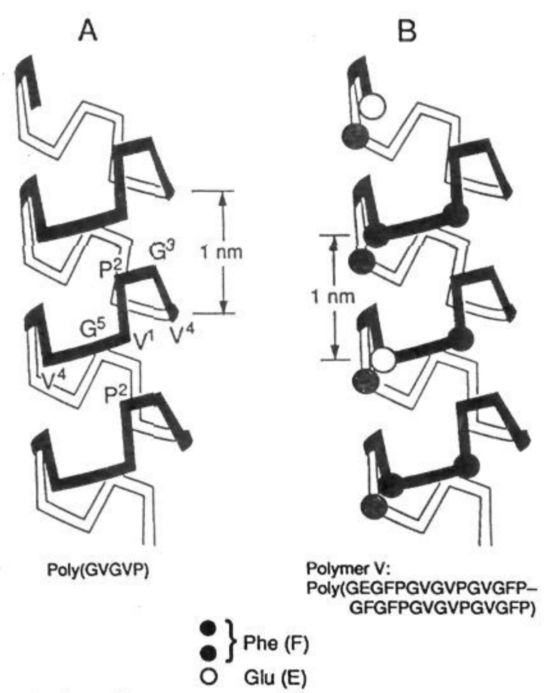

Figure 1. Controlling pK_a by design at nanometric dimensions: Schematic representation of the β-spiral structure proposed for the polypentapeptide poly(Val^1-Pro^2-Gly^3-Val^4-Gly^5), which is equivalent to poly(GVGVP). The Pro^2-Gly^3 β-turn is seen to function as a spacer between the turns of the β-spiral in A, and the hydrophobic folding arises principally from interturn Val^1 γ-CH$_3$ ↔ Pro^2 β-CH$_2$ interactions. In B, the Phe residues are placed proximal to the Glu residues on the basis of a β-spiral with approximately 3 pentamers per turn, i.e., on the basis of tertiary structure.

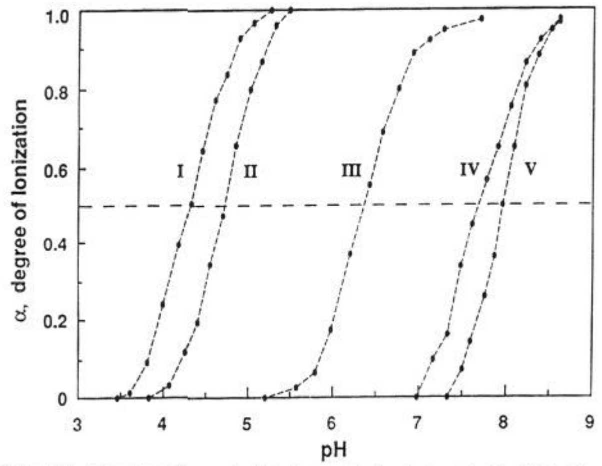

Figure 2. Structure dependent hydrophobicity-induced pK_a shifts: Resolved acid–base titration curves which give pK_a values of 4.3, 4.7, 6.3, 7.7, and 8.1 for polymers I–V, respectively. A remarkable overall pK_a shift of 3.8 pH units is observed. For all curves, the starting concentration was 40 mg/mL and the temperature was 20 °C.

temperatures (T_t) for which vary systematically with composition.[2] Plots of T_t vs f_X are linear, with more hydrophobic residues lowering T_t and less hydrophobic residues increasing T_t. This property has been used to develop a hydrophobicity scale for amino acids.[5] The values of T_t, extrapolated to $f_X = 1$, range from −90 °C for poly(GWGVP) to 250 °C for poly(GEGVP) with Glu-(COO$^-$). The mean residue hydrophobicities, $\langle T_t \rangle$, calculated using this hydrophobicity scale and the amino acid analysis data are 30, 23, 20, 22, and 21 °C for polymers I–V, respectively, in the Glu COOH state, yet the pK_a values differ remarkably.

Previous studies have shown that increased hydrophobicity increases pK_a,[2,6,7] yet in this molecular system tertiary structure dominates over primary structure in achieving the largest pK_a shift. Mean residue hydrophobicity calculations using a sliding window of 11 residues,[5] $\langle T_t \rangle_{11}$, give 15 for polymer IV and 20 for V for the Glu COOH state, and 35 for IV and 40 for V for the Glu COO$^-$ state. Thus, on the basis of primary structures, the Glu residues in polymer IV would experience the greater hydrophobicity and would be expected to give the larger pK_a shift. The pK_a shift is greater, however, for polymer V. Only when the proper, β-spiral folding is taken into account does the spatial proximity become apparent, and this Glu–Phe proximity, as shown in Figure 1B, provides the understanding for the larger pK_a shift exhibited by polymer V.

Clearly, the differences in pK_a do not arise from the commonly considered electrostatic interactions.[8,9] The pK_a shifts instead are an expression of a repulsive free energy of interaction which exists between the hydration shells of hydrophobic and polar (COO$^-$) moieties when sufficiently proximal as discussed in more detail elsewhere.[2] The change in Gibbs free energy per mole obtained from the change in chemical potential, $\Delta\mu$, required to maintain 50% ionization of the side chain is given by $\Delta\mu = -2.3RT\Delta\mathrm{p}K_a$. At 20 °C with a $\Delta\mathrm{p}K_a$ of 3.8 pH units, $\Delta\mu$ is 5.1 kcal/mol; there is observed a repulsive Gibbs free energy of interaction arising out of the proximity of Phe and ionized Glu side chains in polymer V.

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Synthesis, Self-Assembly, and Photophysical Dynamics of Stacked Layers of Porphyrin and Viologen Phosphonates

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Organic thin films are of ongoing interest as photoconductors, photovoltaics, electrochromics, and nonlinear optical elements.[1] Photo- or electroactive species in such films would be best utilized if assembled repetitively in specific sequences or orientations in durable matrices. The self-assembly of transition metal phosphonates on surfaces[2] provides an attractive means of constructing thermally and solvolytically stable films of controlled thickness with spatially defined molecular components. Recently we reported the synthesis, multilayer formation, and nonlinear optical behavior of a polar chromophoric phosphonic acid that self-assembles on Zr phosphate surfaces.[3] Mallouk et al. have incorporated electroactive species into inert phosphonate matrices by ion exchange to form a rectifying film.[4] Film components capable

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of photoindued vectorial electron transport would be desirable for applications where spatial charge separation is required. Photoinduced interlayer electron transfer, however, has not yet been shown to occur in this class of materials. Furthermore, even in the related, much less stable Langmuir–Blodgett films, such a process has only been reported at single interfaces.[5]

Here, we describe a novel photoelectron donor, 5,10,15,20-tetrakis(4-phosphonophenyl)porphyrin (**1**), and an electron acceptor, *N*,*N*′-bis(3-phosphonopropyl)-4,4′-bipyridinium (**2**), each of which forms a solvolytically stable Zr-based self-assembled surface multilayer, and which may be fixed in arbitrarily selected sequences perpendicular to the substrate. We further report fluorescence-quenching data indicative of photoinduced vectorial electron transfer from **1** to **2** across a single Zr phosphonate bilayer interface. A superassembly of these bilayers was also constructed, in which identical photophysical dynamics were observed.

Compound **1** was synthesized from 4-bromobenzaldehyde by acetalization, lithiation, and treatment with diethyl chlorophosphate, followed by removal of the acetal, cyclotetramerization with pyrrole, and deethylation with bromotrimethylsilane. The viologen **2** was prepared from 4,4′-bipyridine and diisopropyl iodopropylphosphonate followed by ion-exchange chromatography and dealkylation.[6] Layers were deposited on Si wafers or quartz disks by heating the phosphorylated, zirconated substrates at 85–90 °C in 0.5 mM solutions of **1** or **2** in 95% DMSO–5% H_2O for 30 min,[7] followed by sequential rinsing in hot DMSO, deionized H_2O, and EtOH. To maximize layer density, each layer of **1** was treated with 1 mM 1,12-dodecanediyldiphosphonic acid (DDPA) in hot DMSO followed by rinsing as above. Multilayers were prepared by treatment of phosphonate-terminated surfaces with 5 mM aqueous $ZrOCl_2$ and repeating the deposition procedure.

Plots of the ellipsometric thickness vs layer number for both **1** and **2** were linear, with slopes of 21 and 13 Å, respectively. Thus, the Zr phosphonate surface multilayers may be formed from two-dimensional or charged chromophores, as well as the previously investigated one-dimensional rigid rods[7] and polymethylenes.[2] The 21 Å per layer observed in the porphyrin film suggests that the porphyrins are significantly vertical, and that one or two phosphonate groups on each molecule are bound toward the substrate. Films of **2** were apparently packed imperfectly or considerably tilted. The plot of the absorbance at the porphyrin Soret band (420 nm) versus the number of layers of **1** was also linear, with an increment per deposition (on both sides of the quartz disk) of 0.039 per layer.

In dilute DMSO solution, a single exponential decay is observed for the fluorescence of **1** with a singlet excited state lifetime of $\sim$13 ns, while the lifetime of solid **1** is 4 ns. In a homogeneous monolayer, the decay is multiexponential and subnanosecond, suggesting highly efficient intermolecular energy transfer quenching of porphyrins in various aggregation states distinct from clusters of the solid. Multilayer lifetimes (constant for 2–10 layers) were shorter than for monolayers, indicating that there are both intralayer and interlayer quenching components.[8] Dilution of the porphyrin layers by codeposition with DDPA (deposition solution 0.1 mM in **1** and 0.4 mM in DDPA, absorbance increment of 0.020 per layer) led to a substantial increase in emission intensity and lifetime and a sharpening of the absorbance peaks, indicating greater isolation of the porphyrins.

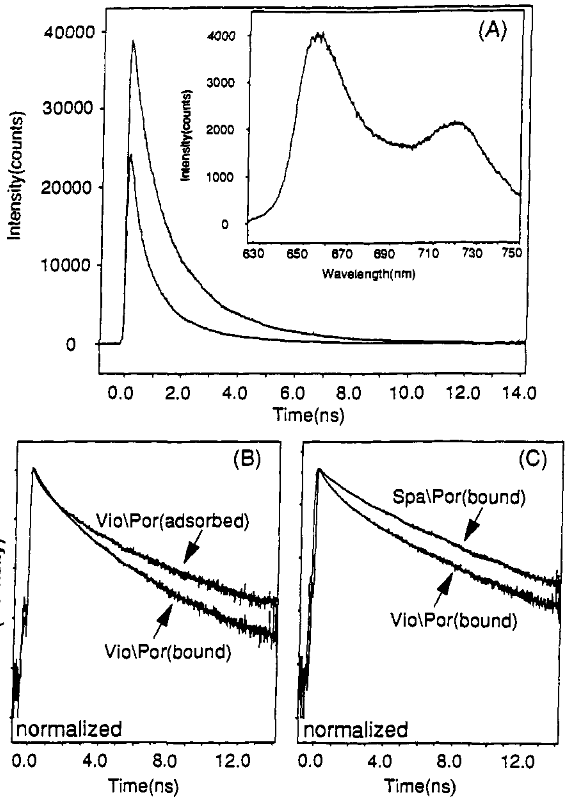

Figure 1. Fluorescence decays of **1** in "dilute" monolayers. Excitation at 420 nm, emission at 650 nm. (A) Upper trace: deposition on DDPA. Lower trace: deposition on **2**. Insert: emission spectrum. (B) Normalized logarithmic decay comparison between trivially "adsorbed" **1** and Zr-"bound" **1** on **2**. (C) Normalized logarithmic decay comparison between Zr-bound **1** on DDPA ("Spa\Por") and on **2** ("Vio\Por").

This "heterogeneous" layer type was used for electron-transfer experiments to allow decoupling of donor–donor and donor–acceptor transfer. Figure 1A, upper trace, illustrates the fluorescence decay of such a layer deposited on top of a single layer of DDPA; the curve could be fit to a double exponential with lifetimes of 1.0 and 3.5 ns (54% and 46% relative contributions, respectively).[9] Treatment of a layer of **2** with the **1**–DDPA solution *without* prior zirconation led to the physisorption of a small amount of porphyrin on quartz ($\sim$20% of the usual deposited amount as judged by optical absorption) with no significant increase in ellipsometric thickness on Si. This material likely substitutes for water or ions in poorly packed regions of the layer. The fluorescence of this randomly adsorbed porphyrin is strongly quenched, although with different decay dynamics compared to a Zr-bound layer (Figure 1B). Application of **1**–DDPA after zirconating the **2** surface in the usual way gave a thickness increase of 19 Å, consistent with the porphyrin molecules being directed upward from the viologens. The expected absorbance increment of 0.020 at 420 nm was observed. The emission decay of this layer structure (Figure 1A, lower trace, and 1C) was best fitted by a triple exponential, with lifetimes of 0.3, 1.0, and 3.0 ns (49%, 44%, and 7% relative contributions, respectively). The integrated fluorescence intensity of the porphyrin monolayer is diminished by ca. 60% in the presence of the viologen layer. Since there is no overlap between the porphyrin emission spectrum and the viologen absorption, the quenching mechanism is most likely due to photoinduced electron transfer. The fact that the Zr-bound porphyrin is quenched as well as or more efficiently than the trivially adsorbed porphyrin indicates that the latter does not facilitate quenching of the "bound" porphyrin. Additionally, no significant quenching is observed when a layer of DDPA was deposited between the donor and acceptor species, indicating the DDPA serves as an effective barrier to both electron transfer and the penetration of **1** during deposition. Finally, superassemblies with the structures (DDPA-**1**-DDPA-DDPA)$_5$ and (**2**-**1**-DDPA-DDPA)$_5$, respec-

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(6) NMR and UV spectra were consistent with the assigned structures. In addition, **1** was characterized by FAB mass spectroscopy, and **2** by elemental analysis.

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(8) Broadening of the absorbance bands of **1** was also observed in the film layers, providing further evidence of intermolecular association and/or aggregation.

(9) The functional form was chosen arbitrarily; a more detailed analysis of the excitation and electron-transfer dynamics is underway.

tively, were prepared, giving correspondingly amplified ellipsometric thickness and absorbance. Respective emission decays were identical to those of the unquenched and quenched bilayer structures discussed above.

In summary, we have reported the synthesis, film-forming properties, and photophysical data on **1** and **2**. The films are stable to hot solvents and may be built up repetitively with reproducible thickness per layer and fluorescence behavior. Thus, we introduce a photocharge-generating element to a material class where nonlinear optical, rectifying, and insulating components could also be present at arbitrary positions. Work is in progress to observe and measure lifetimes of the photoinduced charge separated species directly, and to explore the electrical and optical properties of multiple-component superlattices prepared by Zr phosphonate deposition.

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Supplementary Material Available: Synthetic schemes for **1** and **2** (2 pages). Ordering information is given on any current masthead page.

Supramolecular Chemistry of $[Mn(CO)_3(\mu_3\text{-OH})]_4$: Assembly of a Cubic Hydrogen-Bonded Diamondoid Network with 1,2-Diaminoethane

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Predictable self-organization of molecules into one-, two-, or three-dimensional hydrogen-bonded architectures is an area of supramolecular chemistry that is of great current interest.[1] Such research is particularly relevant in the context of solid-state chemistry since rational design, i.e., crystal engineering, of solids has important ramifications for the development of new materials with unusual physical properties.[2] An aspect of this chemistry that is particularly pleasing from an aesthetic perspective and has a number of potential applications, particularly in the area of host–guest chemistry, concerns the construction of three-dimensional hydrogen-bonded diamondoid open networks. The concept was delineated by Ermer in 1988, who demonstrated that if tetrafunctionalized organics with approximate tetrahedral symmetry have the capability to associate via hydrogen bonds, then diamondoid networks may result.[3] Unfortunately, the relative sizes of the cavities formed by adamantane-1,3,5,7-tetracarboxylic acid and 3,3-bis(carboxymethyl)glutaric acid ("methanetetraacetic acid") facilitate interpenetration of five[3a] and three[3b] networks, respectively, thereby precluding formation of internal chambers. However, Ermer subsequently demonstrated that enclathration can be attained with double-diamond 2,6-dimethylideneadamantane-1,3,5,7-dicarboxylic acid networks,[4] and in a significant development, Wuest recently demonstrated that tecton **1** can self-assemble to form a diamondoid network that does not interpenetrate and is capable of enclathration.[5] In this communication we develop the theme further by outlining an alternate approach to assembly of diamondoid networks: assembly of a rigid tetrafunctional hydrogen-bond donor with complementary difunctional hydrogen-bond-acceptor molecules (Chart I).

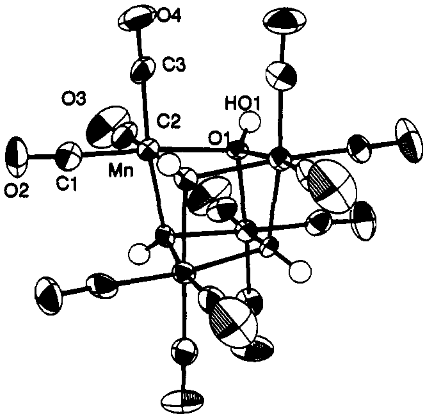
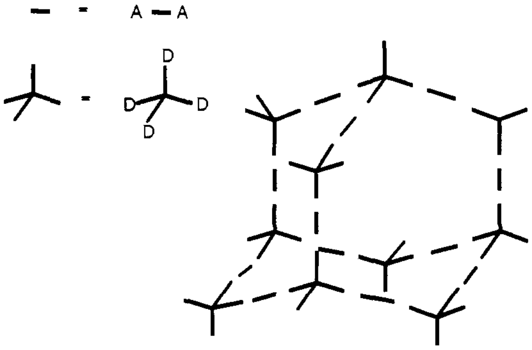
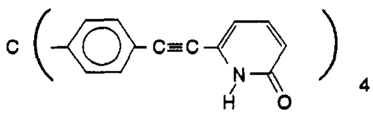


Figure 1. Perspective view of a molecule of **2** as it exists in **3**. Intramolecular distances and angles are within expected ranges.[6,7]

Chart I





1

A molecule which possesses S_4 symmetry and the requisite four H-bond donors[6] is the cubane-like cluster $[Mn(CO)_3(\mu_3\text{-OH})]_4$, **2**, which can be synthesized quantitatively in one step from $Mn_2(CO)_{10}$.[7] Reaction of **2** with excess 1,2-diaminoethane, en, in toluene immediately affords a yellow-orange precipitate, which may be recrystallized from $CHCl_3/CH_3CN$ to afford cocrystals of composition **2**·2en, **3**.[8] X-ray crystallographic analysis[9] reveals

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(6) **2** is able to form isolable 1:4 adducts with H-bond acceptors as diverse in nature as water and triphenylphosphine oxide: Clerk, M. D.; Copp, S. B.; Subramanian, S.; Zaworotko, M. J. *Supramol. Chem.* **1992**, *1*, 7.

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(8) In a typical reaction, a recrystallized yield of **3** of 80% is afforded. IR (KBr, cm^{-1}): ν_{CO} 2011 s, 1916 s; $\nu_{NH,OH}$ 3375 bs. Anal. Found: (calcd) C, 26.12 (25.84); H, 2.68 (2.69); N, 7.26 (7.53).

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