from $[Ir_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$,[19] and on the basis of analogies in the two systems, we favor this route for the sulfide-bridged species also. In an attempt to determine whether or not species **4** was involved in HD formation, this species was also reacted with a H_2/D_2 mixture under the same conditions as for **1**. The results indicate that the H_2:HD ratios obtained by starting from either **1** or **4** are essentially indistinguishable.

Conclusions

Ligand attack in A-frame complexes can occur either at one of the two enclosed sites proximal to the adjacent metal or on the "outside" of the complex at either of the two sites distant from the adjacent metal; examples of each have been reported.[21-23] If the metals are to interact with substrate in a cooperative manner, it is essential that the substrate be bound in close proximity to both metals. We have clearly shown that H_2 attack on the sulfide-bridged A-frame, **1**, occurs at one of the enclosed sites, suggesting the possibility of metal-metal cooperativity in the subsequent chemistry of related species. We see no evidence of attack at either distal site. Although H_2 attack probably occurs at one metal to give a species such as **2c**, exchange of hydride ligands between the two metals, within the enclosed "pocket" of the complex, is extremely facile.

Subsequently, much slower rearrangement takes place, first at one metal to give an unsymmetrical dihydride (**3**) in which one hydride ligand is in the pocket and the other occupies one of the outside sites and then at the second metal to give **4**, in which both hydride ligands occupy the outside sites of the A-frame. This rearrangement may occur via cleavage of one of the Ir-S bonds to yield a dipolar intermediate.

The production of HD from mixtures of H_2 and D_2 in the presence of either **1** or **4** suggests the involvement of a dihydride-dideuteride species analogous to the tetrahydride previously observed in the reaction of $[Ir_2(CO)_2(\mu\text{-}Cl)(DPPM)_2]^+$ with H_2.[10,20]

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Band Structure Calculation of Extended Poly(copper phthalocyanine) One-Dimensional and Two-Dimensional Polymers

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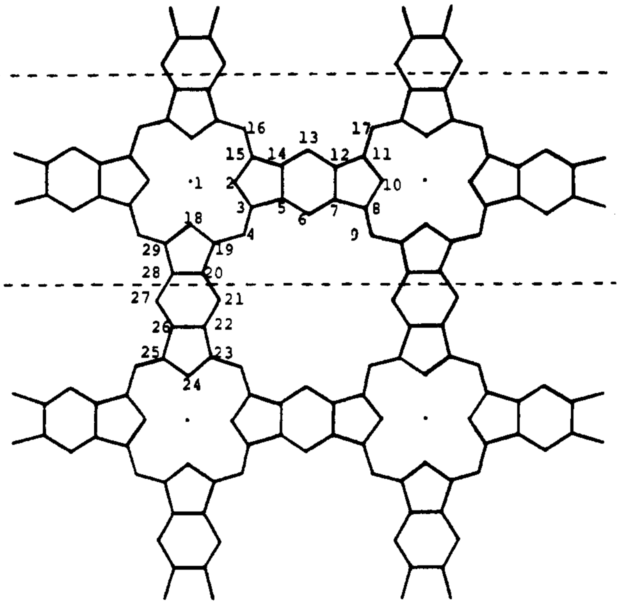
A variety of metallophthalocyanine (MPc) polymers have been experimentally[1-4,9] and theoretically[5-8] studied due to the interest in them as potential conductors and semiconductors. Among them, the linearly stacked chains have been studied most extensively.

In these conducting polymeric Pc's the electrons are delocalized along the π-π stacked Pc chains and the corresponding bandwidths are large ($\approx$1 eV according to ref 5). A less obvious question is the mechanism of electron transport between the individual conducting macromolecular chains.



BOND DISTANCES (Å)	
Cu1-N2	1.97
N2 -C3	1.37
C3 -N4	1.33
C3 -C5	1.48
C5 -C6	1.39
C5 -C14	1.30

BOND ANGLES			
1	2	3	125
2	3	4	130
3	4	19	122
2	3	5	108
15	2	3	108
3	5	14	108
14	5	6	120
5	6	7	120

Figure 1. Labeling of the atoms in the square (4/*mm*) unit cell of the poly(copper phthalocyanine) layer $CuC_{20}N_8$. Unit cell dimension: a = 10.773 Å. The dotted line indicates the limits of the one-dimensional polymer **1a**. For polymer **1b**, C atoms 21, 22, 26, and 27 were included in the calculation, together with the four corresponding H's.

We suggest that the obtainment of fused-ring Pc polymers, from one-dimensional models (**1a, 1b**), to two-dimensional systems such

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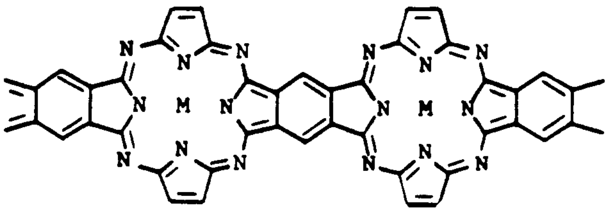
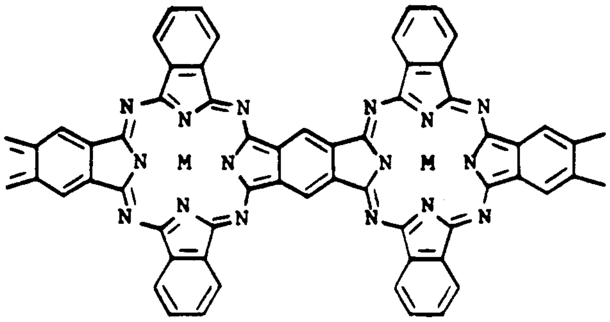
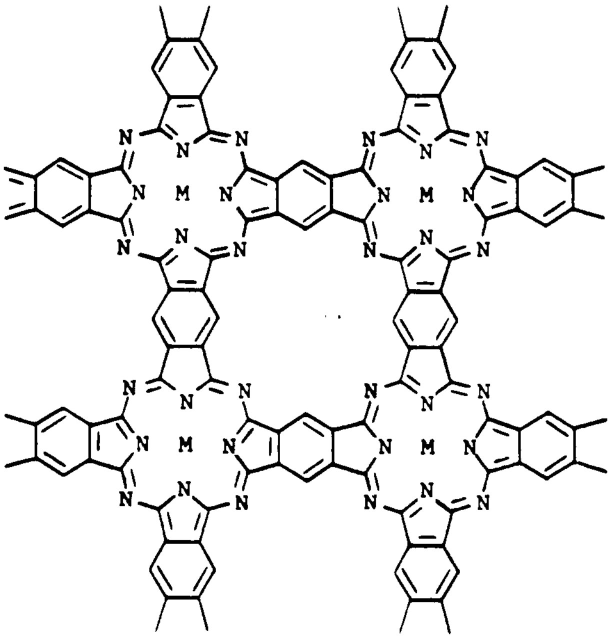


1a

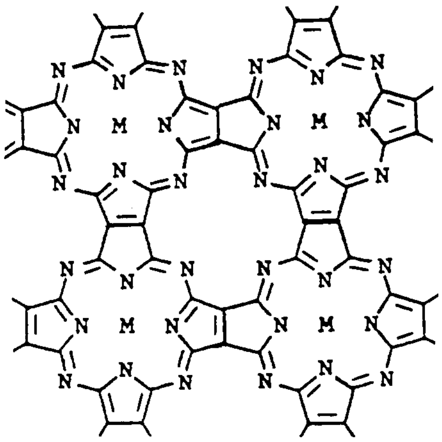


1b

as **2a** and **2b**, would eliminate the need for interstack hopping and should lead to large in-plane bandwidths. Thus, such systems may display intrinsic metallic properties.



2a



2b

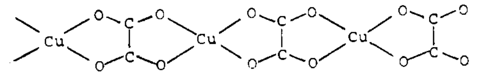
Some compounds related to these systems have been prepared earlier[9] but have not been fully characterized structurally.

Method

In this paper we report our calculations for compounds **1** and **2**, based on the extended Hückel theory (EHT, or tight-binding method)[10] in its band-theoretical form[10b,c] applicable to the solid state, using parameters listed in ref 11.

Figure 1 shows the labeling of atoms for the CuPc polymers studied as well as bond distances and angles chosen according to typical values.[3b,13] The dotted line indicates the limits of the one-dimensional polymer **1a**, which can be obtained from the two-dimensional ones (**2**) by replacing C(20)–C(21), C(27)–C(28), and symmetry-related bonds with C–H bonds, while keeping the C(5)–C(6)–C(7)–C(12)–C(13)–C(14) benzene ring. For polymer **1b**, C atoms 21, 22, 26, and 27 were included in the calculation, together with the four corresponding H's.

Polymers **1a** and **1b** bear some resemblance to a group of planar linear polymers with μ-oxalato groups coordinated equatorially to transition metals[12] as shown in **3** and to other semiconducting ladder polymers[14] containing transition metals, of which **4** is an example.



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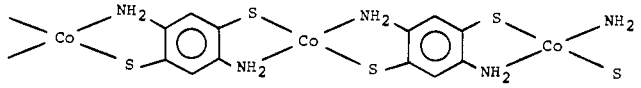

4

For our calculations we assumed ideal D_{4h} geometry (thus, perfect planarity of the rings) and applied a first-neighbor approximation, well justified given the large size of the unit cells. The 1s orbitals on the H's and the 2s and 2p valence atomic orbitals on the C's and N's as well as the 4s, 4p, and 3d AO's of Cu and Co were included in the calculations.[11]

One-Dimensional Planar Pc Chains

The band structure of **1a** (Figure 2a) implies that the system would not be a good conductor because band $\pi 2$ has a very narrow bandwidth although it is half-filled (**1a** has 129 electrons in the unit cell). This band is characterized by large orbital coefficients localized mostly on the two five-membered rings not bisected by the translational axis. However, if these rings are fused with two six-membered rings, as in **1b**, the system becomes a good conductor. This can be explained by constructing the band structure of **1b** from that of **1a**, employing a perturbational orbital approach. The addition of two six-membered rings to the structure of **1a** perturbs band $\pi 1$ upward and band $\pi 3$ downward, since they interact with the orbitals being added in an antibonding and bonding manner, respectively. $\sigma 1$ is not perturbed at all while band $\pi 2$ is perturbed upward strongly enough to surpass $\sigma 1$, and consequently $\sigma 1$ becomes partially filled for structure **1b** (165 e/unit cell). In this case (Figure 2b), the half-filled band ($\sigma 1$) cuts across a broad, empty band ($\pi 3$, bandwidth 0.78 eV), and the polymer should be a conductor.

Two-Dimensional Planar Pc Layers

The band structure of the two dimensional CuPc 2a is shown in Figure 2c. The model contains 135 e/unit cell, and the Fermi level is indicated by E_F. The $\Gamma(0, 0) - X(0.5, 0)$ line is the fraction of the Brillouin zone relevant for comparison with the one-di-

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(11) Atomic parameters used in the calculations (Coulomb parameters in eV). Cu: EXPs = 2.20, COULs = –11.40, EXPp = 2.20, COULp = –6.06, EXPd = 5.95, COULd = –14.00, C1 = 0.5933, EXPd2 = 2.30, C2 = 0.5744. Co: EXPs = 2.00, COULs = –9.21, EXPp = 2.00, COULp = –5.29, EXPd = 5.55, COULd = –13.18, C1 = 0.5679, EXPd2 = 2.10, C2 = 0.6059. N: EXPs = 1.95, COULs = –26.00, EXPp = 1.95, COULp = –13.40. C: EXPs = 1.625, COULs = –21.40, EXPp = 1.625, COULp = –11.40. H: EXPs = 1.30, COULs = –13.60.

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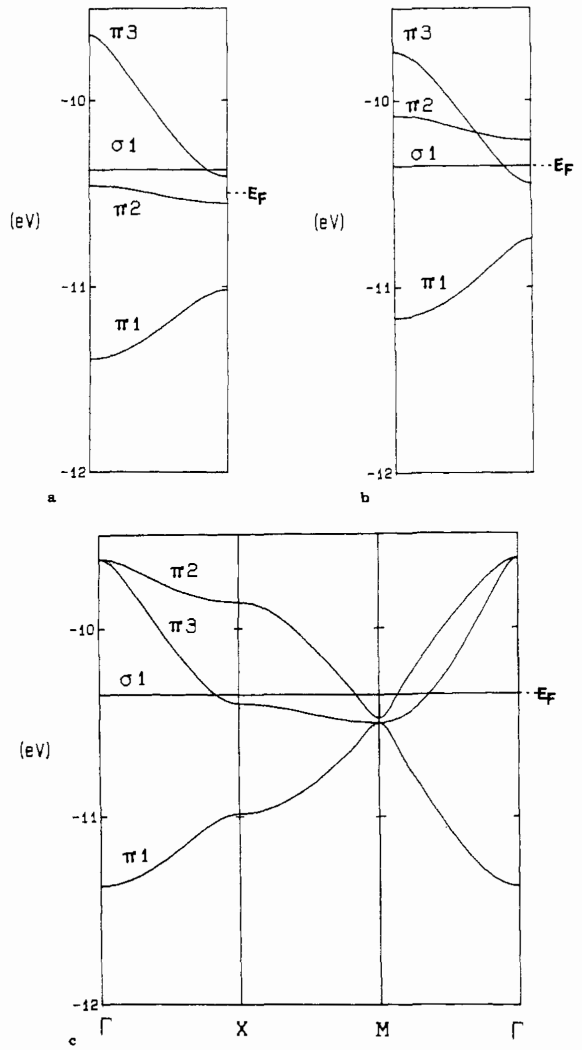

Figure 2. (a) Energy band structure for the one-dimensional CuPc of type **1a**. Labeling starts arbitrarily at the band labeled $\pi 1$. (b) Energy band structure for CuPc of type **1b**. (c) Energy band structure of system **2** (M = Cu) along the Γ–X–M–Γ line of the simple tetragonal Brillouin zone. Labeling starts arbitrarily at the band labeled $\pi 1$. E_F is the Fermi level.

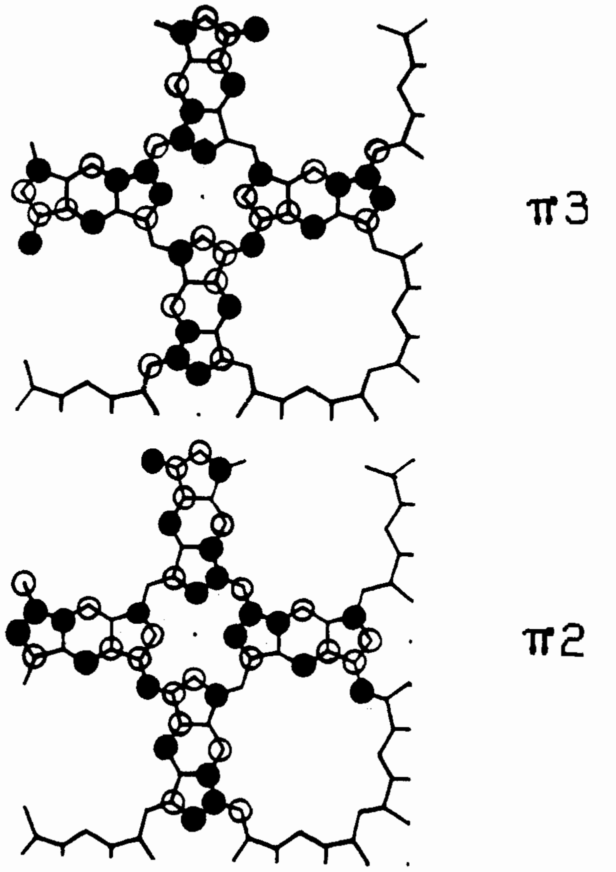

Figure 3. LCAO representation of the highest occupied bands, $\pi 2$ and $\pi 3$ at the Γ point. Circles denote p_z orbitals, and only atomic orbitals contributing significantly to the band have been included. The coefficients for the d_{xz} and d_{yz} AO's from Cu are approximately 5 times smaller than those of the p_z orbitals included here.

mensional calculations discussed above.

The band structure is similar to that of the one-dimensional models except for band $\pi 2$, which is now even higher in energy than for **1b** and forms a degenerate pair with $\pi 3$ at the Γ point (Figure 3) (note that only at points Γ and M is there 4-fold symmetry in the two-dimensional Brillouin zone).

As was the case for the one-dimensional models, the flat σ band at −10.37 eV is mostly Cu($d_{x^2-y^2}$) in character, with some contribution from p(σ) orbitals on the four N atoms coordinated to Cu. This flat band could be the source of magnetism (see e.g. ref 15). Along the Γ–M line, two broad bands instead of one cut across this partially filled flat band. Thus, we conclude that the two-dimensional CuPc would be an isotropic two-dimensional conductor, not requiring any doping to display metallic behavior.

One could argue that the σ band is very likely to be more strongly affected by slight changes in the geometry of the CuPc unit than the π bands. Concerning this point, it is helpful to compare our calculations with those of Schaffer et al. on monomeric CuPc.[13] An antibonding $\sigma(d_{x^2-y^2})$ orbital parallel in nature to our σ band was found in those calculations at −9.6 eV, higher in energy than ours due to the slightly shorter Cu–N bond considered there. When distortions from D_{4h}, attributed to packing effects, were taken into account by Schaffer et al., the overlap between Cu and N decreased and so did the energy of the antibonding σ level (−10.7 eV), whereas the π orbitals remained almost unaffected. In our case, the lower symmetry argument does not apply, given the intrinsic D_{4h} symmetry of the lattice, forced by covalent bonds. On the other hand, the value of the Cu–N bond distance used in our calculation (1.97 Å) is an upper bound, and its shortening would only result in a stronger overlap between Cu and N with a concomitant increase in the energy of the σ band. This would still leave the broad $\pi 3$ band partially filled and therefore would still be consistent with intrinsic two-dimensional conduction in the layer. Indeed, a calculation performed on a model of type **1a** with a Cu–N distance of 1.93 Å (the value used in ref 13a) showed how only the σ band was substantially affected (−10.11 eV at the Γ point) by the change in bond distance, whereas the π bands remained practically unaffected. Therefore, within the limits of reasonable changes in geometry, we predict a $(\text{CuPc})_n$ layer of type **2a** to have intrinsic metallic conductivity.

Figure 3 shows the major atomic orbital coefficients contributing to bands $\pi 2$ and $\pi 3$ at the Γ point (two-dimensional polymer). Both bands are predominantly π^* in nature (p_z(ligand)), with a very small contribution from d_{xz} and d_{yz} atomic orbitals from Cu. A projected density of states (DOS) curve for the Cu atom shows no significant contribution to the total DOS from Cu at the Fermi level, where carbon and nitrogen $2p_z$ orbitals are the major contributors. In this case the metallic atom can be regarded as providing the right number of electrons to bring up the Fermi level to a conducting state but does not take part in the formation of the conduction bands.

Effect of Metal Substitution

Within the limitations of the rigid-band approximation,[10c] we can draw some qualitative conclusions about the effect of substituting the Cu atom by other metals on the conducting properties of these polymers. Thus, by replacing Cu with Co, for instance, all four structures of **1** and **2** would become conductors because the broad band $\pi 1$ (Figure 2a) would be partially filled. This exemplifies how an adequate choice of the metal in these polymers would help in tuning the electronic properties of the materials.

The above qualitative conclusion rests on the assumption that the band energies are not substantially affected by replacing the metal by another one. We have performed a calculation on a $(\mathrm{CoPc})_n$ compound of type **1a** to confirm this point.[11] The results of this calculation showed that the σ band is higher in energy for this Co polymer as compared with the Cu one (-8.35 eV at the Γ point), but the energies of the π bands changed by less than 0.05 eV in all cases, thus confirming the above conclusion. Therefore we did not provide further details of the calculation with Co in place of Cu.

Ladder Polymers

Systems **1** and **2** may be considered as conducting ladder polymers, in analogy to semiconducting ladder polymers of type **4**, which are reported[14] to have conductivities of up to 2 S cm^{-1}. We have performed band structure calculations on a model of **4** based on the structure of a monomeric analogue.[16] These calculations showed that, even though there is a half-filled band to support metallic properties, it is rather narrow (bandwidth = 0.33 eV). The corresponding orbitals are extended over the S–Co–S fragment and the phenyl rings, which is consistent with some degree of band conduction for **4**. We expect that **2**, with its broader and more delocalized bands, would support even higher conductivities.

π–Electron delocalization throughout the extended organic network is responsible for the expected conducting properties of polymers **1b** and **2**. This extended network makes the difference between the title compounds and the μ-oxalato chains mentioned above (**3**): in the latter case the ligand molecules are isolated from each other by Cu atoms and the compound should not be expected to be a conductor.[12a]

Concluding Remarks

The experimental conductivity data available until now on CuPc polymeric films[9] correspond to phases not very well characterized, making a direct comparison with our calculation infeasible, but indications are that high conductivities (5–8 S cm^{-1}) can be reached[9e] for some of these compounds. Smaller conductivity values have been reported for systems prepared under different conditions[9d], but these may be due to the presence of oligomeric or monomeric units[9f] rather than extended polymeric layers in the phases obtained or to the presence of mixtures or impurities. Our prediction is that if a pure phase with a layered structure of type **2** could be prepared, intrinsic metallic behavior should be expected.

One may envision a number of structures that are similar to **1** and **2a** and have intrinsically metallic properties. One such is **2b**, in which the connecting six-membered rings have been eliminated. We have performed EHT energy band calculations also for **2b** and found that there are partially filled broad π-bands around the Fermi level leading to an intrinsically metallic electronic structure.

Finally, we would like to comment on the problem of electron transport between individual columns of metal phthalocyanines in previously described stacked polymers. We consider that, contrary to the models presented here, the conduction in the equatorial direction (perpendicular to the stack) in those polymers is likely to be poor and would limit the overall conducting properties of the materials. In the case of ZnPcCl,[4] for example, semiconductivity is observed, which cannot be explained by band conduction. This is due to the very small interdimer resonance integral, which we estimate to be around 10 meV using extended Hückel theory (EHT).[10a,7]

Our calculations suggest that one-dimensional CuPc **1b**, but not **1a**, will be a conductor if it can be synthesized, and this illustrates the significance of choosing appropriately the contents of the unit cell in the synthesis of conducting polymers. The two-dimensional polymers **2a** and **2b** are also predicted to be conductors.

Acknowledgment. This work has been supported by the Camille and Henry Dreyfus Foundation. Further support by the NSF (Grant DMR-8702148) is gratefully acknowledged. We also thank Professor G. B. Jameson for his support and the Comite Conjunto Hispano-Norteamericano para la Cooperacion Cultural y Educativa for a fellowship awarded to P.G.-R. We thank an anonymous reviewer for suggesting the study of **2b**.

Registry No. Poly(copper phthalocyanine), 26893-93-6.

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Reaction of Protons and Molybdenum Dimers in an Ambient-Temperature Molten Salt

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We have recently reported the electrochemical interconversions of several molybdenum dimers in the ambient-temperature molten salt AlCl$_3$–1-ethyl-3-methylimidazolium chloride (ImCl).[1] The results of the study performed in a basic melt are summarized in Scheme I.

Acidic melts are defined as melts where the AlCl$_3$:ImCl molar ratio is greater than one, and basic melts are melts where this ratio is less than one.[2] These previous studies were hampered in part by the presence of protonic impurities in the melt. We have since found that the addition of EtAlCl$_2$ to AlCl$_3$–ImCl melts effectively removes these protonic impurities, forming AlCl$_3$, a component of the melt.[3] We have applied this purification method to melts containing molybdenum dimer and wish to report several interesting reactions involving the addition and removal of hydrogen to the Mo–Mo quadruple bond in $\mathrm{Mo_2Cl_8}^{4-}$.[4]

Experimental Section

ImCl was synthesized as previously described.[5] Melts were prepared by gradual addition of sublimed AlCl$_3$ (Fluka) to ImCl with stirring. Mo$_2$(OAc)$_4$[6] and ImHCl$_2$[7] were prepared by using literature procedures.

The electrochemical cell consisted of a glass vessel. The working electrode was a Bioanalytical Systems Pt electrode consisting of a 0.08-cm-radius Pt disk sealed in Kel-F. The counter and reference electrodes consisted of Al wire immersed in 1.5:1.0 AlCl$_3$:ImCl melts contained in separate glass-fritted compartments. Cyclic voltammetry was performed on an EG&G PARC Model 173 potentiostat/galvanostat with a EG&G PARC Model 175 wave form generator and a Hewlett Packard Model 2000 XY recorder. Normal-pulse voltammetry was performed with an EG&G PARC Model 273 potentiostat/galvanostat, which was controlled by a computer system similar to that described elsewhere.[8] All electrochemical experiments were performed at 27 °C under a purified He atmosphere in a Vacuum Atmosphere drybox with an HE 493 Dri Train.

Visible spectra were obtained on a Tracor Northern 6500 spectrometer equipped with a photodiode array. All spectra were measured by using 1 mm quartz cells.

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