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Assemblies of “Hinged” Iron−Porphyrins as Potential Oxygen Sensors

Gonen Ashkenasy,[†] Albena Ivanisevic,[§] Rami Cohen,[‡] Clifford E. Felder,[†] David Cahen,[‡] Arthur B. Ellis,[§] and Abraham Shanzer*,[†]

Contribution from the Department of Organic Chemistry and the Department of Materials & Interfaces, Weizmann Institute of Science, Rehovot, Israel, 76100, and the Department of Chemistry, University of Wisconsin−Madison, Madison, Wisconsin 53706

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Abstract: Sequential self-assembly of a two-component system on a solid support is described with respect to structure and function. Two ligands, which bind to the semiconductor surface through one end and axially ligate a heme analogue at the other end, are described. Monolayer assemblies of complexes formed by these ligands and iron-porphyrin perform reversible binding of molecular oxygen. In the monolayer, a metalloporphyrin (the sensing unit) is held by the intervening ligand that serves as a “hinge”, away from the solid surface. Sensing events based on porphyrin chemistry are communicated via the ligand to the solid support. The transduction manifests itself as a change in the solid’s surface electronic properties. Synthesis of the ligands and analysis of its complex formation with Fe^{III}-porphyrin are described. The anisotropic orientation of the porphyrin ring within the ligand cavity, due to restricted rotation around the $Fe^{III}-N$ imidazole bonds, was probed by ^1H NMR measurements in solution. We show that the porphyrin substituents stand as barriers for the free rotation even at room temperature. Molecular modeling supports the NMR evidence and reveals the stable conformations for the porphyrin’s orientation relative to the solid support. The complexes were assembled as films on the (0001) surface of etched n-CdSe single crystals, and the films were characterized using transmission Fourier transform infrared (FTIR) and X-ray photoelectron (XPS) spectroscopies. Contact potential difference (CPD) and steady-state photoluminescence (PL) measurements of the derivatized CdSe show that the intervening ligands yield better conjugation and stronger binding of the sensing unit to the semiconductor surface, relative to direct adsorption of metalloporphyrins. Furthermore, the PL changes in the CdSe can be used to follow the interaction of the surface-bound Fe^{III}-porphyrin−ligand complexes with molecular oxygen. A model is proposed to explain the electronic changes resulting from binding of O_2 to the monolayer.

Introduction

Assembling molecular functional components into supramolecular architectures is envisioned to yield artificial “devices” of technological relevance, such as sensors, heterogeneous catalysts, and photosensitizers.[1] The efficacy of the molecules with special functions, such as recognition sites, photoactivity, or redox activity, can be modified significantly by making them part of well-ordered monolayers.[2] The first advantage that this strategy provides is a means to orient the active species in a predetermined configuration relative to the surface and to neighboring molecules. The second advantage is the ability to use such assemblies for sensing chemical events based on headgroup chemistry that is then communicated via the tail of the molecule to the chosen solid support.[3−8] This transduction event can manifest itself as a change in the solid’s surface electronic properties, such as the work function and redox potential. We have studied during the past few years the modification of semiconductor (SC) work functions and electron affinities through chemical adsorption of organic ligands with polar headgroups and/or suitable LUMO levels.[9−13] In other work we synthesized and used ligands that can bind metal ions in a predetermined location above electrically conductive surfaces.[14,15]

The versatile functions presented by metalloporphyrins in biological, as well as synthetic, systems make these molecules the first choice for incorporation into new assemblies as active components. Attempts have been made to create monolayer

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[†] Department of Organic Chemistry, Weizmann Institute of Science.

[‡] Department of Materials & Interfaces, Weizmann Institute of Science.

[§] University of Wisconsin−Madison.

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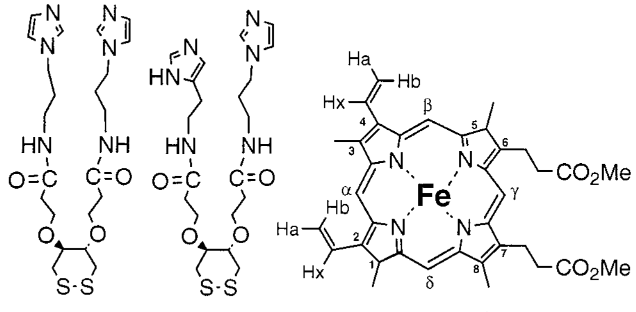
structures by binding (metallo) porphyrin moieties directly to a solid surface.[16−23] This approach resulted in assemblies of mixed porphyrin orientations and did not prevent chromophore aggregation. Optimal uniform orientation is crucial to achieve a unique interaction between the porphyrin and the surface and to minimize chromophore aggregation in the direction parallel to the surface, which is needed to reduce lateral energy dissipation. Recently, the possibility of binding metalloporphyrins to conductive surfaces coordinatively, through the central metal, was demonstrated. Collman et al. utilized single-stranded alkanethiols terminated with imidazoles to bind Ru− and Os−porphyrins,[24] and Willner and co-workers bound hemin groups to a four-bundle synthetic protein on gold.[25]

Recently, we showed that one can use pre-designed dipodal ligands to axially coordinate metalloporphyrins and, consequently, locate them in a well-defined environment, mainly perpendicular to conducting surfaces. Monolayers prepared in this way differ from most other systems in that the metalloporphyrin unit is not in direct contact with the surface. Rather, it is held by the intervening ligand, the "hinge", that also "protects" its open faces, thus eliminating π-stacking with other porphyrin moieties. Although the porphyrins are about 1 nm from the surface, electron-transfer capability is retained, as is evident from our earlier electrochemical results.[26,27]

It occurred to us, by following biological trends, that if these iron porphyrin complexes are to bind dioxygen, a nonsymmetric environment that creates two nonequivalent porphyrin faces (and coordination unsaturation) is needed. This nonsymmetric environment may be induced into our two-component system by binding either a symmetric ligand to a nonsymmetric iron porphyrin or a nonsymmetric ligand to a symmetric (or nonsymmetric) iron porphyrin. We introduce two bifunctional ligands, **1** and **2** (Chart 1), capable of binding to an appropriate surface through one end and to axially ligate a heme analogue at the other end. The complexes formed by **1** or **2** and a heme analogue, and their structural features, were characterized in solution, by UV−vis and ^{1}H NMR spectroscopy, prior to the adsorption onto a semiconducting surface. To probe the anisotropic orientation of the porphyrin ring within the cavity formed by the ligands, we used a combination of dynamic NMR and molecular modeling.

The 1:1, ligand:Fe^{III}-porphyrin complexes were assembled on the (0001) surface of an etched single crystal of n-type cadmium selenide (n-CdSe), and the films formed were characterized by transmission Fourier transform infrared spectroscopy (FTIR). Contact potential difference (CPD) and steady-state photoluminescence (PL) measurements served to identify electronic effects resulting from ligand binding to the surface, and from binding Fe^{III}-porphyrin to the ligands. Advantages of using the linker ligands, over direct binding of the porphyrin to the surface, which include stronger porphyrin−surface binding and better conjugation with the surface, are clearly evident from these measurements. Further we demonstrate the molecular functionality of the assemblies: by following CdSe PL changes, we show that the surface-bound Fe^{III}-porphyrin−ligand complexes interact *reversibly* with O_2. A model is presented to explain the mechanism of O_2 binding to the assemblies.

Chart 1



1 **2** $FePPMe^+$

Experimental Section

Synthesis. Compound **2** was prepared by a modification of the procedure that was described for compound **1**.[26] In the final step the disulfide di-pentachloro phenolate was coupled to 1-(3-aminopropyl)-imidazol (0.9 equiv) and histamine (1.2 equiv), one after the other with no intermediate separation. The nonsymmetric product was separated from the two symmetric ones on a silica gel column ($CHCl_3$:CH_3OH). The overall yield was ca. 25%. **2:** ^{1}H NMR (400 MHz, CD_3OD) δ 7.68 (s, 1H), 7.60 (s, 1H), 7.15 (s, 1H), 6.96 (s, 1H), 6.87 (s, 1H), 4.02 (t, 2H, $J = 7.2$ Hz), 3.82 (m, 4H), 3.43 (t, 2H, $J = 7.5$ Hz), 3.25 (br., 1H), 3.18 (t + ABq, 4H), 2.82 (t + ABq, 4H), 2.42 (m, 4H), 1.98 (qui, 2H, $J = 5.0$ Hz). MS (FAB) *m/z* 496.

$Iron^{III}$ protoporphyrin IX dimethyl ester chloride (FePPMeCl) was synthesized by (i) methylation of protoporphyrin IX (0.53 mmol) with trimethylsilyl diazomethane (2 mmol; 2 N in hexane) and (ii) insertion of iron as $FeCl_2$ (5 molar equiv) and oxidation to Fe^{III} during washing with concentrated NaCl solution. FePPMeCl: IR ($CHCl_3$) $\upsilon(COOCH_3)$ 1733 cm^{-1}. UV−vis ($CHCl_3$) λ_{max} 402 nm; $\epsilon = 7.6 \times 10^4$ $M^{-1}cm^{-1}$. MS (FAB) *m/z* 644 ($MH^+ - Cl$).

UV−Vis Spectroscopy. All measurements were made on a Beckman DU-7500 diode array spectrophotometer. Characterization of free-base PPMe, FePPMeCl, and complexes of the latter with **1** or **2** was done in $CHCl_3$ and DMF, respectively, at room temperature.

NMR and Calculation of Activation Parameters. ^{1}H NMR measurements of the low-spin complex **1-FePPMeCl** were carried out on a Bruker AMX-400 spectrometer. The samples of 1:1 ligand-to-porphyrin solutions (22−25 mM in $CDCl_3$) were measured at 12 different temperatures (−40 to +50 °C). All chemical shifts are reported in δ units from TMS as internal standard. The peak width and chemical shifts of signals, which were split below the coalescence temperature (27 °C), permitted calculation of the exchange rate between two or more conformations, as explained elsewhere for similar systems.[28] To simplify the calculation, signals of lightly populated conformations (less than 0.2 in intensity, relative to the main conformation) were omitted.

Molecular Modeling. Molecular mechanics calculations with Lifson's EFF force field were used to complement the experimental measurements.[29,30] Force parameters for the heme and imidazole groups

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were added to the basic parameter set with the help of structural information derived from Cambridge Structural Database searches and ESP partial atomic charges from MOPAC quantum calculations.

The initial coordinates for the ligand−porphyrin complexes were built in stages. First, the hemin core was built, and the vinyl and propionic acid side chains were added in an extended conformation, which was not scanned further. The ligating nitrogens of the imidazole groups were attached to the ends of an imaginary axis through the iron, perpendicular to, and 2 Å from the plane of the hemin. To determine which meso carbon is located between the ligand's arms, the hemin was rotated over four 90° intervals about this axis, in separate calculations. Independently, the imidazolyl groups were also rotated in 22.5° intervals about this axis out to ±90° from their initial positions. For each position of the hemin and imidazoles, a pseudo-C_2-symmetry-constrained conformational scan of the complex was done (36 separate calculations). The condition of ring closure across the cyclohexyl ring base was set about the pseudo-C_2-axis, in the hemin ring plane, passing from the Fe through one of the four porphyrin meso carbons. The energy minimization was done without any symmetry constraint.

Film Preparation. Single-crystal, vapor-grown c-plates of n-CdSe with resistivity of ~2 ohm·cm were obtained from Cleveland Crystals, Inc. The semiconductor samples were etched in Br_2/MeOH (1:15 v/v), revealing the shiny Cd-rich (0001) face that was used to deposit films onto. Films of the metalloporphyrin and of each ligand were prepared following a previously reported procedure.[26] Bifunctional ligands **1** and **2** were deposited as films onto the CdSe surface from $CHCl_3$ solution. The metalloporphyrin was reacted with these films to form discrete ligand−metalloporphyrin complexes (e.g., **1-FePPMeCl**) in this two-step manner. The discrete complexes were also preformed in solution by simply mixing equimolar solutions of ligand and metalloporphyrin, dip-coating the CdSe with the mixture, and a short rinsing with pure $CHCl_3$.

FTIR Measurements. FTIR spectra were taken with a Bruker FX30 spectrometer in the transmission mode. The (mercury cadmium) telluride (MCT) detector was cooled by liquid nitrogen. The resolution of the spectra was 2 cm^{-1}. The instrument was programmed to run 128 scans with the reference (the etched, bare CdSe) and then 128 scans with the relevant sample. The spectrum of the **1-FePPMeCl** film without rinsing was compared to the isotropic spectrum in KBr, in the region 800−3500 cm^{-1}. Short rinsing of that film removed excess porphyrin and left a monolayer. These assemblies were kept in a vacuum chamber for a few days over which negligible change in the spectrum was observed. We also monitored the monolayer quality following longer exposure to pure $CHCl_3$. There, FePPMeCl was removed first (after about 1 min) and only much later was the ligand monolayer destroyed.

Steady-State Photoluminescence (PL). A Melles Griot He−Ne laser (633 nm) provided excitation of the semiconductor. Incident intensities ranged from 5 to 20 mW/cm^2. Emission spectra were monitored using an Oriel Instaspec II silicon diode array spectrophotometer or Oriel Instaspec IV CCD spectrophotometer. A cutoff filter was used in the spectrophotometer to permit collection of the band-edge PL at $\lambda_{max} \sim 720$ nm ($E_g \sim 1.7$ eV). The entire PL spectrum was monitored, while tracking the PL intensity at a particular wavelength, typically the band maximum, as a function of time; the band maximum did not shift under the low-resolution (0.5 nm) spectral conditions employed. The signal collected was used for computer analysis utilizing InstaSpec1.1 for Windows 95. Binding constants were calculated using the Langmuir adsorption isotherm based on the data as previously described.[31]

A gas flow apparatus was assembled using Tygon tubing that allowed mixtures of nitrogen and oxygen to flow over the semiconductor surface while the solid was illuminated. Flow meters were used to introduce variable percentages of each gas (N_2 or O_2) into the sample cell. Partial pressures of the gases were controlled by adjusting the flow rates of the incoming gases. The total gas flow rates varied from 80 to 250 mL/min, and the total gas pressure was 1 atm. The sample of CdSe was mounted on a glass rod between two Teflon rings within a glass cell. The cell was equipped with a sidearm, through which either solutions or gases could be introduced without disturbing the optical alignment.

Contact Potential Difference (CPD) Measurements. We used the CPD method as previously described.[11] Bare CdSe surfaces, surfaces covered with ligand, and those covered with the complex monolayer (**1-FePPMeCl**) were measured immediately after the adsorption process (described in the film preparation section above). Except for one set of experiments, which was done in an inert atmosphere (N_2), all other measurements were done in air.

XPS Measurements. The XPS data were collected using a Perkin-Elmer PHI 5400 ESCA system with a Mg Kα X-ray source powered at 300 W. The aperture size was 1 mm × 3 mm, and the pass energy was 89.45 eV. The data acquisition time for each run was 4.17 min. Samples were prepared by dipping a crystal of CdSe into an appropriate solution of either ligand or metalloporphyrin, as described in the film preparation section, and rinsing with either $CHCl_3$ or toluene.

Results and Discussion

(a) Design, Synthesis, and Solution Behavior. Two essential components were integrated into the skeletons of ligands **1** and **2**: (i) a six-membered cyclic disulfide for surface attachment and (ii) two extended imidazolyl residues capable of binding metalloporphyrins at the 5th and 6th coordination sites. Synthesis of **2** was achieved as described earlier for ligand **1**.[26] It is based on the preparation of disulfide di-activated ester, followed by coupling to the appropriate amino imidazole derivatives. The disulfide and the imidazoles were deliberately placed on opposite sides of the molecules to avoid their mutual interaction with metalloporphyrins. The same cyclic disulfide serves as the anchoring group of molecular monolayers to gold, as well as to semiconductor surfaces.[11,14] By using this anchor one prevents segregation of the upper arms even if S−S cleavage occurs prior to the surface binding,[2] and one avoids tilt of the molecule relative to the surface, along an axis parallel to the S−S bond. While ligand **1** has C_2 symmetry, bearing N-alkyl imidazole on both arms, ligand **2** lacks this symmetry having two different imidazoles, NH and N-alkyl. Ligation of iron(III) protoporphyrin IX dimethyl ester chloride (FePPMeCl, Chart 1) by either **1** or **2** was expected to create complexes that lack symmetry, due to the nonsymmetric porphyrin substitution. In early works it was shown that *N*-methyl imidazole binds Fe^{III}-porphyrins about 3 orders of magnitude weaker than unhindered NH imidazoles.[32] Thus, the complex of **2** with FePPMeCl presents a minimal approach to mimic binding by proximal and distal histidines in myoglobin. Here, the N-alkyl imidazole arm is bound weakly and can be replaced by an oxygen molecule.

Complexes of **1** or **2** with FePPMeCl were also prepared by simple mixing of a 1:1 solution in $CHCl_3$ or DMF. The formation of the desired complexes was evidenced by UV−vis measurements (λ_{max} 411 and 534 nm). ^{1}H NMR spectra of **1-FePPMeCl** solutions (>20 mM, 30 °C) were obtained, and the low (8 to 20 ppm) and high (−7 to 0) field spectra were resolved by comparing them to simpler FePPMeCl-His_2 models.[33] Only one set of signals was obtained, reflecting complete (>99%) 1:1 complexation.

The ^{1}H NMR measurements of the low-spin complex **1-FePPMeCl** were also performed at various temperatures, from −40 to +50 °C, to search for the different orientations of the porphyrin fragments relative to the ligand chains, due to rotation around the Fe−Nim bonds. Only one set of signals was observed

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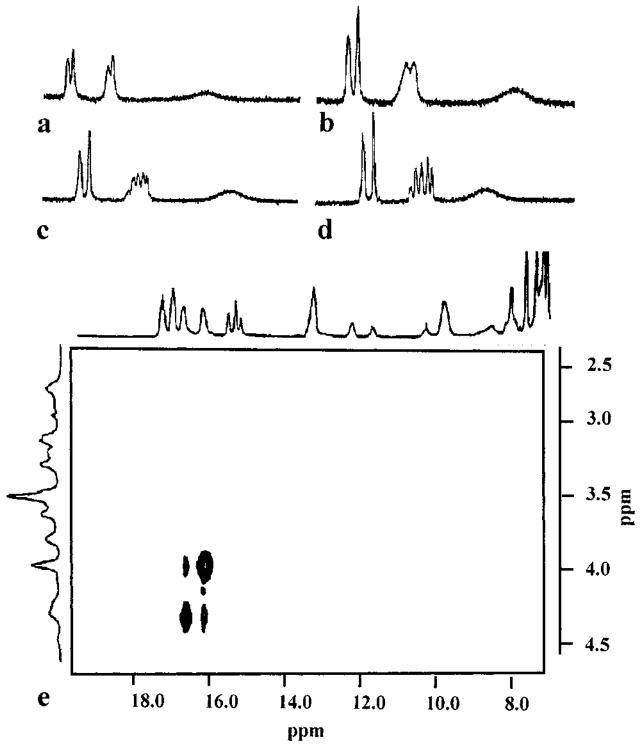

Figure 1. ^{1}H NMR of 23 mM **1-FePPMeCl** in $CDCl_3$: 1D high field at (a) 46.0, (b) 30.0, (c) 22.2, and (d) 0.0 °C and (e) 2D NMR NOESY, NOE coupling between CH_2-Im of the ligand and two meso protons at 15.0 °C. All 1D signals appear below 0 ppm, and are presented one below the other after compensation for the Curie temperature-dependent shifts.

above 30 °C (Figures 1a and 1b), and these were attributed to rapid rotation. But, at or below room temperature (coalescence temperature = +27 °C) signals of certain protons, undoubtedly located in the vicinity of the paramagnetic center, split (Figures 1c and 1d). The same experiment was carried out with a complex of ligand with one extra spiro carbon, positioned between the two arms.[34] This ligand created a cavity equivalent to that formed by a ligand that is "1/2" carbon per chain longer. We observed free rotation at room temperature and a coalescence temperature of ∼+5 °C. The peak separation, in **1-FePPMeCl**, below room temperature was resolved for the ligand CH_2-Im protons (intensity ratio 1:1), and for methyl-3 (∼0.5:1:1.2) and one of the vinyl group protons (∼0.2:1:1.2) which belong to the porphyrin. The other type of vinylic proton signals did not split in this range of temperatures, as shown in Figure 1a−d. The separation of the former vinylic protons (δ −3.2, −3.4 ppm, respectively, at 22 °C) below the coalescence temperature permitted calculation of the activation parameters for the chemical exchange, by adaptation of conventional procedures to the paramagnetic system. The values obtained are the following: $\Delta G^{\#} = 72.2$ kJ mol^{-1}, $\Delta H^{\#} = 86.7$ kJ mol^{-1}, and $\Delta S^{\#}/T = 0.048$ kJ mol^{-1}. The relatively large $\Delta G^{\#}$ value demonstrates that the ligand arms, which are long enough to wrap around the porphyrin ring, function as obstacles and block free rotation. The positive $\Delta S^{\#}$ value may indicate that the rotation of the ring is facilitated by a transition state in which one imidazole is (partially) released. The close proximity of the ligand chains and the porphyrin ring was further evidenced by NOE coupling, shown in Figure 1e, between the CH_2−Im ligand protons (16.2 and 16.4 ppm at 15 °C) and two of the four porphyrin meso protons (4.0 and 4.4 ppm).

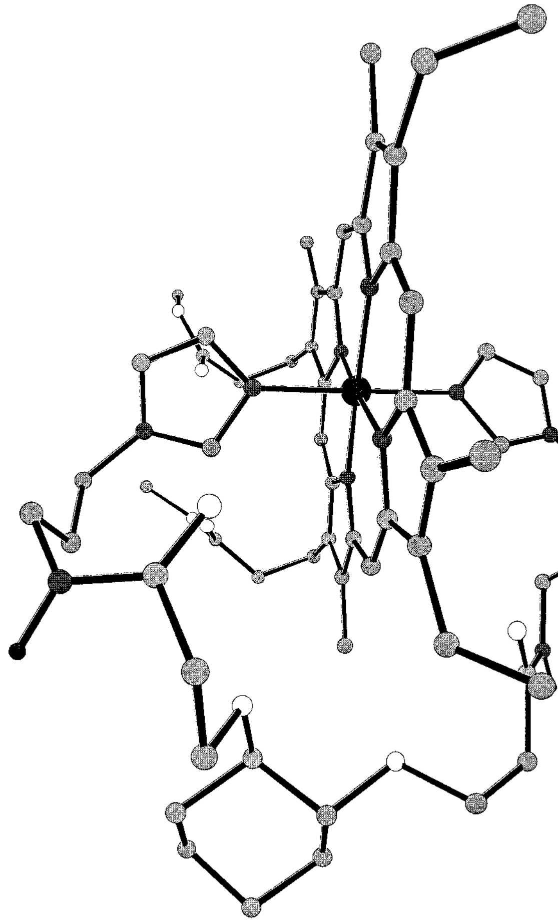

Figure 2. Most stable, calculated, conformation of **1-FePPMeCl**. The view is almost along the porphyrin plane, the two imidazoles are in the center left and right and the anchor base is at the bottom. Atom coding: lightly shaded, carbon; darkly shaded, nitrogen; black, iron; and white, oxygen. The hydrogens are not shown for clarity, but were included in the calculation.

(b) Theoretical Calculations. Molecular modeling, by a conformational tree search, was used to determine the lowest energy conformation of a molecular complex of **1-FePPMeCl**, where the S−S bond is replaced by a C−C bond. A total of 520 initial conformations were minimized to 35 final states within 33 kJ/mol of the minimum. All the structures obtained, as shown in Figure 2 for the most stable one, share the following features: (i) the ligand strands are located above the porphyrin meso-carbons, on opposite faces, between two substituents, (ii) the hemin ester carbonyls are bent over and point toward one of the imidazole rings and the Fe, (iii) the distance between the Fe and the S−S bond is 9.9 ± 0.5 Å, and (iv) the coordination of imidazoles to the iron center is almost perfectly axial, giving octahedral coordination geometry (e.g. all Fe to N bonds are within 90 ± 2° of each other).

Each minimized complex was characterized according to the type of porphyrin meso-carbon that is placed between the ligand arms. In each type of structure the latter are straddling between different porphyrin substituents: α, methyl 3 and vinyl 2; β, methyl 5 and vinyl 4; γ, two propanoic methyl esters; and δ, between methyls 1 and 8 (see Chart 1 for the nomenclature). The γ position is a priori thought to be the least favorable one, due to steric hindrance. Note that the β and δ positions are not the same. Pattern δ was found to be the most stable one, with pattern α first appearing in a conformation 5.9 kJ/mol above the energy minimum. Pattern β is less stable than α by less

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[34] Ashkenasy, G.; Shanzer, A. Unpublished results.

than 0.8 kJ/mol. As expected, pattern γ is not observed in any of the stable conformations.

Ideally, the dipodal ring base C−C and iron-to-imidazole N bonds should be parallel to each other, and both should be perpendicular to the Fe−base midpoint pseudo-C_2 dipodal axis. In the conformations we obtained the two bonds are within 17° of being parallel. Similarly, both bonds are within 21° of being perpendicular to the dipodal axis.

We searched, in a similar way, for the stable conformations in a complex of FePPMeCl and a di-imidazolyl ligand that is shorter at each arm by one methylene unit. The stability order of the four possible patterns was found to be the same, but with much larger energy differences between the patterns. Also, the shorter chain length leads to a less twisted structure. As all the structures appear to have a well-characterized geometry, we would expect a structure like **2-FePPMeCl**, with mixed length spaces (which, lacking a pseudo-C_2 symmetry, is beyond the capability of our current conformational scanning programs), also to have a well-characterized geometry, and in particular a very good octahedral coordination geometry about the iron center.

The three stable conformations we assigned in solution, or by the modeling, exposed a coherent picture. These might affect the orientation of the porphyrin with respect to the surface. Although there are some significant changes in the molecular structure due to the adsorption process, we suggest that these orientations have a crucial influence on the effective interaction of the iron active center and the surface. The findings that both ester carbonyls interact with one imidazole, and that there is a short-lived state in which one imidazole is released, suggest that the two imidazoles are not equivalently binding to the iron. The one farther from the heme esters binds more weakly than the other, and can be displaced more easily by small molecules such as oxygen.

(c) Surface Modification. Complexes of **1** or **2** with FePPMeCl were assembled onto CdSe surfaces from chloroform solutions in two alternative pathways: (i) as discrete preformed **1-FePPMeCl** or **2-FePPMeCl** complexes in a single step, after the complex was formed in solution, and (ii) in a two-step manner, in which a monolayer of **1** or **2** is first adsorbed from chloroform, followed by addition of FePPMeCl to this solvent. In the following we describe the characterization of the resulting films by three independent methods. FTIR and XPS are used to probe the existence of the expected species, and the extent of coverage. The third method, steady-state PL, allows calculating how strong the binding of Fe^{III}-porphyrin is, through the ligands, to the SC surface. In addition, PL reveals the electronic interactions that occur following the binding, an interaction that is further elaborated using the CPD changes.

Figure 3 shows the FTIR spectra of **1** (c) and of **1-FePPMeCl** (b) assemblies on CdSe, after subtraction of the etched bare surface absorbance spectrum in the 1300 to 1800 cm^{-1} region. For comparison, the spectrum of **1-FePPMeCl** in KBr (Figure 3a) is shown as well. All four strong vibrations expected in this region are seen clearly in the **1-FePPMeCl** spectrum. The ligand assemblies looks similar and, as expected, lack the 1733 cm^{-1} vibration of the porphyrin methyl-ester carbonyl symmetric vibration, and the aromatic stretches at ca. 1430 cm^{-1}. Such a comparison also exposed similarities between these spectra in the alkyl vibration region (2800−3200 cm^{-1}) and at ~1100 cm^{-1} corresponding to the ligand ether bond. The strongest vibrations, the carbonyl esters and amides, showed absorbance of about 5×10^{-4}, which includes the contribution from each molecule of two of these functional groups and of the two opposite faces of the CdSe wafer that are covered. This value was correlated previously, on similar systems, to coverage of one monolayer or less (0.4−0.95).[11,15]

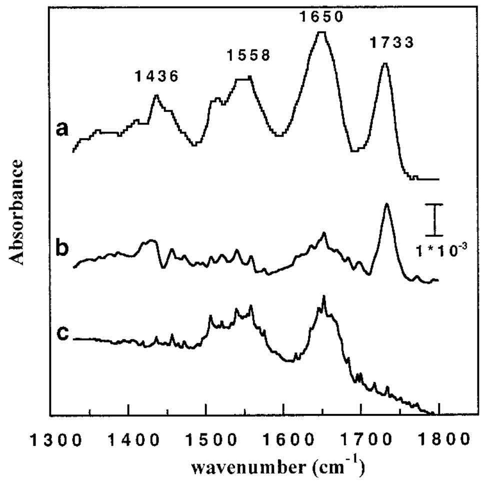

Figure 3. Transmission FTIR spectra of (a) **1-FePPMeCl** in KBr and (b) **1-FePPMeCl** and (c) **1** on an etched (0001) n-CdSe surface. Spectra b and c are relative to the etched CdSe bare surface spectrum (which was used as reference). The intensity scale refers only to spectrum b, while the other two spectra were reduced.

In the two-step method, adsorption of the ligand alone resulted in higher surface coverage, as calculated from the amide 1650 cm^{-1} vibration. Subsequent adsorption of the porphyrin allowed partial ligation and caused slight removal of ligand. This could be reduced to a minimum by shortening the adsorption time of the porphyrin (<5 min) in the second step. The ligand molecules within the assembly adopted an unstrained conformation that created a cavity, not perfectly fitted for porphyrin ligation. We demonstrated earlier, on gold, the same phenomenon, where the preformed method resulted in a more highly ordered monolayer and a larger Fe^{III}-porphyrin capacity than the two-step method.

The monolayers of **1** and **1-FePPMeCl** were analyzed further by XPS. The spectrum of CdSe derivatized by **1** showed the characteristic binding energies of the ligand's atoms, C, O, N, and S. An indication of substantial coverage by the ligand came from the large intensity ratio of these peaks relative to the Cd and Se peaks. The important signal belongs to the S_{2p} binding energy (160 eV), which was absent in the spectrum of the bare surface and is not expected to result from common impurities. In the monolayer of **1-FePPMeCl**, which was made in two steps, an additional doublet of the iron binding energies was observed at ~712 and 725 eV. The 712 eV peak split into two peaks (centered at 710.9 and 712.1 eV) which, from comparison to other systems, both belong to the $2p_{3/2}$ of Fe^{3+}.[22] Interestingly, XPS of a surface that was exposed directly to **FePPMeCl** and rinsed with $CHCl_3$ revealed that so little iron had been bound that the 712 eV signal was not observed in the limit of our signal-to-noise.

The surface modification processes induce changes in the CdSe band-edge PL intensity,[31] at $\lambda_{max} = 720$ nm in response to 633 nm excitation; the porphyrin complexes have negligible absorbance at these wavelengths. Figures 4a and 4b show the PL quenching upon **1-FePPMeCl** adsorption onto the CdSe surface, using either the preformed (Figure 4a) or two-step (Figure 4b) method. In both cases the quenching is compared to that obtained when the CdSe surface is exposed to FePPMeCl alone. Significantly larger quenching is obtained when **1** served to link the porphyrin to the surface. From Figure 4b, the

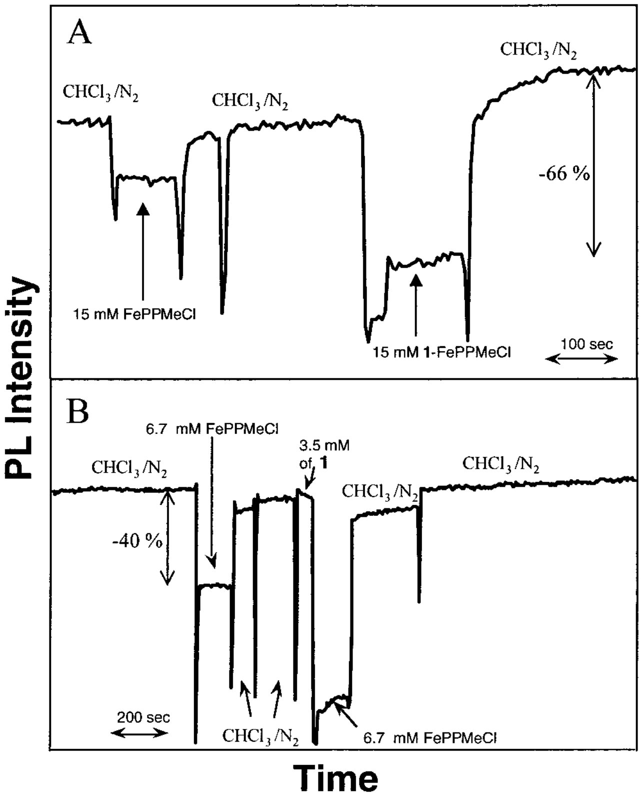

Figure 4. Changes in PL intensity of an etched (0001) n-CdSe sample resulting from exposure to chloroform solutions of **1,** FePPMeCl, and **1-FePPMeCl**. In panel A, the sample is first exposed to FePPMeCl, rinsed with solvent, and then exposed to **1-FePPMeCl**. In panel B, the sample is exposed sequentially to FePPMeCl, solvent, **1**, FePPMeCl (forming **1-FePPMeCl),** and solvent. The downward spikes are an artifact of draining the sample cell to change solution ambient. For all experiments, the PL was excited at 633 nm and monitored at 720 nm. The data in panels A and B were collected using two different CdSe samples.

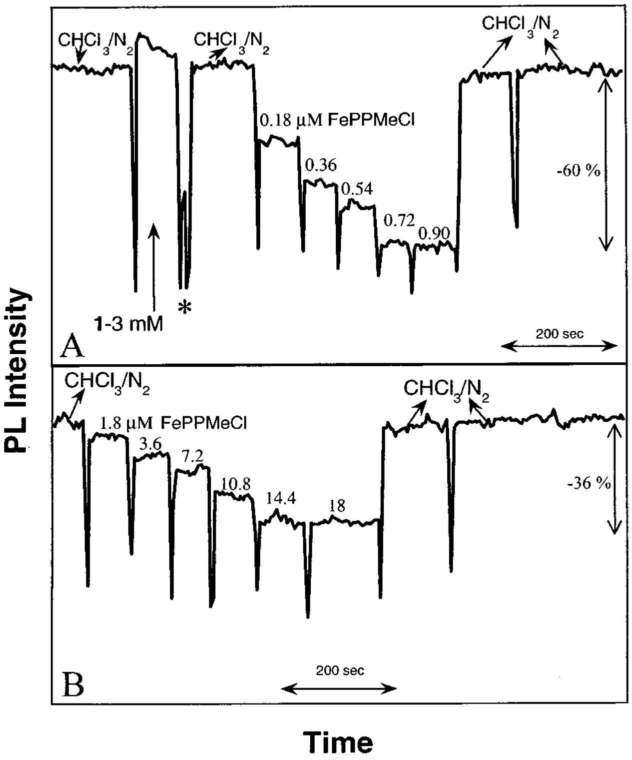

Figure 5. Changes in the PL intensity of an etched n-CdSe crystal resulting from exposure to (A) a 3 mM solution of **1**, followed by FePPMeCl dissolved in N_2-saturated $CHCl_3$ to form **1-FePPMeCl** on the surface, and (B) FePPMeCl dissolved in N_2-saturated $CHCl_3$. The asterisk on panel A indicates the position where ligand **1** was left to dry out on the surface. The PL was excited in each case with 633 nm light and monitored at 720 nm. The downward spikes result from draining the sample cell when changing solutions. The data on panels A and B were collected on the same CdSe surface.

adsorption of ligand **1** alone caused only a very small enhancement in the PL intensity. The same result was observed for **2** (data not shown).

While preparing the complexes in the two-step method, we followed the PL changes due to introduction of different concentrations of FePPMeCl to surfaces of CdSe treated with **1** or **2**. These are shown, for the case of **1**, in Figure 5a. Langmuir double reciprocal plots led to estimates for the binding constants, *K*, of $(1.8 \pm 0.11) \times 10^6$ and $(2.4 \pm 0.19) \times 10^6$ M^{-1} for binding FePPMeCl to adsorbed ligands **1** and **2**, respectively.[31,35] These values are substantially larger than the $\sim 7.5 \times 10^4$ M^{-1} value calculated, from the PL changes in Figure 5b, for the binding of FePPMeCl alone to CdSe. The slightly better binding to **2** fits with the favored binding of its NH-imidazole, relative to N-alkyl, to the heme.[32] The good fit of the PL quenching to the single binding site Langmuir model indicates that the FePPMeCl binds solely to the imidazoles. The equilibrium constant values for binding FePPMeCl to the surface treated with the ligands are larger here than the values we obtained earlier for complex formation in solution.[26] This result is attributed to a smaller entropy loss during complexation when the ligand is already assembled in a confined location onto the surface.

PL results obtained with the two preparative methods that we used were consistent. Larger PL quenching and the higher binding constant of ligand−porphyrin complexes to the surface, relative to only porphyrin, demonstrate two main advantages of the use of ligands **1** and **2**: (i) the metalloporphyrins are bound more strongly to the surface than if used directly, due to chemical bonding of the iron to the linker ligands, and (ii) assuming that similar absolute coverages are involved the electronic interaction of the porphyrin with the surface is enhanced, perhaps due to "through-bond" interactions.

Under photosaturation conditions, CPD on dry samples, in ambient atmosphere, provides additional information on the origin of the PL quenching for adsorption of FePPMeCl onto CdSe derivatized with a monolayer of **1**.[10] While the first step, binding ligand **1** to the CdSe surface, caused a small and inconsistent change in the band bending, V_s, the subsequent adsorption of FePPMeCl revealed an increase in V_s of 80−130 mV. Exposure of the bare CdSe surface to FePPMeCl alone yielded a similar V_s increase. This change in band bending during the derivatization process is in agreement with the notion that the interaction of the Fe^{III}-porphyrin, or maybe its chloride counterion, with the surface reduces the probability for charge recombination, as reflected by the PL quenching. Time-resolved PL (TRPL) measurements show insignificant change in the PL decay, indicating that the surface recombination velocity is unchanged upon porphyrin adsorption and suggesting that quenching is arising from the increase in depletion width accompanying adsorption.[13]

(d) Binding Molecular Oxygen. Films of **1-FePPMeCl** and **2-FePPMeCl** on CdSe were prepared by dip coating in chloroform solution, allowing the solvent to evaporate, and

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[35] Ivanisevic, A.; Ellis, A. B. *J. Phys. Chem. B* **1999**, *103*, 1914−1919.

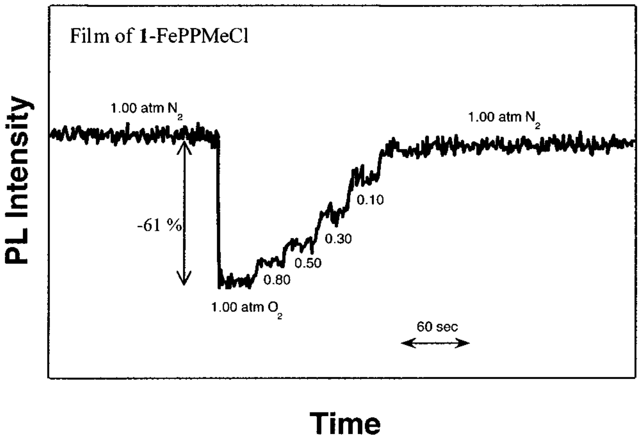

Figure 6. Changes in PL intensity of an etched n-CdSe crystal, coated with a film of **1-FePPMeCl**, resulting from exposure to various pressures of O_2. The equilibrium constant that was calculated from these data using the Langmuir adsorption isotherm model is 3.7 ± 0.2 atm^{-1}. When the crystal was coated with the ligand alone no changes were observed in the PL intensity after exposure to 1 atm of O_2.

quickly rinsing in chloroform to remove the weakly bound excess complex. To follow their response to O_2, these samples were exposed to various mixtures of N_2 and O_2, as shown in Figure 6 for film of **1-FePPMeCl**. In contrast to the uncoated surface and to **1**- or **2**-coated CdSe, which show no PL response ($<5\%$) to these gaseous mixtures, the **1-FePPMeCl**- and **2-FePPMeCl**-coated samples exhibit PL quenching that increases with O_2 partial pressure, and saturates at ~1 atm (Figure 6). The quenching was completely reversible upon returning to a pure N_2 ambient. Using the Langmuir one-site adsorption isotherm model, we estimated film-binding constants for O_2 from the changes in PL quenching. The values calculated for K are 3.7 ± 0.2 and 7.4 ± 0.5 atm^{-1} for **1-FePPMeCl** and **2-FePPMeCl** respectively. The results suggest slightly stronger oxygen binding to **2-FePPMeCl** than to **1-FePPMeCl**, and the binding constants are similar to those previously reported for the binding of oxygen to several divalent metalloporphyrin films, adsorbed directly on CdSe.[35] In conducting these experiments, we have not tried to optimize the PL response of the films but from our results, one can see that O_2 can be detected below 0.1 atm (Figure 6).

The reversible film response to oxygen is intriguing and could reflect several possible binding scenarios. Direct binding to Fe^{3+} sites by oxygen is unlikely, based on studies of compounds such as the globins or cytochrome P-450,[36] thus we gathered the experimental data to suggest other alternatives. The XPS results for air-exposed samples containing films of **1-FePPMeCl** display a double $2p_{3/2}$ Fe peak around 711.5 eV, indicating the presence of two different Fe^{3+} species. While this might be due to X-ray-induced damage, these peaks may otherwise belong to "free" and oxygen-bound Fe^{3+} porphyrins. The experimentally found increase in PL quenching upon exposure to dioxygen, which corresponds to an increase in band bending, i.e., to an increase in negative charge on the surface, is in agreement with the ability of the oxygenated complex to withdraw additional electron density from the semiconductor bulk.

It occurred to us that some of the iron centers might be reduced to Fe^{2+} under our experimental conditions, if the n-type CdSe surface can provide electrons under dark and/or illuminated conditions. Divalent Fe porphyrins are well-known to undergo oxygen binding, and reversibility depends critically on the ability of the surrounding ligands to prevent irreversible oxidation. This reaction sequence is summarized in the scheme below:

$$\text{Fe}^{+3}\text{-por} \xrightarrow{e^-} \text{Fe}^{+2}\text{-por} \overset{O_2}{\rightleftharpoons} \text{Fe}^{+3}\text{-por-}O_2^{\;-}$$

Note that the binding of neutral O_2 resulted in a complex, which is more negative than the originally adsorbed Ferric one. This was further supported by CPD measurements, which showed negligible change (<15 mV) in band bending, following the adsorption of FePPMeCl in an inert atmosphere.

Alternatively, oxygen could bridge adjacent ferric centers to form a μ-peroxo complex. This process, as we understand, dose not take place here because the metal ions are located far from each other, and in the presence of imidazoles the oxygen bridges are known to be broken.[37] Experiments with different analytes and metalloporphyrins are in progress to further elucidate the origin of the PL response to dioxygen

Conclusions

The results presented here show how bifunctional ligands, made of alkyl chains rather than a peptide backbone, can be used to "fix" metalloporphyrins into films. Slow conformational changes of the porphyrin within the ligands' cavities, in solution, gave clues to how the porphyrins are oriented when the complexes are assembled onto surfaces. The use of the linker ligands was found to be crucial in enhancing the interaction of the active moieties with the electronically conductive substrate. Due to this enhancement, oxygen binding to the headgroup of such films, the Fe^{3+} porphyrins, could be monitored about 1.5 nm away by tracking changes in the semiconductor substrate's PL properties. The oxygen binding is completely reversible and obeys the Langmuir single-site adsorption model. Clearly, these findings have implications for sensing other small gaseous analytes. These, and systems in which the metalloporphyrins are even further separated from the surface (2−10 nm), are currently under investigation.

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