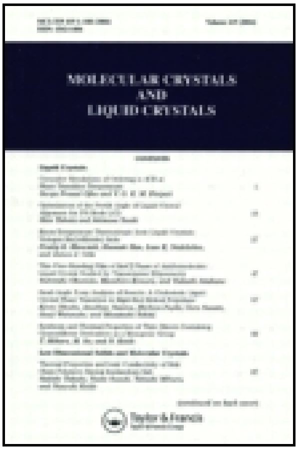

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Photoelectron Spectroscopy of a New Type Electron Acceptor, 5,6,11,12-Tetraazanaphthacene

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Photoelectron spectra of a newly synthesized compound, 5,6,11,12-tetraazanaphthacene are measured. Because of large spectral onset energy its very strong electron accepting ability is highly expected.

Keywords: electron acceptor; electronic structure; photoelectron spectroscopy

INTRODUCTION

Electron acceptors such as tetracyanoquinodimethane (TCNQ) or fullerenes (represented by C_{60}) exhibit high electric conductivity upon complex formation with organic donors [1,2] or alkali metals [3,4] and superconductivity is achieved in alkali metal-C_{60} complexes [5]. Usually spectral onset of ultraviolet photoelectron spectra (UPS) of electron acceptors in the solid state is far from the Fermi level because of their large ionization energy (deep-lying valence band). When electron acceptors receive electrons to their lowest unoccupied molecular

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orbital (LUMO), a new band is to be observed just under the Fermi level in their photoelectron spectra [6–8]. This band can be responsible for high conductivity of the complexes. Recently a heterocyclic aromatic hydrocarbon, 5,6,11,12-tetraazanaphthacene (TANC), has been synthesized and its salt [Cu(TANC)]$F_{0.5}$ showed the conductivity of 54 S cm^{-1} at room temperature [9]. When the salt was cooled, the conductivity decreases; its activation energy from room temperature down to 40 K was estimated to be 40 meV [10]. What sort of change takes place in the electronic structure of TANC upon the [Cu(TANC)]$F_{0.5}$ formation is of a great concern, but photoelectric study of the radical ion salt is not easy task because of sample preparation for the photoelectron spectroscopic measurements. For the future measurement on [Cu(TANC)]$F_{0.5}$, determination of the electronic structure of neutral TANC itself in the solid state is an immediate issue. In this article, we present both ultraviolet and X-ray photoelectron spectra of TANC.

EXPERIMENTAL AND THEORETICAL

Photoelectron spectra were recorded with a Gammadata Sienta SES100 electron energy analyzer attached to a newly designed permalloy chamber. Base pressure of the chamber was 6×10^{-8} Pa. Light sources were a MB Scientific MBS L-1 high intensity VUV photon sources for He I and II radiation , and a twin anode Thermo VG Scientific XR3E2 X-ray source for MgKα. The resolution of UPS was 100 meV, and the spectra were referred to the Fermi level. TANC was vacuum-deposited on gold deposited copper substrate disks from a resistive heating quartz crucible. Molecular orbital calculation was performed with a Fujitsu WINMOPAC program module, and MNDO parameterization was adopted. Calculated Eigen values were broadened with Gaussian functions to obtain a simulated spectrum.

RESULTS AND DISCUSSION

Figure 1 shows He I and II photoelectron spectra of TANC. Spectral onset is 2.55 eV below the Fermi level. This value is very close to that of TCNQ (2.6 eV) [11] and much larger than that of C_{60} (2.0 eV) [6]. Ionization potential (threshold energy for electron ejection) was estimated to be 7.10 eV. These indicate good electron accepting capability of TANC. According to solid state physics, the Fermi level lies at the middle of valence and conduction bands. When this rule is applied to the present result, the energy gap of TANC is estimated to be 5.1 eV. This is too large and inconsistent with its optical absorption

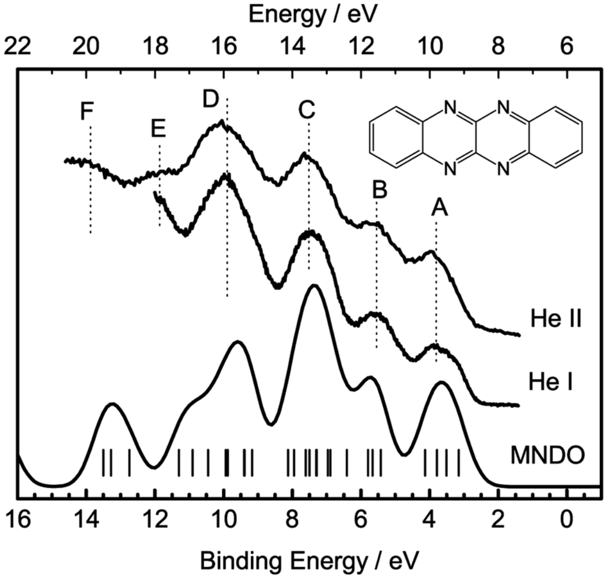
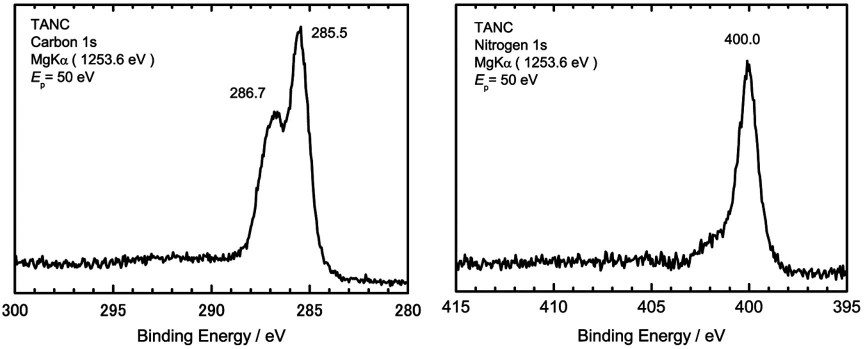


FIGURE 1 He I and II spectra of tetraazanaphthacene (lower scale) and a simulated spectrum obtained by MNDO calculation (upper scale). Bars indicate the position of Eigen values obtained by the calculation.

spectrum. As absorption spectral edge of Vis-UV spectrum of TANC is 500 nm, its energy gap could be around 2.5 eV. Similar results have been observed in fullerenes [12]. As for C_{60}, estimated band gap from UPS spectral onset is 4.0 eV, which does not correspond with optical absorption edge of 650 nm (1.9 eV). These facts indicate that the rule does not stand for electron acceptors.

He I and II spectra of TANC are essentially the same, as most organic compounds are. That is, photoelectron emission in TANC is dominated by k-vector independent indirect transition. There are four distinct and two possible structures labeled A–F. A simulated spectrum obtained from MO calculation is also shown in Figure 1. Energy scale of the simulated spectrum was shifted so that peak positions of the UPS and the simulated spectrum show the best fit. The simulated spectrum reproduces the UPS well, particularly for structures A–D. MO calculation also reveals that four nitrogen atoms participate to construct the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).

Figure 2 shows XPS of C1s and N1s core levels. The C1s spectrum is split into two peaks located at 285.5 eV and 286.7 eV with intensity ratio of 4:3. This splitting is due to chemical shift induced by



(a) (b)

FIGURE 2 X-ray photoelectron spectra of tetraazanaphthacene. C1s (a) and N1s (b) spectra.

neighboring nitrogen atoms. There are six carbon atoms neighboring nitrogen atoms (α-carbon atoms) and eight carbon atoms that do not have neighboring nitrogen atoms (non α-carbon atoms). Ratio of α- and non α-carbon atoms is reflected in the C1s spectrum. MNDO calculation indicates α-carbon atoms are positively charged by 0.07 electrons per atom compared with non α-carbon atoms. An empirical relation between the calculated charge and binding energy [13] gives peak shift of 1.2 eV, which is in good correspondence with the observed splitting of the two peaks.

The N1s spectrum comprises of a single peak and a tail at higher binding energy side. Its binding energy of 400 eV is larger than that of pyridine (398 eV) [14], which is due to the difference in electron density on nitrogen atom: MNDO calculation suggests nitrogen atom in pyridine has about 0.1 excess electrons compared with that in TANC. While the origin of the tail is not clear, it may be attributed to π–π^* shake-up satellites since energy separation of 2–3 eV from the main peak is close to optical absorption energy [10].

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