Platinum oxide formation in the vicinity of the SERS-active sites only commences at ca. 0.9 V in both the absence and presence of CO as seen from the appearance of the ν_{PtO} band (Figure 8). The disappearance of both the ν_{CO} and ν_{PtO} bands at potentials close to this point therefore suggests that the electrooxidation of the SERS-active CO involves reaction with nearby oxygen or hydroxide species which constitute the "PtO" film. Consistent with this interpretation is the observation that electrooxidative loss of the preponderant, infrared-active, adsorbed CO commences at potentials, ca. 0.7 V, close to the onset of oxide formation as sensed by voltammetry (vide supra).

The structural origin of the relative inertness of the SERS-active sites toward CO electrooxidation and oxide formation is unclear. However, examination of both the former[33] and latter[34] processes on low-index single-crystal platinum faces indicates that they are both sensitive to the surface stereochemistry, although a simple correlation between the onset potentials for CO and surface oxidation is not observed.[33]

Concluding Remarks

The present results constitute novel evidence that the strategy of coating suitably roughened gold surfaces with molecularly thin transition-metal films provides a means of obtaining surface Raman spectra for species adsorbed at the transition metal–solution interface with intensities that are comparable to those obtained for conventional SERS-active gold or silver electrodes. As such, then, this simple approach appears to provide a relatively general means by which SERS can be applied to a broad range of transition-metal systems. One inevitable limitation is that it is difficult to eliminate entirely the presence of adsorbate bound to exposed substrate rather than to overlayer sites. The approach may therefore be limited to the examination of adsorbates that bind more strongly to the transition-metal overlayer rather than to the underlying substrate.

Nevertheless, the unique advantages offered by SERS, especially the freedom from bulk-phase interferences and the availability of wide frequency ranges, provide persuasive reasons to consider utilizing this approach to examine reactive as well as stable adsorbates on transition-metal surfaces. The use of multichannel array detectors, in particular, should enable SERS to provide an interesting new means of examining electrocatalytic reaction pathways on transition-metal surfaces. Studies of this type, involving a range of other transition-metal overlayers and including gas-phase as well as electrochemical systems, are currently in progress in our laboratory.

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A New Series of Molecular Semiconductors: Phthalocyanine Radicals[1]

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Abstract: The electrical properties of thin films and single crystals of bis(phthalocyaninato)lutetium (Pc_2Lu) and lithium monophthalocyanine (PcLi) have been determined. Undoped single crystals of Pc_2Lu show a room temperature conductivity of 6×10^{-5} Ω^{-1} cm^{-1}, more than 6 orders of magnitude higher than that for standard divalent ion metallophthalocyanines (PcM: M = Cu, Ni, ...). The conductivity of Pc_2Lu thin films is of the same order of magnitude (10^{-5} Ω^{-1} cm^{-1}), demonstrating that structural disorder is ineffective in creating deep charge carrier traps. Single crystals of PcLi are even more conductive (2×10^{-3} Ω^{-1} cm^{-1}), but thin film conductivities are drastically depressed (10^{-4}–10^{-5} Ω^{-1} cm^{-1}). By comparing magnetic and electrical properties of Pc_2Lu and PcLi, it has been shown that strong interunit interaction energy occurs in PcLi (bandwidth of the order of 1 eV), but it is weak in Pc_2Lu (50 meV). Dielectric spectra of Pc_2Lu thin films in the frequency range 10^{-3}–10^4 Hz have permitted us to confirm the previous result that disorder does not create deep traps in Pc_2Lu. A space charge limited current model enabled us to calculate that the effective mobility of charge carriers is $\theta\mu = 1.3$ $cm^2/(V\cdot s)$ for thin films of Pc_2Lu. This is the highest value ever found for thin films of a molecular material at room temperature.

Inorganic materials with conductivities intermediate between those of metals and those of insulators form a homogeneous class of materials possessing a low density of intrinsic charge carriers associated with high mobilities and a temperature activated conductivity. These materials may be p- or n-doped and may be used to form junctions and associated electronics devices such as photoconductors or field effect and bipolar transistors. Many attempts have been made to obtain similar characteristics with molecular compounds.[2–4] While intermediate conductivities very often have been encountered, members of the molecular family show very disparate properties; in particular, the chemical processes involved in the charge transport and in the formation of junctions were not known in detail. The object of the present paper is to give a precise definition of molecular semiconductors and to describe two members of a new series of molecular semiconductors.

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MOLECULAR
UNIT

chemical nature
shape
redox properties
HOMO-LUMO
dipoles,multipoles
polarizability
magnetism
chirality

MOLECULAR
MATERIAL

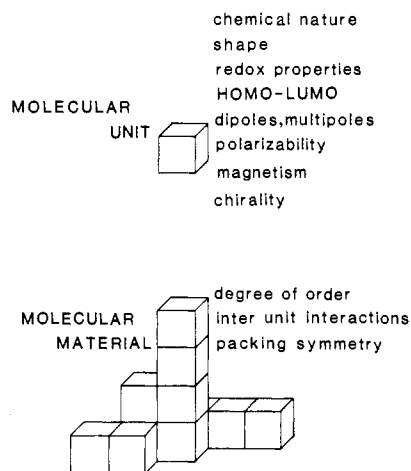degree of order
inter unit interactions
packing symmetry

Figure 1. Schematic representation of the definition of a molecular material: a molecular unit characterized by its individual properties is subsequently organized into a condensed phase.

A preliminary publication has related the electrical properties of Pc_2Lu thin films doped with electron acceptors or electron donors by the co-sublimation technique.[1]

Molecular materials differ from three-dimensional covalent (Si, Ge, ...) or iono-covalent (AsGa, InP, ...) materials in being constituted of molecular units that can be individually characterized by their properties: chemical nature, shape, redox potentials, polarity, ... The molecular units are organized in a second step to give a condensed phase: amorphous or polycrystalline films, liquid crystals, single crystals[5,6] (Figure 1). In the field of molecular materials, the notion of a molecular semiconductor may be defined as follows: it must possess an *intrinsic* conductivity in the semiconducting range, and it can be doped with electron acceptors and electron donors to yield highly conducting materials. When these criteria are fulfilled, it can be demonstrated that electronics type devices may be elaborated.[7] Within these hypotheses, neither molecular crystals—from naphthalene to pentacene—nor macromolecular systems—polyacetylene, polydiacetylene, ...—belong to the molecular semiconductor class.[2-4] In many cases, intermediate conductivities have been obtained but always as a result of doping, fortuitously or not; i.e., these systems all behave as "doped insulators". This assumption may be verified by determining under which conditions a molecular unit may lead to a semiconducting material.

The intrinsic generation of charge carriers within a molecular material may be represented as a disproportionation reaction

$$2A \rightleftharpoons A^+, A^-$$
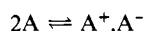
if A is the constituting molecular unit. The energy that is necessary to generate the ionized pair A^+, A^- may be estimated from the redox potentials in solution.[8]

$$A + e^- \rightleftharpoons A^- \qquad E_{1/2}^{red}$$

$$A \rightleftharpoons A^+ + e^- \qquad E_{1/2}^{ox}$$
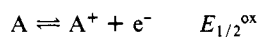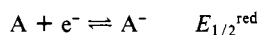
These equations are valid for isolated molecular units in solution. It is then postulated that the difference in dielectric constants between the solution and the condensed phase is sufficient to estimate the concentration of generated ion pairs in the solid. In particular, the interaction energy between the molecular units must be low enough to allow one to neglect the role of collective electronic states in the transport properties. It may be readily demonstrated that the thermal activation energy ($E/2$) for intrinsic
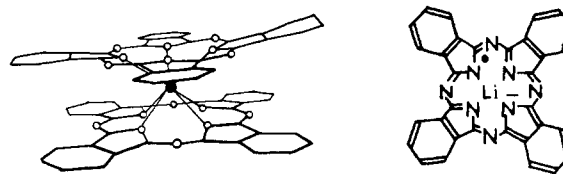

Figure 2. Bis(phthalocyaninato)lutetium (Pc_2Lu) and electronic structure of PcLi.

conduction in the equation $\sigma = \sigma_0 \exp(-E/2kT)$ may be evaluated by[8]

$$E \sim \left(E_{1/2}^{ox} - E_{1/2}^{red}\right) + (S^+ + S^-)\left(1 - \frac{1 - 1/\epsilon_2}{1 - 1/\epsilon_1}\right) \quad (1)$$

Here S is the difference between ion solvation energy and neutral molecular unit solvation energy in solution, ϵ_1 is the dielectric constant of the solution in which the redox potentials have been measured, and ϵ_2 is the dielectric constant of the thin film or the crystal.

In all the previously mentioned mesomolecular or macromolecular systems, the difference between the oxidation and reduction potentials is equal or greater than 1.5 eV.[4] They are consequently insulators when undoped. Phthalocyanine radicals seem to be exceptions to that rule.[9-11] It was thus tempting to study the electrical properties of the corresponding materials.

Experimental Section

Pc_2Lu and PcLi were synthesized following previously described procedures.[20,34]

Elemental microanalysis and spectral data are in agreement with the proposed structures.

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Table I. Electrical Properties of Single Crystals (SC) or Thin Films (TF) of Various Metallophthalocyanines (PcM or Pc$_2$M)

		solid state				solution		
	σ_{RT}, Ω^{-1} cm^{-1}	E,[h] eV	μ_e, cm^2/(V·s)	ref	$E_{1/2}^{ox}$, V	$E_{1/2}^{red}$, V	E_{calcd}, eV
PcH$_2$	SC $<10^{-12}$	2.00	1.2	21, 22	+0.86[a]	-0.58[a]	
	TF		10^{-2}–10^{-3}	23			
PcCu	SC $<10^{-12}$	2.00	7	24–26	+0.98[b]	-0.84[c]	2.2
	TF $<10^{-10}$	1.98	10^{-2}	27, 28			
PcNi	SC $<10^{-12}$	2.28		29	+1.05[f]	-0.85[g]	2.6
Pc$_2$Lu	SC 6×10^{-5}	0.64			+0.03[d]	-0.45[d]	0.9
	TF $\sim 10^{-5}$	0.52	1.3				
PcLi	SC 2×10^{-3}	0.2			+1.0[e]	+0.17[e]	1.1
	TF 10^{-4}–10^{-5}						

[a] vs. NHE in dimethylformamide (ref 30) ($\epsilon = 36.7$). [b] vs. SCE in chloronaphthalene (ref 4) ($\epsilon = 5.04$). [c] vs. SCE in DMF (ref 4). [d] vs. ferrocene in CH$_2$Cl$_2$ ($\epsilon = 9.08$) (ref 11). [e] vs. SCE in THF–chloronaphthalene 1:1 ($\epsilon \sim 6.2$) (ref 20). [f] vs. SCE in chloronaphthalene (ref 4). [g] vs. SCE in dimethylformamide (ref 4). [h] E in the equation $\sigma = \sigma_0 \exp(-E/2kT)$.
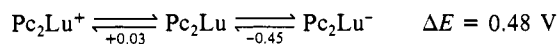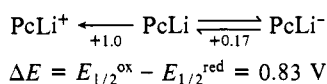
The sandwich cells were fabricated under vacuum (10^{-5}–10^{-7} Torr) by successively evaporating on a glass substrate a gold layer, the phthalocyanine, and the gold counterelectrode.[35] The cells were studied without breaking the vacuum at any stage. It has been previously shown that, under these conditions, the intrinsic properties of the materials may be determined.[35] Quartz crystals were used to determine the thicknesses of the materials evaporated. The phthalocyanine layers were about 2 μm thick. The ac electrical measurements were performed with a semiautomatic apparatus already described.[36] In the frequency range 10^{-3}–10 Hz the ac probing voltage never exceeded 0.1 V. For higher frequencies a standard General Radio bridge was used. The conductivity of the Pc$_2$Lu layer was checked by using a planar configuration in which a Pc$_2$Lu thin film was evaporated onto two electrodes separated by 0.1 mm. Very consistent results were found in all cases.

The dc conductivity of single crystals of Pc$_2$Lu was measured both with two and with four contacts, giving similar results. For PcLi, only the two-contacts method could be used because of the small dimensions of the crystals (typically 0.03 × 0.03 × 1 mm^3).

Results and Discussion

Two different types of stable phthalocyanine radicals have been described in the literature: bis(phthalocyaninato)lutetium[12-14] (Pc$_2$Lu), and lithium monophthalocyanine, (PcLi).[15-18] In the first case, a lutetium(III) ion is sandwiched between two macrocyclic rings; the overall molecule is neutral and magnetic studies indicate one spin per molecule.[14,19] Although the lithium derivative contains only one macrocycle,[18] the magnetic properties of the individual unit are similar to those of Pc$_2$Lu (Figure 2).

The peculiar electronic nature of these two compounds seems to favor their ease of oxidation *and* reduction.

$$\text{PcLi}^+ \xleftarrow[+1.0]{} \text{PcLi} \xrightarrow[+0.17]{} \text{PcLi}^-$$

$$\Delta E = E_{1/2}^{ox} - E_{1/2}^{red} = 0.83 \text{ V}$$

$$\text{Pc}_2\text{Lu}^+ \xrightleftharpoons[+0.03]{} \text{Pc}_2\text{Lu} \xrightleftharpoons[-0.45]{} \text{Pc}_2\text{Lu}^- \qquad \Delta E = 0.48 \text{ V}$$

The potentials were determined in THF/chloronaphthalene (vs. SCE) and dichloromethane (vs. ferrocene), respectively. In the case of standard molecular crystals such as divalent complexes of phthalocyanine, PcM (M = Zn, Ni, Cu, ...), the difference between oxidation and reduction potentials is of the order of 1.8–2.0 V. Correlatively, the activation energies of conduction of PcM (M = Cu, Ni) or PcH$_2$ are expected to be much higher than those found for Pc$_2$Lu and PcLi. The conductivity of thin films and single crystals of PcM has been reported in the literature. The room temperature conductivity is in all cases less than 10^{-10} Ω^{-1} cm^{-1} with an activation energy of the order of 2 eV (Table I). The agreement between experimental activation energies and those calculated from eq 1 is very good. The conductivities of Pc$_2$Lu and PcLi have been determined for thin films and single crystals.

The room temperature conductivity of a Pc$_2$Lu thin film fabricated and studied under vacuum is about 10^{-5} Ω^{-1} cm^{-1}, more than 5 orders of magnitude higher than that for PcCu or PcH$_2$. The experimental activation energy of conduction, 0.52 eV, is in

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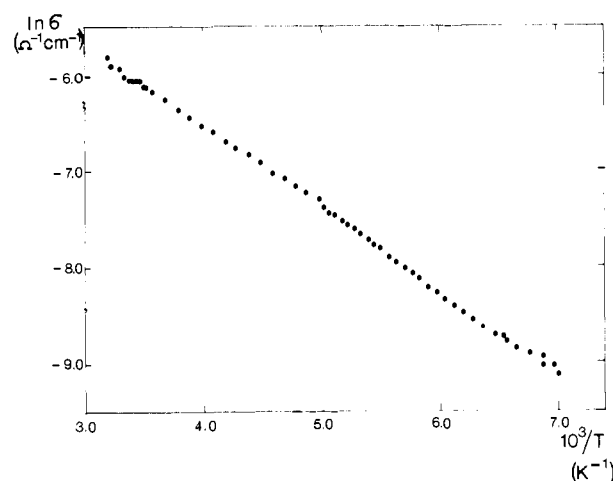(36) Guillaud, G.; Rosenberg, N. *J. Phys. E.* **1980**, *13*, 1287.

Figure 3. Conductivity of a single crystal of PcLi as a function of temperature (ln σ vs. 1000/T).

good agreement with the one calculated from eq 1. The conductivity of Pc$_2$Lu appears to be rather insensitive to the degree of organization of the material since the single-crystal conductivity (6×10^{-5} Ω^{-1} cm^{-1}) is of the same order of magnitude as that for a thin film.

The conduction properties of a single crystal of PcLi in the temperature range -130 to 40 °C were determined (Figure 3). The room temperature conductivity was 2×10^{-3} Ω^{-1} cm^{-1} with an activation energy of 0.2 eV. Contrary to the previous case, there is a strong disagreement between the experimental and calculated activation energies of conduction ($E_{calcd} = 1.1$ eV). This clearly indicates a strong interaction between PcLi units, and collective electronic energy levels must be present. As a matter of fact, the magnetic behavior of PcLi observed by ESR indicates strong coupling between molecular units.[31] X-ray measurements on single crystals of PcLi show an interplanar distance (3.24 Å) significantly smaller than the van der Waals value (3.4 Å).[18]

The dielectric spectra of Au/Pc$_2$Lu/Au sandwich cells were determined as a function of temperature (Figure 4). The range of temperature studied (102–160 K) was chosen in order to avoid the effect of the metallic electrode contacts on the electrical properties. The capacitance varied slowly with temperature and frequency, indicating that there was no significant ionic contribution to the conductivity. The conductivity was approximately constant below 1 Hz and corresponded to the bulk characteristics in agreement with the dc values.

At high frequencies, the conductance approximately followed a $\omega^{0.8}$ law, which is characteristic of a hopping mechanism between disorder induced trapping of the charge carriers.[32] Contrary to the results on thin films, the conductivity of a single crystal of Pc$_2$Lu was frequency independent (σ_{dc} was approximately equal to σ at 10 GHz). This confirms that the frequency dependence found for thin films is related to structural disorder.

The electrical behavior of Au/Pc$_2$Lu/Au sandwich cells was studied as a function of temperature and applied external voltage
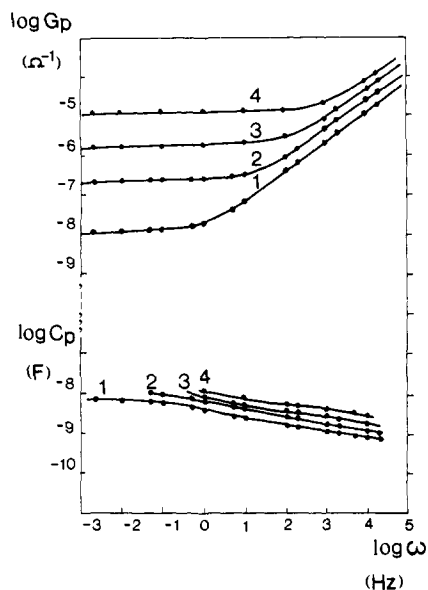
Figure 4. Dielectric spectra of $Au/Pc_2Lu/Au$ sandwich cells fabricated and studied under vacuum: (1) 102 K; (2) 122 K; (3) 140 K; (4) 160 K.

(Figure 5). At high temperature and low voltage ($V < 0.2$ V), an ohmic regime was observed. At higher voltages, a space charge limited behavior took place and $I \propto V^2$. In the shallow trap approximation, justified when traps are generated by disorder, the space charge limited current is given by[33]

$$I_{SCL} \sim \epsilon_r(\Theta\mu)(V^2/L^3) \qquad (2)$$

where ϵ_r is the relative dielectric constant, μ the mobility of charge carriers, L the thickness of the sample, V the external voltage, and Θ the proportion of free charge carriers.

The product $\Theta\mu$ can be calculated from the slope of the $I-V^2$ curve. For Pc_2Lu, $\Theta\mu = 1.3$ cm^2/(V·s), a value that may be compared with those obtained with standard metallophthalocyanines: $\Theta\mu = 10^{-2}-10^{-3}$ for PcH_2[23] and $\Theta\mu = 10^{-2}$ for $PcCu$[27,28] (Table I). Since $\Theta < 1$, the $\Theta\mu$ value is an underestimate of the mobility of free charge carriers. In the case of Pc_2Lu, the value found is exceptionally high for thin films of molecular or even inorganic materials.

Conclusion

Lutetium bisphthalocyanine (Pc_2Lu) and lithium phthalocyanine (PcLi) show electrical properties drastically different from all molecular compounds studied so far. Standard mesomolecular or macromolecular systems are all insulators when undoped or not involved in a charge-transfer material. This is related to the difficulty of creating free charge carriers in these materials and therefore to the energy difference between the HOMO and LUMO orbitals. Pc_2Lu and PcLi are easily reduced and oxidized and the HOMO–LUMO difference is correspondingly significantly smaller. This is clearly related to their peculiar electronic nature. On the other hand, the interunit interaction energy is small in Pc_2Lu but large in PcLi. From spin dynamic measurements,[19]
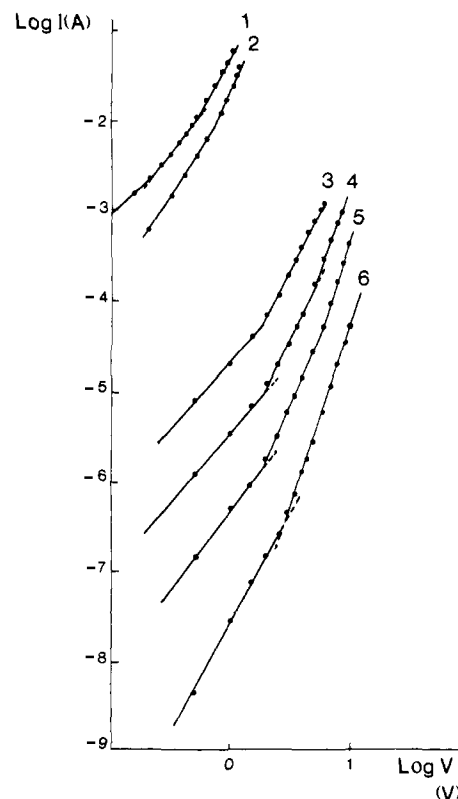

Figure 5. Current–voltage curves for $Au/Pc_2Lu/Au$ cells: (1) 323 K; (2) 291 K; (3) 160 K; (4) 140 K; (5) 122 K; (6) 102 K. The thickness of the cell was approximately 2 μm.

the bandwidth was estimated to be of the order of 50 meV for Pc_2Lu and more than 1 eV for PcLi. These materials are therefore the first two members of the class of molecular semiconductors having either localized or collective electronic levels. Structural disorder was rather ineffective for creating traps in Pc_2Lu whereas it had drastic effects in PcLi as it may be expected from the magnitude of the interunit interaction energy.

The effective mobility of charge carriers found in thin films of Pc_2Lu, as determined from space charge limited currents, was exceptionally high, being more than 2 orders of magnitude higher than for other molecular compounds. This observation is of the utmost importance in considering how to obtain well-behaved devices, in particular bipolar transistors, in which the switching time is inversely proportional to the mobility of carriers. The obtaining of such high mobilities could open the domain of high speed thin film electronics devices based on molecular materials. Such studies are in progress.

Registry No. Pc_2Lu, 79079-35-9; PcLi, 37740-59-3.