Discovery of Sodium-Doped Triphenylene Superconductors by Searching the Organic Material Database

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ABSTRACT: Over the past few decades, there has been a lot of research on organic molecule-based materials for future advanced technology. The superconductivity has also been reported in various carbon-based organic materials in line with this trend. In particular, polycyclic aromatic hydrocarbons (PAHs) have been intensively studied in recent years because of the highly conjugated characteristics of the delocalized electrons supplied by alkali metal doping. Here, we report on a PAH superconductor, sodium-doped triphenylene (nominal composition of Na3triphenylene), which was discovered by searching the database of PAH molecules with a small energy difference between the lowest unoccupied molecular orbital (LUMO) and LUMO + 1 states. As the first sodium-doped PAH superconductor, it shows the superconducting transition at $T_c \approx 15$ K under ambient pressure. The discovery of the new PAH superconductor suggests the promising possibility of superconductivity from more diverse molecular structures and the realization of high-$T_c$ organic superconductors furthermore.

1. INTRODUCTION

After the first discovery of superconductivity in graphite intercalation compounds (GICs) in 1965, carbon-based superconductors have received much attention, including carbon nanotubes and graphene. They possess a relatively low $T_c$ value as a limitation in comparison to inorganic superconductors, such as copper (or iron)-based superconductors, for which $T_c$ reaches 133 K in HgBa$_2$Ca$_2$Cu$_3$O$_{8+\delta}$ and 56 K in Sr$_{0.5}$Sm$_{0.5}$FeAsF$_6$ at ambient pressure. Nevertheless, they are still being studied intensively because of their low toxicity, abundant quantity, cheaper price, lighter weight, and mechanical flexibility, especially those that are important requirements for next-generation electronics. Development of carbon-based superconductors holds significance not only for extending to organic molecular materials from inorganic materials for high-$T_c$ superconductors but also for studying their fundamental but veiled physical and chemical properties. One of the core categories of carbon-based materials is hydrocarbon molecules composed only of carbon and hydrogen atoms. In particular, polycyclic aromatic hydrocarbons (PAHs) made up of sp$^2$ carbons and fused benzene rings have attracted significant interest. Their extended π-bonding orbitals can delocalize the externally supplied electrons by alkali metal vapor intercalation and the small size of crystallites. Thus, successful synthesis of new PAH superconductors with high reproducibility is very crucial in terms of securing the research on the high-$T_c$ superconductivity of organic crystals.

The above-mentioned limitations in the synthesis of PAH superconductors make it difficult to explore and discover new PAH superconductors. In this study, we used the computational approach to explore the vast number of PAH molecules and find out the candidate molecules that have the possibility to show superconductivity. Since it has been reported that the small splitting between the lowest unoccupied molecular orbital (LUMO) and LUMO + 1 energy levels is a necessary condition for the multi-band Fermi liquid nature and possible superconducting phase, we used $\Delta = E_{\text{LUMO+1}} - E_{\text{LUMO}}$ as a key parameter to extract the superconducting candidate molecules. Among several candidates of PAH molecules with small $\Delta$, we experimentally confirmed that sodium-doped triphenylene (Na$_3$triphenylene) shows superconductivity with $T_c \approx 15$ K. Note that sodium is first intercalated to synthesize a PAH superconductor by annealing after grinding molten sodium and the powder precursor directly. This work demonstrates the search for superconductive alkali metal vapor intercalation and the small size of crystallites. Thus, successful synthesis of new PAH superconductors with high reproducibility is very crucial in terms of securing the research on the high-$T_c$ superconductivity of organic crystals.
2. METHODS

2.1. Triphenylene Purification and Preparation of Sodium-Doped Triphenylene. Triphenylene powder (98.0% purity, Sigma-Aldrich) was purified by the sublimation method and loaded at the end of a Pyrex glass tube (16 mm diameter, 300 mm length). The tube was connected to a center hole (12 mm diameter) perforated blank flange by a torr seal (Agilent technologies) to create a vacuum of up to $8.0 \times 10^{-7}$ Torr. It was then placed at the center of a tubular furnace after vacuum sealing. The temperature increased up to 130 °C in 1 day and the tube was kept for 6 days at this temperature. An ampoule containing sodium (99.5% purity, Alfa Aesar) was heated to purify and melt the sodium using a hot plate. To prevent the oxidation of precursors, all sample preparation processes were carried out in a glovebox (with oxygen and moisture less than 0.5 ppm). A glass pipet (1 mm diameter) was fixed with a plastic syringe (1 mm volume) by a glue gun. The pipet was used to suck out the melted sodium metal in the vacuum-sealed glass tube under 8.0 °C.

Purified triphenylene was poured into the Pyrex mortar and directly ground with sodium to induce preintercalation of sodium into triphenylene for a specific time. Only short-time grinding is needed to avoid the loss of crystallinity (see the Supporting Information, Figure S1). The color of the sample changed from white to gray depending on the grinding time (see the Supporting Information, Figure S2). The ground sample was added to the Pyrex glass tube and annealed in the vacuum-sealed glass tube under $8.0 \times 10^{-7}$ Torr for 20 h at 198 °C in an oven. The color of the doped samples was completely changed to black. The nonsuperconducting sodium-doped triphenylene was prepared (for unknown reasons) in the same way and confirmed by measurement of its magnetic properties.

2.2. Measurement of Magnetic Susceptibility of Sodium-Doped Triphenylene. The magnetic properties of sodium-doped triphenylene were measured by a SQUID MPMS (MPMS XL-7, Quantum Design). A gelatin capsule (AGC1, Quantum Design) filled with doped black powder crystals was fixed using clear plastic straws (AGC2, Quantum Design) to measure the magnetic susceptibilities.

2.3. Heat Capacity Measurement. Sodium-doped triphenylene was mixed with pure copper powder (99.999% purity, Sigma-Aldrich), and then made into a pellet (CuTPH in this text) using a hand press to maintain its form for measurement. The heat capacity of CuTPH was measured by PPMS (DynaCool, Quantum Design) after the measurement of grease (N grease, Apiezon), which can facilitate heat conduction. All processes except measurements were carried out in the glovebox (with oxygen and moisture less than 0.1 ppm).

Figure 1. Calculation of $\Delta$ for 200 PAH molecules. Energy difference ($\Delta$) versus the number of carbon atoms for (a) 200 PAH molecules (some points are located in the area outside the graph) and (b) the molecules corresponding to the area under the dashed line in (a) with markings representing the stacking type. (c) A table depicting the molecular structure of numbered molecules in (b).

2.4. Powder Characterization. All X-ray diffraction (XRD) patterns shown in Figure 3a were measured at the Pohang Accelerator Laboratory (PAL, SD XRS GIST beamline). First, sodium-doped triphenylene powder samples were ground finely to add into the capillary tubes (purchased from CTS, Quartz Glass Capillary Tubes 1.0, outer diameter 1.0 mm, length 80 mm, wall thickness 0.01 mm). To maintain inert conditions, the other end was sealed by a torr seal. The X-ray diffraction pattern was obtained in the 2θ range from 5 to 40°. The beam exposure times of pristine triphenylene and sodium-doped triphenylene were 1 and 4 s, respectively. The scan step was 0.02° for both samples, and powder indexing was done by Materials Studio using the DICVOL 91 program in the Reflex module. X-ray diffraction patterns for only ground samples were measured by an in-house machine (Rigaku D/Max 2500 with 40 kV, 100 mA). The powder was placed on the SiO$_2$ substrate covered using a Kapton film and sealed by Kapton tape.

2.5. Raman Spectroscopy Measurement. Raman scattering measurement was carried out with a Raman microscope (Witec) equipped with a 633 nm laser (Research Electro-Optics, Inc.). Capillary samples were prepared using the same methods as for the X-ray diffraction experiment. The laser power was fixed at 0.32 μW to prevent the burning of sodium-doped triphenylene powder crystals.

2.6. Structure Optimization and Electronic Structure Calculation. In the structure relaxation using the Vienna $ab$ initio simulation package (VASP),11 we optimized the cell using the GGA-PBE12 and vdW-DF/revPBE14 functional. We used 6 × 2 × 2 k points inside the first Brillouin zone and an energy difference cut-off of $1 \times 10^{-3}$ eV for both ionic relaxation and electronic relaxation.

To calculate the electron–phonon coupling (EPC) of sodium-doped triphenylene, we performed electron–phonon coupling calculations of sodium-doped triphenylene to estimate superconductivity based on the density-functional perturbation theory15 using Quantum Espresso software.16 EPC matrix elements were placed in the first Brillouin zone on the 1 × 1 × 1 mesh with the Gamma point mesh for electronic states with a plane-wave basis set cut-off of 100 Ry.

$$T_e = \frac{\Omega_{eg}}{1.2} \exp \left(-\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right)$$

where $\mu^*$ is the effective Coulomb interaction parameter, and the normalized weighting function of Eliashberg theory18 is
3. RESULTS AND DISCUSSION

3.1. Search for Candidate Molecules of PAH Superconductors. To search for candidate molecules of PAH superconductors, we first collected the molecular structure of 200 PAH molecules from the Cambridge Structural Database (CSD)\(^1^9\) and PubChem.\(^2^0\) The distribution of 200 PAH molecules with respect to their molecular sizes is shown in the Supporting Information (Figure S3). They have various molecular sizes and geometrical shapes. After their molecular structures were optimized using Gaussian 09,\(^2^1\) exchange–correlation functional and 6-31G(d,p) basis, their molecular energy differences, \(\Delta\), were obtained.

In Figure 1a, the distribution of \(\Delta\) as a function of the number of carbon atoms is shown, and there is no significant correlation between \(\Delta\) and the size of the molecules. The reported PAH superconductors, phenanthrene,\(^7\) picene,\(^8\) and coronene,\(^9\) are marked as circles. Since \(\Delta \approx 0.2\) eV is the largest among those for the reported PAH superconductors so far, we filtered 34 molecules (see the Supporting Information, Table S1) with \(\Delta\) smaller than 0.2 eV. (1,2,8,9-dibenzo pentacene\(^2^5\) has a larger \(\Delta\) but a small energy gap between LUMO + 1 and LUMO + 2 levels, which is explained in detail in the Supporting Information, including the case of \(p\)-terphenyl.\(^2^6\)) The filtered molecules were again categorized according to the reported stacking types of the crystals, as shown in Figure 1b. The stacking types of herringbone, \(\gamma\)-type, and \(\beta\)-type are indicated with circles, diamonds, and squares, respectively. Previously reported superconductors, indicated with filled symbols, have a stacking type of herringbone or \(\gamma\)-type, which is also similar to \(\beta\)-type. PAH molecules with unknown stacking type are indicated by a cross. Candidate PAH molecules with small \(\Delta\) and a similar stacking type to those for the reported superconductors are listed in Figure 1c. Among the final 10 candidates, phenanthrene (1), picene (2), and coronene (8) are the experimentally reported superconductors, and benzene (7) was theoretically predicted to be a superconductor under high pressure.\(^2^7\) Note that triphenylene (3) was confirmed to be a superconductor by doping sodium in this work.

3.2. Magnetic Susceptibility of Na\(_3\)triphenylene. Sodium-doped triphenylene was prepared via annealing after direct powder grinding of triphenylene with sodium. Figure 2 shows the overall diamagnetic properties of Na\(_3\)triphenylene. The field-cooling (FC) and zero-field-cooling (ZFC) measurements of Na\(_3\)triphenylene as a function of temperature under 10 Oe are depicted in Figure 2a. In the ZFC curve, a conspicuous decrease of \(M/H\) versus \(T\) occurred below 15 K, which was the same as from the FC measurement, which means the shielding effect against the applied magnetic field and the corresponding shielding fraction can be estimated to be about 0.65% (assuming the density of Na\(_3\)triphenylene to be 1.302 g/cm\(^3\)). This shows that the Meissner effect is manifested in the Na\(_3\)triphenylene sample, which is the key evidence of superconductivity. The small shielding fraction seems to be caused by the smaller grain size of crystals than the penetration depth of the magnetic field (\(H\)) as discussed by Mitsuhashi \textit{et al.} The \(M/H\) curve from Na\(_3\)triphenylene shown in Figure 2a has moderate transition behavior with an onset temperature of \(T_{\text{onset}} \approx 30\) K and a critical temperature of \(T_C = 15\) K, as indicated in Figure 2a. In the last step of the experiment, the superconductivity through the consecutive...
rapid ZFC measurements was confirmed in 3 of 10 samples made under optimized conditions for the reproducibility test, as shown in the Supporting Information, Figure S4. The magnetic field \( (H) \) dependence of \( M/H \) versus \( T \) shows the drastic suppression of diamagnetic properties above 100 Oe, as shown in Figure 2b. Although the superconducting phase of the powder is gradually destroyed above 100 Oe, the decrease of \( M/H \) showing the superconductivity is still observed up to 2000 Oe. One interesting thing to note is that only the shielding fraction seems to be affected by the applied magnetic field. Upon several attempts of heat capacity measurements, no distinct thermodynamic evidence was observed, which appears to be due to the low shielding fraction (see the Supporting Information, Figure S5). In Figure 2c, the lower critical field \( (H_{\text{c1}}) \) of Na\(_3\)triphenylene is estimated to be about 95 Oe, which is less than those of K\(_3\)picene \( (H_{\text{c1}} \approx 380 \text{ Oe}, T_{\text{c}} \approx 18 \text{ K}) \)\(^{9,10}\) and K\(_3\)phenanthrene \( (H_{\text{c1}} \approx 175 \text{ Oe}, T_{\text{c}} \approx 4.95 \text{ K}) \).\(^{9,10}\) Na\(_3\)triphenylene shows type-II characteristics clearly, like other reported PAH superconductors. Figure 2d shows the magnetic susceptibility of (non-)superconducting sodium-doped triphenylene and pristine triphenylene in a wide range of temperature from 2 to 300 K. While certain K\(_3\)dibenzopentacenes are reported to have several \( T_{\text{c}} \) values,\(^{11,12}\) the superconducting Na\(_3\)triphenylene in this work has a single \( T_{\text{c}} \) value of 15 K. In addition, the pristine triphenylene has a negligible magnetic response unlike the paramagnetic or diamagnetic sodium-doped triphenylene samples. The inset of Figure 2d shows the magnetic susceptibility of potassium-doped triphenylene and non-superconducting sodium-doped triphenylene (nominal composition of K\(_3\)triphenylene and Na\(_3\)triphenylene). K\(_3\)triphenylene shows clear Curie behavior of magnetic susceptibility, which implies that the system has local spin moments with possible Mott insulator behavior. On the other hand, the nonsuperconducting Na\(_3\)triphenylene shows almost constant Pauli behavior of magnetic susceptibility and this system is believed to remain metallic. This difference suggests that the size of the alkali metal atom would play an important role in producing the superconductivity in alkali metal-doped PAHs because smaller sodium atoms will result in a metallic state with broad bandwidths of conducting orbitals.

### 3.3. Crystal Structure and Raman Scattering Spectra of Na\(_3\)triphenylene

The crystal structures of pristine triphenylene and Na\(_3\)triphenylene were measured and analyzed using X-ray diffraction (XRD) and Raman spectroscopy (Figure 3). Each powder sample was filled in the capillary for XRD and Raman measurements. The lattice constants of pristine triphenylene are estimated to be \( a = 13.1964, b = 16.77912, \text{ and } c = 5.2859 \text{ Å with } \beta = 90^{\circ} \), which is similar to the reported orthorhombic crystal structure with a space group of \( P2_12_12_1 \).\(^{16}\)

In superconducting Na\(_3\)triphenylene, the main XRD peaks remained to have lattice parameters of \( a = 13.1901, b = 16.7708, c = 5.2760 \text{ Å, and } \beta = 90^{\circ} \). Negligible change of volume by sodium doping is consistent with the case of K\(_3\)phenanthrene.\(^{16}\) Unfortunately, we observed NaH-related peaks in the range of 29–35 cm\(^{-1}\) (marked with asterisks) like other PAH superconductors,\(^{17,24,29}\) which are believed to be caused by the decomposition of some triphenylene molecules during the mixing or annealing in a vacuum with thermal treatment. However, the other peaks related to the pristine triphenylene still remained. Figure 3b shows the Raman spectra of Na\(_3\)triphenylene and pristine triphenylene. In pristine triphenylene, the main peaks at 1607.26, 1458.17, and 1340.98 cm\(^{-1}\) are attributed to the stretching of aromatic C–C bonds, those at 1229.02 and 1062.45 cm\(^{-1}\) to the in-plane bending of C–H bonds, and that at 699.85 cm\(^{-1}\) to the out-of-plane bending of C–H bonds, as listed in Table 1.
Na$_3$triphenylene shows conspicuous downshift of the peaks, which indicates the charge transfer to triphenylene from sodium atoms. The peaks from C–C stretching are 1580.59, 1444.42, and 1324.88 cm$^{-1}$, those from C–H in-plane bending are 1214.78 and 1044.51 cm$^{-1}$, and that from C–H out-of-plane bending is 681.40 cm$^{-1}$. Because three sodium atoms are doped to one triphenylene molecule, 5–6 cm$^{-1}$ of redshift is estimated for one sodium atom. A similar size of redshifts has also been observed in M$_3$C$_{60}$ (M = K, Rb) and potassium-doped phenanthrene. The reason for the broadening of peaks in Raman spectra seems to be the formation of amorphous carbon during the annealing process, which would also be another reason for the low shielding fraction.

### 3.4. Electronic Structures of Na$_3$triphenylene

We optimized the crystal structure of Na$_3$triphenylene and calculated its electronic structures using Quantum Espresso and VASP packages. The unit cell contains 4 triphenylene molecules and 12 Na atoms, and its optimized lattice parameters were predicted to be $a = 5.32150$, $b = 14.48530$, and $c = 17.37210$ Å with $\beta = 90^\circ$. Figure 3c,d shows the crystal structures of pristine triphenylene and Na$_3$triphenylene, respectively. The tilting degree and the position of triphenylene molecules have been slightly changed after the doping of 3 sodium atoms. The optimized positions of the three sodium atoms are determined to be on the top of each end ring of a triphenylene molecule, which is natural since the end rings are equally more electron-rich than the central ring. The sodium atoms are located between two triphenylene molecules within the $ab$-plane, which is a result similar to the case of K$_3$picene and K$_3$coronene.

Based on this optimized crystal structure, we have obtained the electronic structures of Na$_3$triphenylene. Figure 4a shows the band structure of the conduction bands near the Fermi level. In terms of rigid band theory, Na$_3$triphenylene has half-filled LUMO + 1 after the doping of three electrons; therefore, the Fermi level has shifted up and become metallic. The band dispersion also indicates the interaction between the triphenylene molecules. Because of the large dispersion along Y–S and X–I’ directions, unlike the $b^*$ and $c^*$ directions, the triphenylene molecules strongly interact along the $a^*$ direction. As mentioned before, in Figure 3d, the molecules are stacked in parallel along the $a^*$-axis and there are three sodium atoms between them. In terms of the interaction between MOs of aromatic molecules, the three electron-rich end rings of triphenylene molecules are in contact only along the $a^*$ direction. Along the $b^*$ and $c^*$ directions, the electron-pool edges of the molecules are in contact; hence, it shows negligible band dispersion as similarly shown in K$_3$coronene.

Figure 4b shows the density of states of Na$_3$triphenylene. The original band gap of the pristine triphenylene crystal was about 3.1 eV (see the Supporting Information, Figure S6) and Na$_3$triphenylene has a slightly smaller energy gap below the Fermi level (between the lowest conduction bands and the highest valence bands). Looking at the atom-projected density of states, it is clear that the states at the Fermi level are mainly contributed by carbon atoms, with little contribution from the sodium atoms. In Figure 4c, the isosurfaces of charge density for all integrated $k$-points for the lowest 4 bands (L) and the next lowest 4 bands (U) of conduction bands are shown. These 8 bands are mainly contributed from the LUMO and LUMO + 1 states of triphenylene molecules. As shown in the

![Figure 4](https://dx.doi.org/10.1021/acs.chemmater.9b04346)

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charge density plot, L and U bands evenly have the characteristics of both LUMO and LUMO + 1. It implicitly shows that LUMO and LUMO + 1 are well hybridized and almost degenerate with a very small energy difference of 0.54 meV.

Furthermore, we performed electron–phonon coupling (EPC) calculations to estimate the superconducting transition temperature using the Allen–Dynes equation.\textsuperscript{17} Integrated EPC (λ) is predicted to be ∼0.5 and the corresponding superconducting transition temperature is estimated to be ∼1.94 K using an effective Coulomb interaction parameter, μ* = 0.13. The calculated spectral function and the integrated EPC with respect to frequency are shown in Figure 4d, which exhibit frequency-dependent behavior, although there is a quantitative deviation between the calculated and experimentally observed values. We can easily confirm that the lower frequency domain contributed mainly to the coupling, which is the contribution of heavy elements (i.e., sodium). It is worth noting that superconductivity Tc increases with decreasing μ* (μ* = 0.10 gives 3.15 K and μ* = 0.03 gives 6.92 K), which implies that an electron correlation effect at the Fermi level can affect significantly the transition temperature.

4. CONCLUSIONS

In this work, we report the synthesis of a PAH superconductor by doping sodium atoms, which is differentiated from a previous report on the synthesis of PAH superconductors using potassium doping. In the case of C60, which is expected to exhibit superconductivity with sodium doping, the small size of the Na+ ion causes a disproportionation of Na3C60 into Na2C60 and Na6C60 due to poor size matching and freezing at the intercalated site.\textsuperscript{33} By synthesizing a well-characterized molecule, we still have room to increase the intercalated site.\textsuperscript{33} Therefore, we have room to increase Tc of alkali metal-doped triphenylene using other alkali metals as a dopant, because Tc is known to rise in proportion to the size of a unit cell.\textsuperscript{34}

Furthermore, superconductivity in sodium-doped triphenylene was found by applying the computational method based on first-principles calculation with the aid of a material database. As mentioned earlier in this paper, it is difficult and takes too much effort to synthesize an alkali metal-doped PAH material and check the superconductivity only with experiments. The veiled mechanism of superconductivity in the PAH material makes it even more difficult to predict new PAH superconductors. Using the computational search method, however, it is possible to judge quickly as to which PAH molecules have a high possibility of exhibiting superconductivity with simple and meaningful physical or empirical parameters. Among the 200 PAH molecules from the database, 34 candidate molecules are suggested to be the possible superconductors with small Δ (see Supporting Information, Table S1). Finally, our computational approach—applying first-principles calculation in the material database to search target materials—is portable to various fields of materials and would help in finding new candidate materials without high costs. Thus, it is worth synthesizing and checking the superconductivity in other candidates consisting of various alkali metal and PAH molecules using our computational approach, which can help open other pathways to find high-Tc organic superconductors.

■ ASSOCIATED CONTENT

\* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.9b04348.

X-ray diffraction patterns for ground triphenylene with sodium; real images of color changing of the sample; distribution histogram of PAH molecule data; list of candidate PAH molecules; reproducibility test results; heat capacity and specific heat data; band structure of pristine triphenylene; magnetization of K-doped triphenylene (PDF)

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Notes

The authors declare no competing financial interest.

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