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Semiconductor Properties in an Iodine-Doped Platinum(II) Dinuclear Complex

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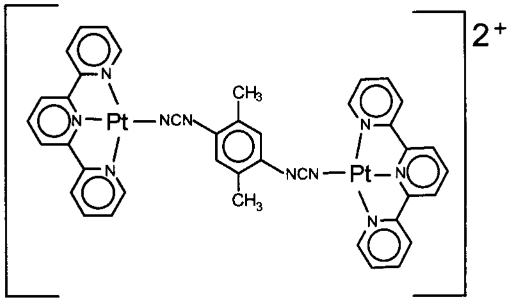
The conducting properties of organic charge transfer salts have been studied for many years and arise from the orientation of conjugated planar organic molecules on top of one another to form “pancake” stack structures within the crystal lattice.[1] The π interactions between molecules making up the stack create a continuum of molecular orbitals (a band structure) and, under the right conditions, can result in conductivity in the direction of the stack. Attempts to combine metal ion chemistry with organic charge transfer salts has mainly focused on metal phthalocyanins and porphyrins, as these complexes naturally form π-stacking architectures in their crystal lattices.[2] These materials all show weak conductivity, but upon doping by either chemical or electrochemical means significant improvement in conductivity is observed ($\sigma_{RT} = 10^{-5}-10^{-1}$ S cm^{-1}).[2] Another important class of materials are the metal *N*,*N*′-dicyanoquinonediimine compounds.[3] For example, [Cu(Me$_2$dicyd)$_2$]$_n$, where Me$_2$dicyd$^-$ is the radical anion of 2,5-dimethyl-*N*,*N*′-dicyanoquinonediimine, exhibited metallic conductivity down to 3.5 K with $\sigma = 500\,000$ S cm^{-1}.[4] The crystal structure of this material showed that the Me$_2$dicyd molecules form π stacks with copper ions interconnected to these stacks by bridging Me$_2$dicyd. Supramolecular methods have also proved successful with the synthesis of tetracyanoquinodimethanide stacks in nickel and copper tetraazamacrocyclic systems.[5] These materials are good semiconductors with powder conductivities of approximately $10^{-3}-10^{-2}$ S cm^{-1}.[5b]

An alternative way to form novel conducting materials is to coordinate a donor or acceptor conjugated planar molecule to a metal ion in a square planar coordination sphere. Provided that the complex is planar, it should be possible to form π stacks in the crystal lattice and, with appropriate doping, create the conditions for conductivity. To demonstrate that this can be a successful strategy, we have synthesized and characterized the dinuclear complex [{Pt(trpy)}$_2$(μ-Me$_2$dicyd)][PF$_6$]$_2$ (**1**), where trpy is 2,2′:6′,2″-terpyridine and Me$_2$dicyd^{2-} is 2,5-dimethyl-1,4-dicyanamidebenzene dianion.

1 was prepared by reacting the thallium salt of Me$_2$dicyd^{2-} with [Pt(trpy)Cl][PF$_6$] in *N*,*N*′-dimethylformamide (DMF) under argon for 1 week. The orange reaction mixture slowly turned a dark purple and precipitated white TlCl. Recrystallization by ether diffusion into a filtered DMF solution of the complex gave deep purple microcrystalline powder in 84% yield.[6] The complex is soluble in only strongly donating solvents, and various attempts to recrystallize the complex has so far yielded only powders. Nevertheless, the ^{1}H NMR spectrum of the complex (see Supporting Information) is entirely consistent with a dinuclear complex, showing chemical shifts of a single terpyridine and a symmetric bridging Me$_2$dicyd^{2-} ligand with appropriate proton integration.[6] In addition, the ^{13}C NMR spectrum of **1** (see Supporting Information) shows the expected 13 line pattern.[6]



The UV−vis spectrum of **1** in DMF (see Supporting Information) shows a terpyridine $\pi \rightarrow \pi^*$ band at 283 nm ($\epsilon_{max} = 44\,300$ M^{-1} cm^{-1}) and Pt(II) → terpyridine metal-to-ligand charge transfer transitions at 334 (28 800 M^{-1} cm^{-1}) and 386 nm (shoulder $\epsilon = 10\,500$ M^{-1} cm^{-1}).[7,8] In addition, a broad band at 588 nm ($\epsilon_{max} = 2800$ M^{-1} cm^{-1}) is assigned to a $\pi \rightarrow \sigma^*$ ligand-to-metal charge transfer transition arising from the Pt(II)−cyanamide chromophore. This band is too low in energy and too intense to be a metal-centered transition, and similar absorption bands have been observed for the mononuclear palladium(II)[7] and platinum(II)[9] terpyridine complexes of phenylcyanamide ligands in which crystal structures clearly show the coordination of the cyanamide group to the metal ion.

The cyclic voltammogram of **1** in DMF solution showed two reduction couples at positive potentials, Me$_2$dicyd$^{-/2-} = 0.694$ V vs NHE (quasi-reversible) and Me$_2$dicyd$^{0/-} = 1.51$ V vs NHE (anodic peak position). The corresponding quasi-reversible free ligand reduction couples are −0.348 and 0.390 V versus NHE in DMF. This approximately 1 V positive shift in ligand reduction potentials upon coordination has been observed before in polyammineruthenium(III) complexes of this ligand.[10] Irreversible waves and fouling of the working electrode were observed when scanning at negative potentials.

Chemical doping of **1** was achieved by exposing a powder sample of **1** to iodine in a developing chamber. This results in the formation of radical anion Me$_2$dicyd$^-$ as was shown by the

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(6) Anal. Calcd for [{Pt(trpy)}$_2$(μ-Me$_2$dicyd)][PF$_6$]$_2$·H$_2$O (C$_{40}$H$_{32}$N$_{10}$F$_{12}$OP$_2$Pt$_2$): C, 35.62; H, 2.39; N, 10.38. Found: C, 35.56; H, 2.33; N, 10.48. IR (KBr disk): ν(NCN) = 2114 cm^{-1}. ^{1}H NMR (400 MHz): 7.94−8.63 (terpyridine-H, multiplets, 22H), 6.73 (phenyl-H, singlet, 2H), and 2.11 ppm (methyl-H, singlet, 6H). ^{13}C NMR (100 MHz): 157.8, 154.5, 150.9, 142.9, 141.9, 137.3, 130.8, 129.4, 127.4, 126.0, 124.4, 123.3, and 17.9 ppm.

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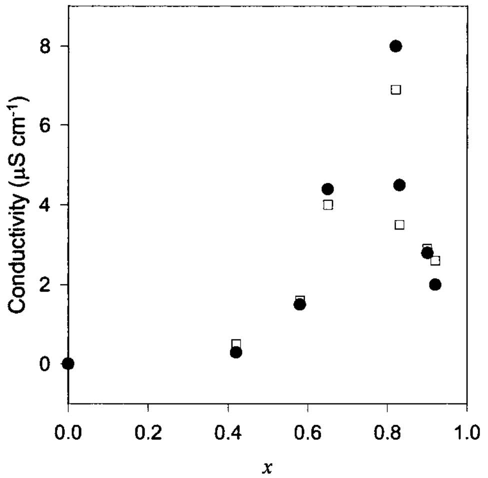

Figure 1. Conductivity versus I_3^- equivalences for $[\{Pt(trpy)\}_2(\mu\text{-}Me_2dicyd)][PF_6]_2[I_3]_x$. The data from two different experiments are plotted.

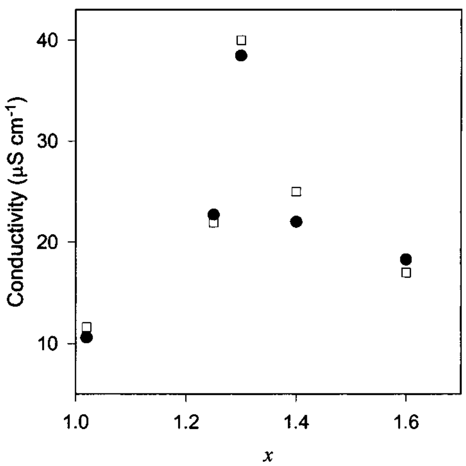

Figure 2. Conductivity versus I_3^- equivalences for $[\{Pt(trpy)\}_2(\mu\text{-}Me_2dicyd)][PF_6]_2[I_3]_x$. The data from two different experiments are plotted.

growth of absorption bands characteristic of the radical anion in the doped complex's DMF solution spectra.[10] At different time intervals, portions were taken for elemental analysis of iodine and conductivity measurements,[11] and the combined results of two separate experiments are plotted in Figures 1 and 2. We have assumed that doping results mainly in the formation of I_3^- by analogy with crystallographic and spectroscopic studies performed on iodine-doped metal phthalocyanin complexes.[2] Accordingly, the value of x in Figures 1 and 2 represents the number of oxidizing equivalents (i.e., $\mathbf{1}\cdot[I_3]_x$).

A powder sample of $[AsPh_4]_2[Me_2dicyd]$ was also doped with iodine. However, conductivity measurements of doped samples taken during the doping process showed no evidence of conductivity.[11] In the crystal structure of $[AsPh_4]_2[Me_2dicyd]$, the Me_2dicyd^{2-} anions are not π stacked and are separated from each other by the tetraphenylarsonium cations.[12]

The novel observation of double maxima in conductivity with doping that is seen in Figures 1 and 2, $x = 0.8$ ($\sigma = 8\ \mu S\ cm^{-1}$), and $x = 1.3$ ($\sigma = 39\ \mu S\ cm^{-1}$), respectively, has been reproduced in two additional conductivity versus doping experiments with very little scatter in data points (see Supporting Information). Indeed, the maximum in Figure 2 corresponds to a charge of -0.7 for Me_2dicyd. This is approximately the same charge found for Me_2dicyd in the molecular metal $[Cu\,(Me_2dicyd)_2]_n$, where XPS and low-temperature X-ray diffraction indicate an average oxidation state of $^4/_3$ for Cu and hence $-^2/_3$ for Me_2dicyd.[3,13]

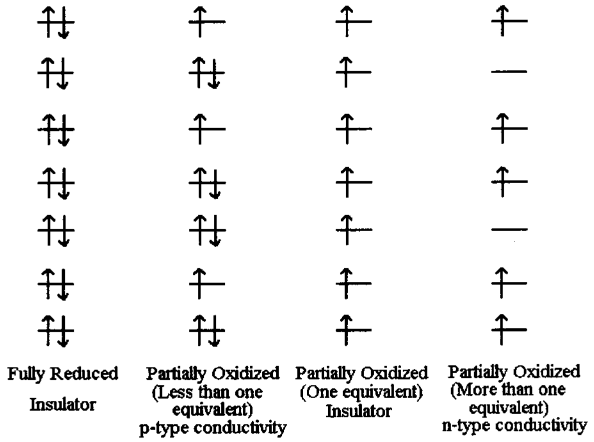

Figure 3. Schematic to explain the mechanism of conduction in π-stacked orbitals depending on orbital occupancy.

While we do not have a crystal structure of **1**[14] and our attempts to grow crystals of doped **1** proved unsuccessful, it is probable that the architecture responsible for conductivity in these materials is π stacking of Me_2dicyd molecules. Assuming π stacking, Figure 3 gives our interpretation of the mechanisms of conductivity for the data shown in Figures 1 and 2. Clearly, electron movement between filled orbitals is not possible, and if the orbitals making up a π stack each possess one electron, there will be a significant Coulombic barrier to electron movement. This can be overcome if partial oxidation occurs (less than or more than 1 equiv, $x = 0.8$ or $x = 1.3$, as shown in Figures 1 and 2, respectively).[15] In the case of $x = 1.0$, conductivity should probably be much lower than observed but is not because of the heterogeneity of doping. It is likely that the surface of a particle of **1** is more strongly doped than the interior. Indeed, it is possible that polyiodides such as I_5^- may form under conditions of excess iodine in the presence of I_3^-.[16]

Powder conductivity is generally 100 times smaller than that of a crystal,[11] but this would still classify these doped materials as weak semiconductors. Nevertheless, the results of this study open up a new family of materials and strongly suggest that supramolecular assembly of π-stacked architectures can lead to conducting materials.

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Supporting Information Available: Four figures showing ^1H and ^{13}C NMR spectra, a quantitative electronic absorption spectrum, and conductivity versus time plots. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Conductivity was measured by using the two-probe method for compressed powders. See: Wudl, F.; Bryce, M. R. *J. Chem. Educ.* **1990**, *67*, 717. The lower limit for our conductivity measurements is $10^{-3}\ \mu S\ cm^{-1}$.

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(14) A crystal structure of the mononuclear complex, $[Pd(trpy)(2,6\text{-dichlorophenylcyanamide})][PF_6]$ (see ref 7), shows that the cation is planar. In addition, Me_2dicyd^{2-} is also planar. See ref 12. It is therefore reasonable to suggest that **1** will be planar as well.

(15) A referee has pointed out that, in order to confirm n-type conductivity, thermopower or Hall-effect measurements should be made. Unfortunately, these measurements would be open to interpretation because of the low conductivity and lack of stability of $\mathbf{1}\cdot[I_3]_x$.

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