Discovery of the K_4 Structure Formed by a Triangular π Radical Anion

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S *Supporting Information*

ABSTRACT: The K_4 structure was theoretically predicted for trivalent chemical species, such as sp^2 carbon. However, since attempts to synthesize the K_4 carbon have not succeeded, this allotrope has been regarded as a crystal form that might not exist in nature. In the present work, we carried out electrochemical crystallization of the radical anion salts of a triangular molecule, naphthalene diimide (NDI)-Δ, using various electrolytes. X-ray crystal analysis of the obtained crystals revealed the K_4 structure, which was formed by the unique intermolecular π overlap directed toward three directions from the triangular-shape NDI-Δ radical anions. Electron paramagnetic resonance and static magnetic measurements confirmed the radical anion state of NDI-Δ and indicated an antiferromagnetic intermolecular interaction with the Weiss constant of $\theta = -10$ K. The band structure calculation suggested characteristic features of the present material, such as a metallic ground state, Dirac cones, and flat bands.

Figure 1. (a) View of the crystal structure of K_4 carbon. (b) Local structure in the K_4 carbon.

Graph theory has predicted the K_4 structure as a new allotrope of carbon, in addition to diamond, graphite, graphene, fullerenes, and nanotubes.[1] Figure 1 shows a view of the K_4 structure, which is certainly no less elegant than that of diamond. However, while diamond has a 3D structure of the cubic $Fd\bar{3}m$ space group, consisting of tetravalent (sp^3) carbons, the K_4 carbon has a 3D chiral structure of the cubic $I4_132$ space group, consisting of trivalent (sp^2) carbons. In the K_4 structure, each carbon atom exists at the center of a triangle formed by the three neighboring carbon atoms, and the neighboring triangles, which share one C—C bond, are twisted with a torsion angle α (= ±70.5°) of $\cos \alpha = 1/3$ (Figure 1b). It is characteristic that the K_4 structure consists of interconnected ten-membered rings with a huge 3D cavity space. The electronic structure of the K_4 carbon is also attractive; the band calculation predicts a metallic ground state in contrast to the insulating properties of diamond.[2] Although attempts to synthesize the K_4 carbon have not succeeded, the K_4 structure itself has been reported in a few
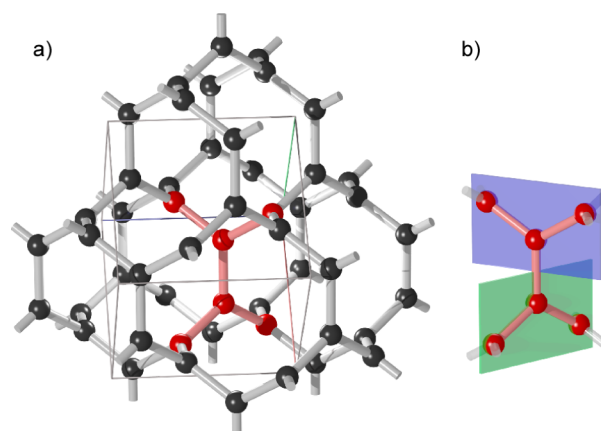
noncarbon materials,[3,4] such as $SrSi_2$.[4] It is still challenging to make this structure and to examine its theoretical predictions.

Recently, Schneebeli et al. reported a beautiful chiral triangular molecule, naphthalene diimide (NDI)-Δ, that consisted of three planar NDI moieties, connected by three cyclohexane moieties.[5] This molecule exhibits reversible six-step reductions on the CV curves due to the strong acceptor ability of the NDI moiety. Although there was no intermolecular π overlap in the crystal structures of neutral NDI-Δ,[5,6] the anionic radical species of NDI-Δ would exhibit three-way branched intermolecular π overlaps due to the exchange interactions (Figure 2). In addition, the bulky terminal cyclohexane moieties in NDI-Δ may prevent an eclipsed π overlap between the NDI moieties and make a twisted π overlap, which is another key factor to create the K_4 structure. In the present communication, we report the electrochemical synthesis and crystal structures of the radical anion salts of NDI-Δ.

The chiral parent compound, (−)-NDI-Δ, was prepared according to a method described in the literature.[5] We then
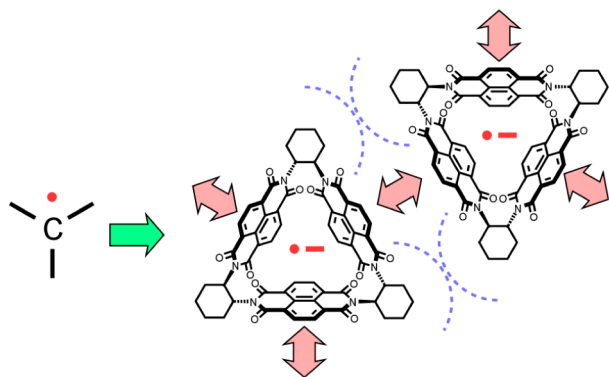
Figure 2. Comparison between the sp^2 carbon and radical anion of NDI-Δ.

Figure 3. Nearest-neighbor intermolecular arrangement (a) and the π−π overlap between the NDI moieties (b) in the Rb salt of (−)-NDI-Δ.

carried out the crystal growth of the radical anion salts by galvanostatic reduction under an N$_2$ atmosphere, using various combinations of solvents and electrolytes. Although the reduction of (−)-NDI-Δ took place with a significant change in solution color, the crystals were grown only when propylene carbonate (PC) was adopted as solvent. In PC, rather air-sensitive crystals with a block shape were grown on the cathode. Table S1 shows the lattice parameters for the crystals prepared with the electrolytes Rb·ClO$_4$, NH$_4$·ClO$_4$, Me$_4$N·ClO$_4$, Bu$_4$N·ClO$_4$, and MePy·PF$_6$ (MePy = 1-methylpyridinium). These crystals belong to the cubic system, having nearly the same lattice parameters.

We carried out X-ray single crystal analysis for the crystals obtained in a PC solution of Rb·ClO$_4$. The crystallographic data for the analysis is shown in Table S2. Fortunately, despite the instability of the crystals, this analysis revealed a 3D network structure of the (−)-NDI-Δ radical anions with a huge 3D cavity and the locations of Rb ions, which were coordinated to the oxygen atoms in (−)-NDI-Δ. However, the refinement for the structure in the cavity was always unsuccessful, probably due to a significant structural disorder within it. Therefore, we flattened the electron densities in the cavity, using the SQUEEZE subroutine of PLATON,[7] and refined only the 3D framework of the (−)-NDI-Δ anions and the Rb ions connected to oxygen atoms. This treatment decreased the reliability factor for the SQUEEZED structure, which confirmed that the primary uncertainties were not caused by the molecular skeleton of (−)-NDI-Δ but by the disorder in the large void space (Table S3). The present data quality and structural analysis are not sufficient for a discussion of the fine molecular structure but are sufficient to conclude the K_4 structure in the obtained crystals.

The crystal structure of the Rb salt of (−)-NDI-Δ belongs to the cubic space group $I4_132$, which is isostructural to the K_4 structure, as we had intended. The structure of the asymmetric unit is shown in Figure S1 and consists of one-sixth of the (−)-NDI-Δ molecule and a Rb ion with an occupancy factor of 0.233(3). This value means that one (−)-NDI-Δ molecule is surrounded by ca. 1.4 Rb ions in average and suggests that (−)-NDI-Δ is approximately in the monoanionic state. Although it is hard to confirm this state from the bond lengths and angles due to their rather large standard deviations, the IR bands exhibit low-frequency shifts, compared with those of the neutral (−)-NDI-Δ (Figure S2). This is consistent with the anionic state of (−)-NDI-Δ. Figure 3a shows the nearest-neighbor intermolecular arrangement, revealing a twisted π−π overlap with an interplanar distance of 3.4 Å. Figure 3b shows the
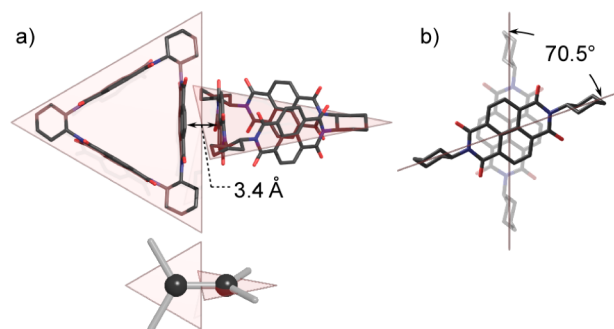
intermolecular overlap between the NDI moieties in which the twisted angle is 70.5°. This angle is coincident with that for the K_4 structure. Since the neutral NDI-Δ does not exhibit such intermolecular π overlap,[5,6] the present π−π overlap must be caused by the exchange interaction between the paramagnetic radical anions of (−)-NDI-Δ. However, the observed interplanar distance is not as short as those for the so-called "pancake bonds"[8] in radical dimers. This suggests a weak interaction between the neighboring (−)-NDI-Δ radical anions.

Figure 4a,b shows the comparisons between the projections of the present crystal and the K_4 structure, along the [111] and
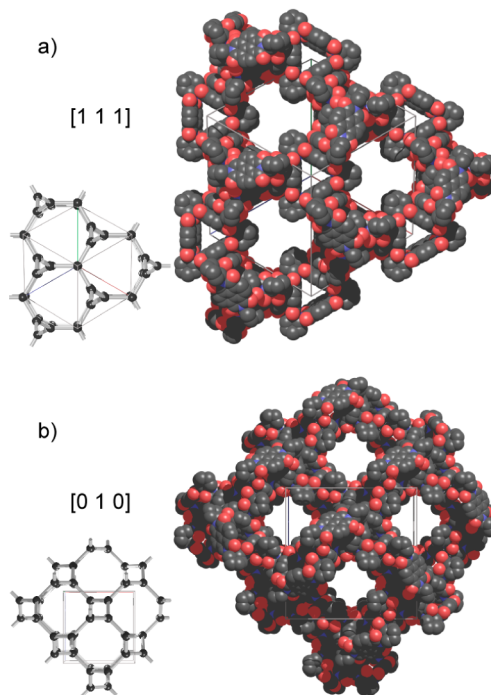

Figure 4. Comparisons between the projections of the K_4 structures of carbon and (−)-NDI-Δ, along the [111] (a) and [010] (b) directions.

[010] directions, respectively. The former lies along a three-fold rotation axis, and the latter along a four-fold screw axis. The structure of the (−)-NDI-Δ radical anion salt can be understood by replacing every sp^2 carbon atom in the K_4 carbon with a triangular (−)-NDI-Δ molecule. It is worth noting here that the K_4 structure of (−)-NDI-Δ is formed only by the unique intermolecular overlap in Figure 3, whereas most molecular crystals consist of several kinds of intermolecular interactions,

such as intra- and intercolumnar interactions. The network structure of (−)-NDI-Δ contains a huge 3D cavity with a volume fraction of 73%, which is comparable to those of metal−organic frameworks (MOFs)[9] and covalent−organic frameworks (COFs).[10]

To understand the chemical contents in the 3D cavity, we carried out an elemental analysis, inductively coupled plasma (ICP) elemental analysis and scanning electron microscope with energy dispersive X-ray fluorescence (SEM-EDX) spectroscopy for the Rb salt. The SEM-EDX spectroscopy indicated that no ClO_4^- was present in the crystals (Figure S3). The elemental analysis gave unexpected results of 26.52% for C, 2.39% for H, and 1.51% for N, meaning that the other elements occupy 69.58 wt %. Since there was no N source except (−)-NDI-Δ, we determined the content rate of (−)-NDI-Δ and calculated the elemental ratio for the other parts except (−)-NDI-Δ as follows: C, 13.57%; H, 1.63%; N, 0%. This indicated a C/H ratio of 8.3, which roughly agreed with that of PC (7.9). These analyses suggested the presence of PC in the cavity, but the source of the large amounts of the non-C, H, and N elements was still uncertain. The ICP measurements for Rb ions indicated a molar ratio of (−)-NDI-Δ/Rb = 1:40 (Figure S4). This abnormal excess amount of Rb ions was semiquantitatively consistent with the presence of the non-C, H, and N elements of ca. 70%. These results strongly suggest the presence of a well-known electrochemical decomposition of PC into dianionic propane-1,2-diolate, etc. (Scheme S1).[11] In fact, the results of the elemental analysis can be explained by the chemical formula, $Rb_{1.4}[(−)$-NDI-Δ]·16.8[Rb_2(propane-1,2-diolate)]·3.1PC with 26.52% for C, 2.93% for H, and 1.51% for N, in which the decomposition compounds of PC, except propane-1,2-diolate, are ignored. As mentioned in the previous section, the crystal growth of the (−)-NDI-Δ salts took place only in the solvent of PC. The presence of a large amount of PC and its decomposed salts, such as Rb_2(propane-1,2-diolate), might assist the formation of the K_4 structure.

The magnetic measurements were performed for the Rb salt of (−)-NDI-Δ. Figure 5a shows the temperature dependence of the
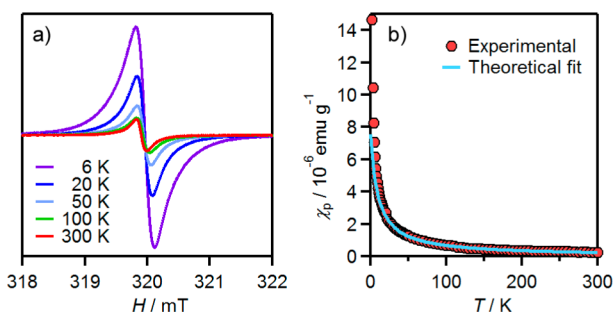

Figure 5. Magnetic data for the Rb salt of NDI-Δ: the temperature dependences of the EPR signals (a) and the static paramagnetic susceptibility (b).

EPR line shape in the range of 6−300 K. These crystals are paramagnetic and exhibit a strong single-line Lorentzian absorption at g = 2.0035 at room temperature. With a decrease in temperature, the EPR intensity exhibits an increase, while the line width and the g-factor depend little on temperature (Figure S5). The temperature dependence of the static magnetic susceptibility was also examined in the range of 2−300 K under the field of 0.5 T. Figure 5b shows the temperature dependence of the paramagnetic susceptibility χ_p, which was

obtained after compensating the diamagnetic susceptibility (Figure S6). This behavior can be fit to the Curie−Weiss law with the Curie constant of C = 7.4 × 10^{-5} emu K g^{-1} and the Weiss constant of θ = −10 K, indicating an antiferromagnetic interaction. If we assume the chemical formula, $Rb_{1.4}[(−)$-NDI-Δ]·16.8[Rb_2(propane-1,2-diolate)]·3.1PC, the molar Curie constant becomes 0.41 emu K mol^{-1}, which roughly agrees with that of the S = 1/2 species.

On the basis of the K_4 structure of the (−)-NDI-Δ, we carried out the band calculation in which intra- and intermolecular transfer integrals were assumed to be −0.029 and −0.258 eV, respectively. These values were estimated by calculating the overlap integrals between the NDI moieties Figure S7 and Table S4). The results are shown in Figure 6, in which the Fermi energy
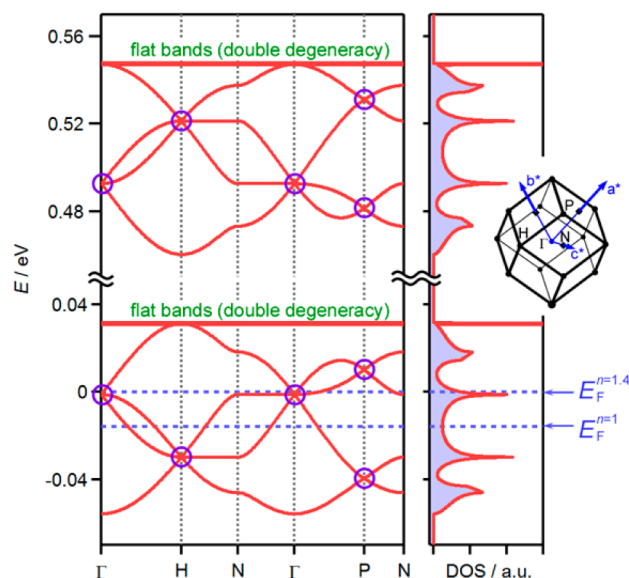

Figure 6. Band structure and density of states (DOS) calculated with the tight binding method for the K_4 structure of NDI-Δ radical anion. The $E_F^{n=1}$ and $E_F^{n=1.4}$ correspond to the Fermi energy for the K_4 structure of Rb[(−)-NDI-Δ] and $Rb_{1.4}[(−)$-NDI-Δ], respectively. The purple circles indicate the Dirac cones. The inset shows the first Brillouin zone for the band structure.

is set for the composition, $Rb_{1.4}[(−)$-NDI-Δ]. In this mixed valence state and even in the monoanion state, namely Rb[(−)-NDI-Δ], the band calculation suggests a metallic ground state. Furthermore, this calculation indicates two very fascinating features. One is the presence of the Dirac cones at the P, Γ, and H points. While Dirac cones are known for the 2D electronic systems in graphene[12] and Bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) salts,[13] the 3D K_4 structure is expected to possess robust Dirac cones. The other striking feature is the presence of the doubly degenerated flat bands, which appear above the Fermi energy. Note here that a partial occupation of the flat bands suggests a ferromagnetic metal state. Since there is no such band structure for simple K_4 carbon,[2] the flat bands reflect the fact that (−)-NDI-Δ has an internal structure consisting of three NDI planes. Although the band calculation suggested a metallic ground state, the preliminary conductivity measurements by the two-probe method indicated semiconductive properties (Figure S8). This electron localization is presumably caused by formation of the Mott state and/or the random potential induced by the structural disorder in the 3D cavity.

In conclusion, we discovered a molecule-based K_4 structure formed by the (−)-NDI-Δ radical anions. The electrochemical reduction for (−)-NDI-Δ in PC solutions produced the beautiful K_4 structure of the anion species, formed by the exchange interactions through the three-way branched $\pi-\pi$ interactions. The band calculation indicated a metallic ground state and two striking features such as Dirac cones and doubly degenerated flat bands. The structural refinement for the 3D cavity and the detailed physical measurements are in progress.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Experimental details, crystallographic details, IR spectra, SEM-EDX spectra, ICP elemental analysis, EPR parameters, DFT (density functional theory) calculation, and conductivity measurements. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b04180.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Heimann, R. B.; Evsyukov, S. E.; Koga, Y. *Carbon* **1997**, *35*, 1654−1658. (b) Iijima, S. *Nature* **1991**, *354*, 56−58. (c) Falcao, E. HL; Wudl, F. *J. Chem. Technol. Biotechnol.* **2007**, *82*, 524−531.

(2) Itoh, M.; Kotani, M.; Naito, H.; Sunada, T.; Kawazoe, Y.; Adschiri, T. *Phys. Rev. Lett.* **2009**, *102*, 055703(1)−055703(4).

(3) Eremets, M. I.; Gavriliuk, A. G.; Trojan, I. A.; Dzivenko, D. A.; Boehler, R. *Nat. Mater.* **2004**, *3*, 558−563.

(4) (a) Janzon, K.; Schäfer, H.; Weiss, A. *Angew. Chem., Int. Ed.* **1965**, *4*, 245. (b) Pringle, G. E. *Acta. Crystallogr., Sect. B* **1972**, *28*, 2326−2328.

(5) Schneebeli, S. T.; Frasconi, M.; Liu, Z.; Wu, Y.; Gardner, D. M.; Strutt, N. L.; Cheng, C.; Carmieli, R.; Wasielewski, M. R.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2013**, *52*, 13100−13104.

(6) Liu, Z.; Liu, G.; Wu, Y.; Cao, D.; Sun, J.; Schneebeli, S. T.; Nassar, M. S.; Mirkin, C. A.; Stoddart, J. F. *J. Am. Chem. Soc.* **2014**, *136*, 16651−16660.

(7) Spek, A. L. *Acta. Crystallogr., Sect. D* **2009**, *65*, 148−155.

(8) Preuss, K. E. *Polyhedron* **2014**, *79*, 1−15.

(9) (a) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334−2375. (b) Kurmoo, M. *Chem. Soc. Rev.* **2009**, *38*, 1353−1379.

(10) (a) Feng, X.; Ding, X.; Jiang, D. *Chem. Soc. Rev.* **2012**, *41*, 6010−6022. (b) Ding, S.-Y.; Wang, W. *Chem. Soc. Rev.* **2013**, *42*, 548−568.

(11) Shkrob, I. A.; Zhu, Y.; Marin, T. W.; Abraham, D. *J. Phys. Chem. C* **2013**, *117*, 19255−19269.

(12) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Katsnelson, M. I.; Grigorieva, I. V.; Dubonos, S. V.; Firsov, A. A. *Nature* **2005**, *438*, 197−200.

(13) Kajita, K.; Nishio, Y.; Tajima, N.; Suzumura, Y.; Kobayashi, A. *J. Phys. Soc. Jpn.* **2014**, *83*, 072002(1)−072002(31).