Infrared Electronic Absorption in a Single-Component Molecular Metal

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Frontier orbital engineering is crucially important in the bottom-up construction of molecular systems with desired electronic functions. It is commonly accepted that the electronic energy of a molecule is much higher than the vibrational energy of a molecule. If a molecule with electronic excitation in the infrared (IR) region can be designed, then the molecular system is expected to have unprecedented electronic properties. To develop a metallic crystal that consists of single-component molecules, we have synthesized molecules with unprecedentedly low electronic excitations (or unprecedentedly small HOMO (the highest occupied molecular orbital) − LUMO (the lowest unoccupied molecular orbital) gaps).

Since the first organic superconductor was discovered about a quarter century ago,[1] numerous molecular metals and superconductors have been reported. There are two essential requirements for designing molecular metals. First, a suitable molecular arrangement that permits the formation of conduction bands of the HOMO and/or the LUMO of the constituent molecules must be realized. Second, charge carriers must be generated by a charge transfer between the molecules that form the conduction band and other chemical species. Consequently, until recently all of the molecular metals developed were composed of more than two chemical species. However, we noticed that the charge transfer between different chemical species is not necessary for generating the carriers.[2,3] Free carriers can be generated even in single-component molecular crystals if the crystal is formed from molecules with a very small HOMO−LUMO gap and multidimensional intermolecular HOMO−HOMO and/or LUMO−LUMO interactions.

In general, the simplest "one-dimensional box model" of π-conjugated molecules predicts that the wavelength of the longest-wavelength electronic absorption (λ_{max}) will become longer as the size of the π molecule increases. However, synthesizing molecules with very long π-systems is not trivial because of synthetic inaccessibility, chemical instability, and poor solubility.[4] Furthermore, a convergent limit behavior of λ_{max} is widely observed due to the effective conjugated length (ECL) effect.[5] Nevertheless, Tsuda and Osuka recently succeeded in preparing fully conjugated linear porphyrin oligomers with electronic absorption bands that reach into the IR region.[4] λ_{max}^{-1} decreases as the number of porphyrins (n) increases, and $n = 12$ (dodecamer) is about 3500 cm^{-1} (∼0.45 eV). On the other hand, the most straightforward way to engineer a small HOMO−LUMO gap is to design a molecule that incorporates covalently linked donor and acceptor moieties.[6] It has been reported that the TTF-fluorene conjugate possesses the smallest HOMO−LUMO gap (∼0.3 eV) for closed-shell organic compounds and exhibits an intramolecular charge-transfer band around 8000 cm^{-1}.

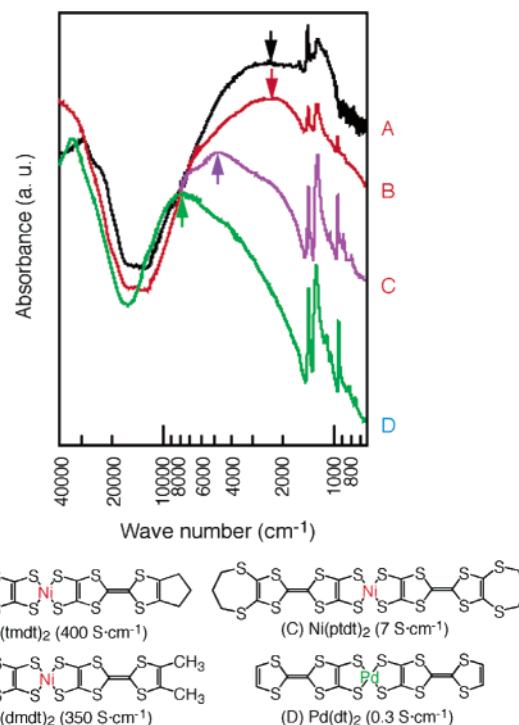[†] The University of Tokyo.
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Figure 1. The visible and IR spectra of Ni(tmdt)$_2$, Ni(dmdt)$_2$, and Pd(dt)$_2$, and the IR spectra of Ni(ptdt)$_2$ measured on crystalline powder samples using a JASCO-MSV-370 spectrometer (40 000−5000 cm^{-1}) and a JASCO-FT/IR-420+IRT30 spectrometer (7800−600 cm^{-1}). The VIS and IR spectra connected smoothly around 6000 cm^{-1}. The broad absorption maximum (arrow) shifts to higher energy from 2200 to 7800 cm^{-1} as the semiconducting properties increased (Ni(tmdt)$_2$, Ni(dmdt)$_2$ → Ni(ptdt)$_2$ → Pd(dt)$_2$). The room-temperature conductivities (σ_{RT}) are in parentheses.

We have synthesized and examined the electronic absorption spectra of the crystals of transition metal complex molecules with extended-TTF ligands M(L)$_2$ [M = Ni, Pd; L = tmdt (trimethylenetetrathiafulvalenedithiolate), dmdt (dimethyltetrathiafulvalenedithiolate), ptdt (propylenedithiotetrathiafulvalenedithiolate), and dt (tetrathiafulvalenedithiolate) (see Figure 1)]. Because a suitable solvent was not found, the visible (VIS) and IR spectra were measured on crystalline powder samples.[7,8] As shown in Figure 1, the IR spectra had molecular vibration peaks and broad electronic absorption. Ni(tmdt)$_2$ and Ni(dmdt)$_2$ exhibited the broadest absorption maxima around 2200 cm^{-1} (λ_{max}^{-1}), which is much smaller than the wavenumber for the porphyrin dodecamer ($n = 12$, λ_{max}^{-1} ≈ 3500 cm^{-1}). It will be extremely difficult to prepare a fully π conjugated porphyrin oligomer longer than icosamer ($n > 20$) without the ECL effect, which is also expected to show a similar low-energy electronic excitation.[4] To our knowledge, this is the smallest electronic absorption energy ever reported for single-
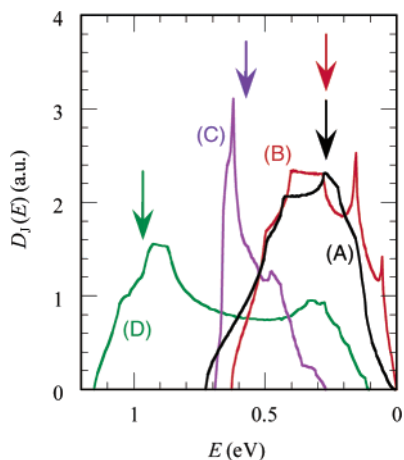
Figure 2. The calculated joint density of states $D_J(E)$: (A) Ni(tmdt)$_2$, (B) Ni(dmdt)$_2$, (C) Ni(ptdt)$_2$, and (D) Pd(dt)$_2$. The E-dependence of $D_J(E)$ is consistent with the observed electronic absorption spectra for each system. The arrows indicate the energy of observed absorption maxima (λ_{max}^{-1}) (see Figure 1).

component closed-shell molecular systems. On the other hand, semiconducting complexes, N(ptdt)$_2$ and Pd(dt)$_2$, exhibited absorption maxima at 4700 and 7800 cm^{-1}, respectively.[8,9] Although the electronic absorptions around 2200 cm^{-1} of Ni(tmdt)$_2$ and Ni(dmdt)$_2$ seem to suggest an extremely small HOMO−LUMO gap (ϵ_{HL}), the M(L)$_2$ peaks blue shifted as the semiconducting properties of the crystal increased, which indicates that the band structure plays a crucial role.

The electronic absorbance is proportional to $D_J\mu^2$, where D_J is the joint density of state and μ is the transition dipole. The bonding and antibonding combinations of the left and right ligand orbitals, respectively ($\phi_{HOMO} \approx \phi_{Ligand1} + \phi_{Ligand2}$; $\phi_{LUMO} \approx \phi_{Ligand1} - \phi_{Ligand2}$ $+ c_M\phi_{d\pi}$, where $c_M\phi_{d\pi}$ is the small contribution from the dπ orbital of the central metal atom), can approximate the HOMO and LUMO of a M(L)$_2$ (M = Ni, Pd, ...; L = extended-TTF ligand) molecule.[2] The wave function of the tight-binding band in Ni(L)$_2$ (L = tmdt, dmdt) crystals, which have one molecule in the unit cell, can be written as $\varphi(k) = (1/N)^{1/2}[\sum \exp(ikR_n) \{c_{HOMO}(k)\phi_{HOMO}(r - R_n) + c_{LUMO}(k)\phi_{LUMO}(r - R_n)\}]$, and the transition dipole μ between $\varphi_{occ}(k)$ and $\varphi_{vac}(k)$ is $(c_{HOMO}^{vac*}(k)c_{LUMO}^{occ}(k) + c_{LUMO}^{vac*}(k)c_{HOMO}^{occ}(k))\mu_{HL}$, where μ_{HL} is $\langle\phi_{LUMO}|r|\phi_{HOMO}\rangle$. Although a substantial HOMO−LUMO mixing in several parts of the Brillouin zone was suggested by Rovira et al.,[10] the HOMO−LUMO mixing around the energy where the density of states (D) has large value was tentatively assumed to be not so serious due to the crossing-band nature of the Ni(L)$_2$ system. Thus, $\mu \approx \mu_{HL}$ and the absorbance is approximately proportional to $D_J(E)$ $(=\sum_k D^{occ}(k, \epsilon(k))D^{vac}(k, \epsilon(k) + E))$, when $\epsilon_F - E < \epsilon(k) < \epsilon_F$ (ϵ_F: Fermi energy). Thus, the E-dependence of $D_J(E)$ can be roughly regarded as the calculated electronic spectrum.

Because it is difficult to accurately estimate ϵ_{HL}, the extended Hückel tight-binding band structures and the joint density of states $D_J(E)$ of M(L)$_2$ were calculated by varying ϵ_{HL} at $\epsilon_{HL} < 1.0$ eV.[11] The calculated spectra agreed with the observed spectra when ϵ_{HL} = 0.14 ± 0.06 eV for Ni(L)$_2$ and 0.12 ± 0.08 eV for Pd(dt)$_2$.[12] That is, ϵ_{HL} seems to be less than ca. 0.2 eV. It should be noted that λ_{max}^{-1} does not correspond directly to the HOMO−LUMO gap (ϵ_{HL}). As shown in Figure 2, the calculated absorption maximum was around 0.3 eV for Ni(tmdt)$_2$ and Ni(dmdt)$_2$, around

0.6 eV for Ni(ptdt)$_2$, and around 0.9 eV for Pd(dt)$_2$,[12] which are consistent with the wavenumbers of the observed absorption maxima: λ_{max}^{-1} = 2200 cm^{-1} (0.27 eV) for Ni(tmdt)$_2$ and Ni-(dmdt)$_2$, 4700 cm^{-1} (0.58 eV) for Ni(ptdt)$_2$, and 7800 cm^{-1} (0.97 eV) for Pd(dt)$_2$.

Thus, the general feature of the IR electronic spectra of M(L)$_2$, especially the blue shift of the IR electronic absorption spectra, is well explained by the calculated joint density of states. It may be said that the recent developments in single-component molecular metals were realized by successfully designing molecules with unprecedentedly small HOMO−LUMO gaps.

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(7) The molecules were synthesized according to the reported methods (ref 2; Binet, L.; Fabre, J. M.; Montginoul, C.; Simonsen, K. B.; Becher, J. *J. Chem. Soc., Perkin Trans.* **1996**, *1*, 783−788. Kumasaki, M.; Tanaka, H.; Kobayashi, A. *J. Mater. Chem.* **1998**, *8*, 301−307). Black crystals were prepared electrochemically.
(8) The electrical properties of M(L)$_2$ crystals are as follows: (1) Ni(tmdt)$_2$, room-temperature conductivity (σ_{RT}) = 400 S cm^{-1} (single crystal), metallic state down to 0.6 K (ref 3), (2) Ni(dmdt)$_2$, σ_{RT} = 350 S cm^{-1} (compacted powder pellet sample), metallic down to 230 K (ref 3), (3) Ni(ptdt)$_2$, σ_{RT} = 7 S cm^{-1} (single crystal), semiconductor with E_a = 0.03 eV (ref 9), (4) Pd(dt)$_2$, σ_{RT} = 0.3 S cm^{-1} (pellet), semiconductor with E_a = 0.09 eV.
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(11) The extended-Hückel molecular orbital calculations of Ni(tmdt)$_2$ were performed by using several parameters sets of atomic orbitals [e.g., the parameters reported by R. Hoffmann et al. were used (*J. Am. Chem. Soc.* **1976**, *98*, 1647−1653; **1976**, *98*, 7240−7254; **1979**, *101*, 592−598; **1987**, *109*, 118−124)]. The calculated HOMO−LUMO gap ϵ_{HL} was scattered between 0.07 and 0.24 eV. Therefore, further calculations were made varying ϵ_{HL} by employing the following parameters of atomic orbitals: valence shell ionization potential H_{ii}(eV) and the exponent ζ_i of the Slater-type atomic orbital c_i are, respectively, −22.0 and 2.122 for S 3s, −10.5 and 1.827 for S 3p, −21.4 and 1.625 for C 2s, −11.4 and 1.625 for C 2p, −13.6 and 1.0 for H 1s, −10.95 and 2.1 for Ni 4s, −3.74 and 2.1 for Ni 4p, −9.19 and 2.190 for Pd 5s, and −5.30 and 2.150 for Pd 5p. The d orbitals of Ni and Pd are represented by a linear combination of two Slater-type orbitals: H_{ii}, ζ_i, c_i, ζ_{ii}, and c_{ii} values are −12.91, 5.98, 0.5264, 2.613, and 0.6372 for Pd 4d and −10.58, 5.75, 0.5681, 2.00, and 0.6294 for Ni 3d, respectively. The calculated values of ϵ_{HL} were 0.10 eV for Ni(tmdt)$_2$, 0.11 eV for Ni(dmdt)$_2$, 0.12 eV for Ni(ptdt)$_2$, and 0.04 eV for Pd(dt)$_2$.
(12) Very recently, Ishibashi has evaluated $D_J(E)$ of Ni(tmdt)$_2$ on the basis of the local density approximation (LDA) band structure calculation using the ab initio plane-wave norm-conserved pseudopotential method, which gave essentially the same spectra around the absorption maximum (private communications).

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