Multilayer Assemblies

Surface-Confined Metalloporphyrin Oligomers**

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The ability to control charge transfer over long distances is an important aspect of nanometer-scale fabrication. Early work on molecular wires utilized metalloporphyrin oligomers,[1,2] whereas more recent work with these materials has been

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directed towards the production of supramolecular rods.[3,4] Metalloporphyrin oligomers in various forms can be used as self-assembling blocks to make discrete, ordered arrays.[5,6] These are then combined with other molecules to create supramolecular structures,[7] which have applications as sensors[8] or as nanoporous materials,[9,10] or which exhibit electronic properties that are unique to fully π-conjugated systems of this size.[11,12] We recently developed a modular method for the assembly of metalloporphyrins on surfaces.[13] Herein we report the preparation of surface-confined, axially-linked metalloporphyrin oligomers and aspects of the electronic coupling along the oligomer backbone.

Our experimental approach is outlined in Figure 1 and is detailed in the Experimental Section. In this modular scheme, we used a monolayer of decanethiol, which contained a low mole fraction of 11-mercaptoundecylisonicotinate (**1**), as the substrate for the chemisorption of a sub-monolayer of metalloporphyrin. Bis(acetonitrile)-*meso*-tetratolylporphyrinatoruthenium(II) (**2**) or bis(acetonitrile)octaethylporphyrinatoruthenium(II) (**3**) were anchored to the surface by the exchange of an axial acetonitrile group for the monolayer-bound isonicotinate group. After attachment of the metalloporphyrin, the remaining axial acetonitrile group was exchanged for a linking bidentate ligand such as *trans*-1,2-bis(4-pyridyl)ethylene (**4**) or pyrazine (**5**). The oligomer was extended by repeating the treatment of the surface-bound conjugate with **2** or **3**, followed by linking with **4**; in such a manner, we prepared oligomers that were up to five repeat units long.

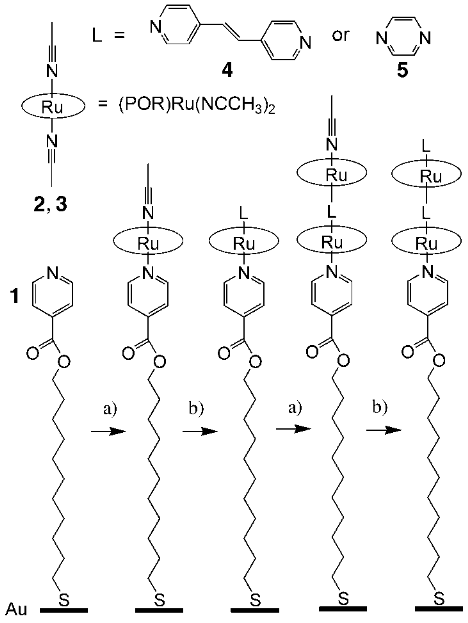

Figure 1. Schematic representation of the modular assembly of ruthenium—porphyrin, (POR)Ru, oligomers onto **1**, which is supported within an alkanethiol monolayer on a Au surface. a) Immersion in a solution of **2** or **3** (1 μM) in toluene for 20 min; b) immersion in a solution of the linker (L), **4** or **5** (1 mM), in toluene for 5 min; steps a) and b) may be repeated to extend the oligomer.

The underlying monolayer of the alkanethiolate and the first monolayer of metalloporphyrin have been characterized extensively by a range of techniques, which include optical ellipsometry, contact angle goniometry, X-ray photoelectron spectroscopy, grazing-angle FT-IR spectroscopy, UV/Vis spectroscopy, and scanning tunneling microscopy.[14] The modular assembly of linkers and metalloporphyrins on top of this substrate was monitored with cyclic voltammetry measurements. Figure 2 shows the cyclic voltammograms of ruthenium-based oxidation and reduction processes in the surface-bound monomer, trimer, and pentamer of **2** linked with **4**. The formal potential of each additional conjugate as another metalloporphyrin is added to the oligomer is similar to that of the original isonicotinate-bound monomer. Integration of the charge under the wave at $E = +0.35$ V allowed the surface coverage of this one-electron couple to be calculated. The surface coverage of **2** in Figure 2a corresponds to $3.4\,\mu\mathrm{C\,cm^{-2}}$, that is, 50% of a compact, non-overlapping metalloporphyrin monolayer.[13] The surface coverage of the first layer of chemisorbed metalloporphyrin was controlled by the variation of the mole fraction of **1** in the underlying alkanethiol monolayer. After a further four cycles of the modular assembly process (Figure 2c), five tiers of metalloporphyrin were present on the surface. The resulting coverage, which is based on the total number of immobilized metalloporphyrins in the stacks, corresponded to 225% of the coverage for a single close-packed monolayer.

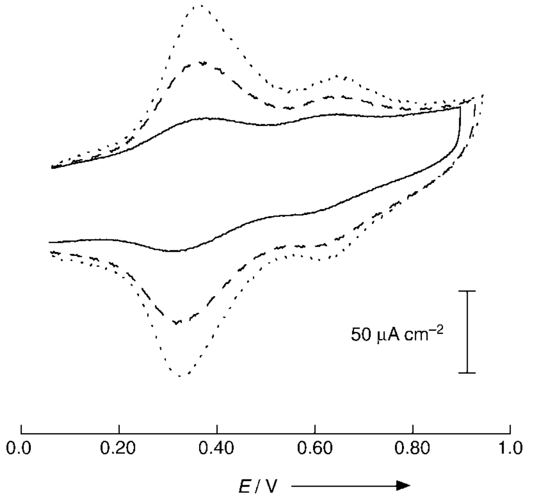

Figure 2. Cyclic voltammograms (*E* versus SCE) of a) the monomer Au–**1**–**2**–**4** (——); b) the trimer Au–**1**–**2**–**4**–**2**–**4**–**2**–**4** (-----); and c) the pentamer Au–**1**–**2**–**4**–**2**–**4**–**2**–**4**–**2**–**4**–**2**–**4** (•••••). Scan rate: $0.8\,\mathrm{V\,s^{-1}}$.

A control experiment was performed in which an electrode was subjected to five sequential treatments of **2** according to step a in Figure 1 without intervening treatment with the linker (step b). This showed that further added metalloporphyrin units formed oligomer stacks, rather than inserting into unoccupied **1** sites on the underlying monolayer. As illustrated in Figure 3, the final surface coverage of the five-layer control assembly of **2** was identical to that of the monomer. This control experiment shows that further elec-

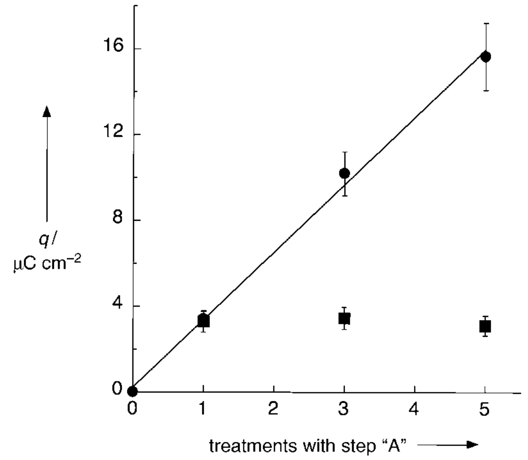

Figure 3. Correlation of the charge under the wave at $E = +0.35$ V with the number of treatments with the metalloporphyrin in Figure 1, step a; ●: metalloporphyrins linked with **4** using steps a) and b); ■: control experiment under the same conditions, but in the absence of a linker—step a) only.

troactive material arised from the elongation of the oligomer, rather than from an increased coverage in the chemisorbed metalloporphyrin monolayer or by the physisorption of the metalloporphyrin onto the original chemisorbed layer.

The electrochemical properties of the oligomer are strongly influenced by the mole fraction of **1** in the underlying alkanethiol monolayer and by the choice of the linking ligand. At higher mole fractions of **1**, a second oxidation wave at $E = +0.65$ V becomes more prominent which eventually yields an integrated area of $\approx 30\%$ of the larger peak observed at $E = +0.35$ V. The increased prominence of this secondary oxidation peak at higher surface coverages of the metalloporphyrin is attributed to the incomplete electrostatic screening of the charge on the oxidized metalloporphyrins in the solvent of low dielectric constant employed here. At higher surface coverages, a greater fraction of unoxidized, neutral metalloporphyrins have a large number of oxidized, cationic nearest-neighbors during the oxidation process; the electrostatic work required to oxidize a neutral metalloporphyrin in an environment of poorly screened positive charge is greater than that required to oxidize an isolated neutral metalloporphyrin.

By the use of a shorter linking ligand such as pyrazine (**5**), a similar effect was observed. Incomplete screening and neutralization of the charge along the backbone of the oxidized metalloporphyrin led to an additional wave of fractional area at more-positive potential. In the case of **5**-linked homogeneous trimers, we observed up to three additional waves. Similar additional waves were observed in the solution-based cyclic voltammetry analysis of axially-linked metalloporphyrin oligomers of undefined length.[1,2,15,16] Whereas the observation of these waves has been taken as evidence of multivalence effects,[15] we believe that these additional waves result from electrostatic artifacts.

Heterogeneous surface-confined metalloporphyrin dimers can also be produced with our modular assembly method. Figure 4 shows the near-identical cyclic voltammograms for the Au–**1**–**2**–**4**–**3**–**4** and Au–**1**–**3**–**4**–**2**–**4** dimers. The waves at $E = +0.14$ and $+0.36$ V correspond to ruthenium-based redox chemistry at **3** and **2**, respectively. The surface coverage of each of the metalloporphyrins is $\approx 1.9\ \mu\text{C}\,\text{cm}^{-2}$, which corresponds to 25% of a compact monolayer. In both cases **3** is oxidized before **2**, regardless of their relative positions in the stack. In a similar fashion, on the return scan **2** is always reduced before **3**. Let us consider the Au–**1**–**2**–**4**–**3**–**4** dimer under an oxidative scan: The first electron-transfer event corresponds to the tunneling of an electron from the outer metalloporphyrin **3** through the linking ligand, the inner metalloporphyrin, and the backbone of the alkane chain to the underlying Au surface at the formal potential of **3**. This event is independent of the identity or the oxidation state of the inner metalloporphyrin **2**. In other words, neither of these structures exhibits current rectification, which is observed in less-tightly coupled systems;[17,18] these structures are not viable redox-switched molecular diodes.

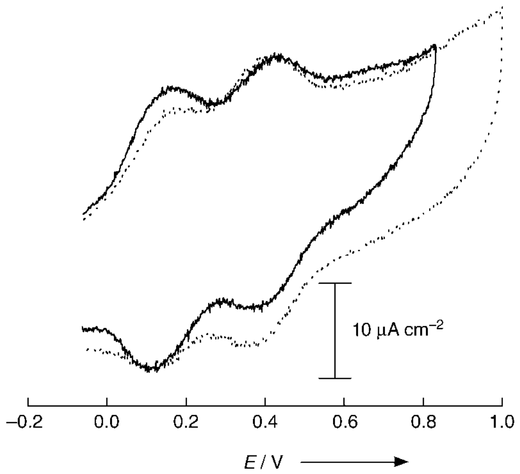

Figure 4. Cyclic voltammograms (E versus SCE) of Au–**1**–**2**–**4**–**3**–**4** (——) and Au–**1**–**3**–**4**–**2**–**4** (•••••) dimers. Scan rate: $0.4\ \text{V}\,\text{s}^{-1}$.

Whereas the present solvent system is not ideal for studying the kinetics of the electron-transfer processes, the minimal splitting of the peak at elevated scan rates suggests facile electron-transfer kinetics. Also, it suggests that the electronic coupling along the backbone of the alkanethiolate is at least as strong as that of $[\text{Ru(NH}_3)_5]^{2+}$ coordinated to pyridine-terminated alkanethiolates of a comparable length to those employed here.[19–21] Furthermore, the lack of any marked decrease in the rate of transfer of an electron from the outer metalloporphyrin relative to the inner metalloporphyrin argues that the coupling between the two metalloporphyrins by the fully conjugated linker is significantly stronger than that offered by an alkane chain of similar length. For reference, fully conjugated, ferrocene-terminated oligophenylenevinylenes display no decrease in their rates of electron-transfer owing to electronic coupling over distances up to 2.8 nm.[22]

As shown in Figure 2, any differences in the formal potentials for metalloporphyrins within the homogeneous oligomer linked with **4** are smaller than we can resolve with cyclic or square-wave voltammetry. On the basis of the minimal peak broadening (as measured by the full width at half maximum) that is observed upon moving from the monomer to the pentamer, we estimate the differences in formal potential to be less than 0.06 V, which corresponds to an upper limit of 10 for the conproportionation constant[23] associated with the reaction (POR represents the porphyrin and L represents the linker):

$$\mathrm{Ru^{II}(POR)\text{–}L\text{–}Ru^{II}(POR) + Ru^{III}(POR)\text{–}L\text{–}Ru^{III}(POR) \rightleftharpoons 2\,Ru^{II}(POR)\text{–}L\text{–}Ru^{III}(POR)} \tag{1}$$

This means that the electronic coupling contribution between the metal centers in the dimer is small and it falls into the Robin–Day class I or a weak-interaction regime.[24] However, as the outer metalloporphyrin can be oxidized regardless of the oxidation state of the inner metalloporphyrin (see Figure 4), the electronic communication along the backbone of the oligomer chain from the outer metalloporphyrin, through the inner metalloporphyrin, along the supporting alkane chain, and into the underlying gold substrate can still be considered as substantial.

In conclusion, we have presented a modular method for the assembly of surface-confined metalloporphyrin oligomers. Such structures exhibit electronic communication along their backbone and offer the potential to control charge transfer over long distances. This is of interest for materials or sensing applications, especially when interfacing with a surface is a concern.

Experimental Section

Compounds **1**,[25] **2**, and **3**[14] were prepared according to reported methods. Polycrystalline Au electrodes were evaporated onto titanium-coated silicon substrates, and then the conjugates were cleaned by immersion in a solution of H_2SO_4:30% aqueous H_2O_2 (3:1 v/v) for 10 s and rinsed with deionized water and ethanol, immediately before use. Supported monolayers of **1** were formed by the immersion of the clean Au electrodes into a solution of decanethiol (1.25 mM) and **1** (0.2 equiv) in ethanol. The electrodes were rinsed with ethanol and blown dry with nitrogen prior to transfer to a glove box. The first monolayer of **2** or **3** was chemisorbed to the electrodes in a solution of the metalloporphyrin (1–3 μM) in toluene for 20 min under a nitrogen atmosphere, and the assembly was rinsed with toluene. The distal axial ligand was exchanged in a solution of **4** (1 mM) or pyrazine (**5**, 1 mM) in toluene for 5 min, and the assembly was again rinsed in toluene. Subsequent additions to the oligomer were performed in a similar fashion. Electrochemistry was performed on the benchtop under air with a Princeton Applied Research model 263 potentiostat and model 250 software by using a cell that was formed by pressing a bored-out cone of poly(tetrafluoroethylene) against the electrode. A platinum counter electrode and a silver quasi-reference electrode were used with a solution of tetrabutylammonium hexafluorophosphate (0.1M) as the supporting electrolyte in CH_2Cl_2. Potentials were checked periodically with a saturated calomel reference electrode (SCE), which was sheathed in the supporting electrolyte and separated from the cell by a cracked-bead junction.

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[1] J. P. Collman, J. T. McDevitt, G. T. Yee, C. R. Leidner, L. G. McCullough, W. A. Little, J. B. Torrance, *Proc. Natl. Acad. Sci. USA* **1986**, *83*, 4581.
[2] J. P. Collman, J. T. McDevitt, C. R. Leidner, G. T. Yee, J. B. Torrance, W. A. Little, *J. Am. Chem. Soc.* **1987**, *109*, 4606.
[3] H. L. Anderson, *Chem. Commun.* **1999**, 2323.
[4] N. Aratani, A. Osuka, Y. H. Kim, D. H. Jeong, D. Kim, *Angew. Chem.* **2000**, *112*, 1517–1521; *Angew. Chem. Int. Ed.* **2000**, *39*, 1458–1462.
[5] L. Baldini, C. A. Hunter, *Adv. Inorg. Chem.* **2002**, *53*, 213.
[6] R. A. Haycock, C. A. Hunter, D. A. James, U. Michelsen, L. R. Sutton, *Org. Lett.* **2000**, *2*, 2435.
[7] J. Wojaczynski, L. Latos-Grazynski, *Coord. Chem. Rev.* **2000**, *204*, 113.
[8] G. A. Mines, B. Tzeng, K. J. Stevenson, J. Li, J. T. Hupp, *Angew. Chem.* **2002**, *114*, 162–165; *Angew. Chem. Int. Ed.* **2002**, *41*, 154–157.
[9] R. K. Kumar, I. Diskin-Posner, I. Goldberg, *J. Inclusion Phenom. Macrocyclic Chem.* **2000**, *37*, 219.
[10] K. F. Czaplewski, R. Q. Snurr, J. T. Hupp, *Adv. Mater.* **2001**, *13*, 1895.
[11] N. Aratani, A. Osuka, *Bull. Chem. Soc. Jpn.* **2001**, *74*, 1361.
[12] J. J. Piet, P. N. Taylor, B. R. Wegewijs, H. L. Anderson, A. Osuka, J. M. Warman, *J. Phys. Chem. B* **2001**, *105*, 97.
[13] T. A. Eberspacher, J. P. Collman, C. E. D. Chidsey, D. L. Donohue, H. Van Ryswyk, *Langmuir* **2003**, *19*, 3814.
[14] D. A. Offord, S. B. Sachs, M. S. Ennis, T. A. Eberspacher, J. H. Griffin, C. E. D. Chidsey, J. P. Collman, *J. Am. Chem. Soc.* **1998**, *120*, 4478.
[15] M. Saito, A. Endo, K. Shimizu, G. P. Sato, *Chem. Lett.* **1995**, 1079.
[16] M. Saito, A. Endo, K. Shimizu, G. P. Sato, *Electrochim. Acta* **2000**, *45*, 3021.
[17] K. Uosaki, Y. Sato, K. Shimazu, I. Yagi, *New Funct. Mater.* **1993**, *C*, 711.
[18] C. R. Leidner, P. Denisevich, K. W. Willman, R. W. Murray, *J. Electroanal. Chem.* **1984**, *164*, 63.
[19] J. F. Smalley, H. O. Finklea, C. E. D. Chidsey, M. R. Linford, S. E. Creager, J. P. Ferraris, K. Chalfant, T. Zawodzinsk, S. W. Feldberg, M. D. Newton, *J. Am. Chem. Soc.* **2003**, *125*, 2004.
[20] D. A. Brevnov, H. O. Finklea, H. Van Ryswyk, *J. Electroanal. Chem.* **2001**, *500*, 100.
[21] H. O. Finklea, D. D. Hanshew, *J. Am. Chem. Soc.* **1992**, *114*, 3173.
[22] H. D. Sikes, J. F. Smalley, S. P. Dudek, A. R. Cook, M. D. Newton, C. E. D. Chidsey, S. W. Feldberg, *Science* **2001**, *291*, 1519.
[23] D. Astruc, *Electron Transfer and Radical Processes in Transition-Metal Chemistry*, Wiley-VCH, Weinheim, **1995**.
[24] M. B. Robin, P. Day, *Adv. Inorg. Chem. Radiochem.* **1967**, *9*, 247.
[25] H. Van Ryswyk, E. D. Turtle, R. Watson-Clark, T. A. Tanzer, T. K. Herman, P. Y. Chong, P. J. Waller, A. L. Taurog, C. E. Wagner, *Langmuir* **1996**, *12*, 6143.