarkably low water contact angles of **1**–**3**, in spite of their hydrophobic end groups, indicate significant porosity to water. Moreover, groups with high hyperpolarizabilities, such as *p*-nitroaniline or merocyanine **4**–**6**, covalently attached to the above diamide handles, do not alter their ability to form stable Z-type films, as confirmed by second harmonic generation (SHG) measurements.[24] SHG is a process converting light from wavelength $\lambda = (2\pi c/\omega)$ to $\lambda/2 = (2\pi c/2\omega)$. It proceeds without specific molecular excitation, rather arising from residual non-centrosymmetrical polarizability within small but supermolecular volumes, being thus both highly dependent on and a sensitive probe of molecular packing. The very good N^2 dependence observed with films of compound **4** (see Figure 1) is direct proof of the formation of Z-type films,[25,3a,c] near (optical) equivalence of the layers, and the long term stability of the films since some of these data were reproduced over a year from the deposition date! Mixed multilayers from compounds **4** and **2**, in 1:1 ratio, also exhibited SHG. In this case there was substantial in-plane inhomogeneity indicating clustering and domain formation but nevertheless allowing stable Z-layer production.[27]

The unusual behavior of the diamide amphiphiles can be explained as follows: the amide groups located along the hydrocarbon chains on the periphery of the crystalline domains may bind water via hydrogen bonds, rendering the surface more hydrophilic. Thus, we suggest that the contact angles depend not only on the structure and nature of the terminal group of an amphiphile but also on the extent and character of the voids[19] between the domains at the surface film. This model is supported by grazing angle X-ray diffraction and reflectivity measurements on a floating monolayer of palmitoyl-R-lysine (**7**) at 20 dynes/cm.[28] The monolayer was found to be a two-dimensional powder comprising crystalline domains of approximately 500-Å diameter. The side chains are inclined at an angle of ≈60° to the water surface thus precluding close packing of neighboring domains. Indeed the Fresnel reflectivity data of **7** indicated that the monolayer coverage is 90%, the remaining 10% representing bare patches of water. The role played by the occluded water in determining the mode of deposition is indicated by the following experiments: **7** yields at 20 dynes/cm Z-type multilayers, whereas at 25 dynes/cm or above, it forms a Y-type film, in keeping with tighter packing of the domains. Drying of a deposited monolayer of monoamide **7** for 24 h at 25 °C raised its advancing contact angle and also caused Y-type deposition of the following layer. A similar treatment of a monolayer of diamide **3** did raise the contact angle but not above 90°, and thus the following depositions continued to be Z-type.

In agreement with this model, is the observation that monolayers incorporating ester groups **8** and **9**, known to bind water less firmly than amides, form Y-type films.

In order to test the generality of the present model, we are preparing new amphiphiles with different groups along the hydrocarbon chain, which should affect retention of water, the tilt of the chains, and size of domains.

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Registry No. 1, 113321-78-1; **2**, 113321-79-2; **3**, 113321-80-5; **4**, 113321-81-6; **5**, 113321-84-9; **6**, 113321-82-7; **7**, 59012-43-0; **8**, 113321-83-8; **9**, 83789-61-1.

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(20) In general, the three-phase line movement during monolayer deposition is not accurately described by quasi-static contact angles.[14] However, such angles are easily measured, being of value as indicators of the expected trend. It should also be noted that the water surface tension is lowered by the presence of a floating monolayer. According to Young's equation, for a monolayer surface pressure of 20 dynes/cm the contact angle with the floating monolayer will invariably drop to 0° for any pure water contact angle below ca. 44.5°.

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(24) Slides covered with mono- and multilayers of compounds **4**–**6** were studied by SHG primarily in the $\theta = 45°$ transmission geometry. Both Nd/YAG and Nd/YLF lasers were used, producing harmonics near 530 nm. Conversion efficiencies were measured relative to a quartz crystal and polarization dependences were investigated.

(25) (a) For surface SHG in the dipole approximation $I_{2\omega} \propto |\bar{e}_{2\omega}\cdot\chi_s^{(2)}\cdot\cdot\bar{e}_\omega\bar{e}_\omega|^2$, a square projection of the surface nonlinear susceptibility (a polar third-rank Cartesian tensor). Modelling $\chi_s^{(2)}$ for LB multilayers as a tensorial summation of N layer-contributions, $\chi_s^{(2)}$ depends on the layers' equivalence, registries and orientations. For idealized X- or Z-type films $I_{2\omega} \propto N^2$. Interference between successive layers in idealized Y-type films results in complete cancellation or a residual monolayer contribution when N is even or odd, respectively. SHG thus provides a critical, unambiguous test of type in well behaved films. Rigorous analysis will be presented elsewhere. (b) Heinz, T. F.; Chen, C. K.; Ricard, D.; Shen, Y. R. *Phys. Rev. Lett.* **1982**, *48*, 478.

(26) It should be commented that the scatter of data at $N = 1$ is a consequence of nonlinear constructive interference by SHG at front and back surfaces of the slide. The slides have been wiped with solvent on one side to remove the second surface layer, but, as was proved by observation and analysis of 'Maker fringe' rotation patterns, it seems that the robust first layer was not completely removed by this procedure.

(27) Details of the SHG conversion also indicate that the "nonlinearly polarizable marker" in **4**, *p*-nitroaniline, is oriented on average at a very large tilt angle from the LB film normal.

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Macroring Contraction Methodology. 4. A Novel Route to Steroid A, B, C Rings by the Transannular Diels-Alder Reaction of the 14-Membered (*E*,*E*,*E*)-Macrocyclic Triene

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Intermolecular reactions on macrocycles can proceed with high stereoselectivity.[1] We recently demonstrated that the transannular [2,3]-Wittig rearrangement of 13-membered diallylic ethers yields germacrane lactones.[2] We wish now to report a novel route to the steroid skeletone (A/B/C/D,cis-anti-trans-anti-trans) via the transannular Diels-Alder reaction of the 14-membered cyclic triene.[3] Intramolecular Diels-Alder reactions are useful synthetic methods, and their regio- and stereoselectivities have been well studied.[4] However, few synthetic studies on transannular

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(3) This account has been presented: Takahashi, T.; Shimizu, K.; Tsuji, J. Presented at the 54th Spring Meeting of the Japan Chemical Society, 1987; Abstract p 1116.

(4) Kocovsky, P.; Turecek, F.; Hajecek, J. *Synthesis of Natural Products: Problems of Stereoselectivity*; CRC Press: 1986; Vol. 1, p 48 and references cited therein.

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