Strong Intramolecular Electron-Phonon Coupling in the Negatively Charged Aromatic Superconductor Picene

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Superconductivity was recently discovered in solid potassium-intercalated picene ($K_3$22ph), in which the picene molecule becomes trianionic ($22ph^{3-}$). In this Letter, we conduct a theory-based study of the superconductivity of $22ph^{3-}$ within the framework of BCS theory. We estimate the density of states $N(\varepsilon_F)$ on the Fermi level to be 2.2 states per (eV molecule spin) by using the theoretical intramolecular electron-phonon coupling l_x and the experimental superconducting transition temperature T_c of 18 K. The theoretical value is consistent with the 1.2 states per (eV molecule spin) determined experimentally for $K_3$22ph with $T_c = 18$ K, indicating the validity of our theoretical treatment and the electron-phonon mechanism for superconductivity. The predicted l_x, 0.206 eV, for $22ph^{3-}$ is larger than any value reported for organic superconductors, so picene may have the largest l_x among the superconductors reported so far.

Modification of the electronic structure of materials with π-electron networks by metal doping is a very important way to bring out novel physical properties, such as superconductivity [1–6]. However, in the case of organic superconductors, no new material systems with high superconducting transition temperatures (T_c's) have been discovered in the past decade [4–6]. Here it is important to say that the electron-phonon interactions between intramolecular vibrations and frontier orbitals play an essential role in the occurrence of superconductivity in organic materials [7–9]. In the previous work, we have theoretically analyzed the electron-phonon interactions and estimated possible T_c's of the monoanions and monocations of various molecular systems such as polyacenes and polyphenacenes, including picene 22ph (Fig. 1). We have suggested a guiding principle for the realization of high-temperature superconductivity in view of the electron-phonon interactions in the monoanions and monocations of various molecules [7–9]. Specifically, we predicted the occurrence of superconductivity in the monoanion of 22ph, with a predicted T_c of around 10 K [8].

Recently, it has been experimentally established that intercalating alkali metal atoms into 22ph produces metallic behavior and superconductivity [10]. Solid potassium-intercalated picene (K_x22ph) has a T_c of 7 or 18 K, depending on the metal content. This is the first aromatic hydrocarbon superconductor. Thus, our guiding principle is available for the study of the organic aromatic hydrocarbon superconductors, which are promising candidates for improved T_c's. In this Letter, we investigate the electron-phonon interactions in the trianion of 22ph in

order to clarify the mechanism of superconductivity in $K_3$22ph. The density of states at the Fermi level [$N(\varepsilon_F)$ [states per (eV molecule spin)]] is estimated on the basis of the calculated electron-phonon coupling constants and
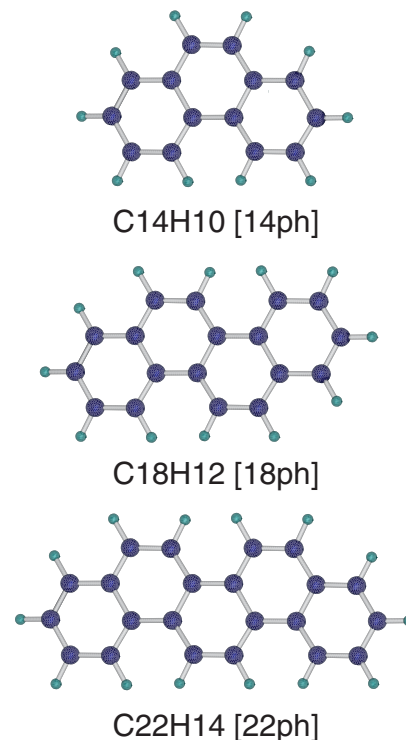

FIG. 1 (color). Schematic representation of hydrocarbon molecules.

experimental T_c's of 7 and 18 K [10]. We approach the
intrinsic feature of aromatic superconductivity by compari-
son with the electronic properties of traditional molecular
superconductors such as alkali-metal-doped C_{60} [1–3] and
bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) [4–6].
We theoretically investigate the trianions of polyphena-
cenes for the first time, which are very important since
$22ph^{3-}$ actually exhibits superconductivity at 18 K.

We investigate the experimentally determined T_c's for
22ph by using an approximate solution (McMillan's for-
mula [11]) of the Eliashberg equation from the calculated
BCS electron-phonon coupling constants. McMillan's
formula is derived in a three-dimensional formalism. The
band structure near the Fermi level in $K_3$22ph molecular
crystals is suggested to include some three-dimensional
character [12], so McMillan's formula may be useful in
discussions of the superconductivity of $K_3$22ph. For values
of the dimensionless electron-phonon coupling constant λ_x
smaller than 1.5, T_c is expressed by McMillan's formula,

$$
\begin{aligned}
T_c &= \frac{\nu_{\ln,x}}{1.2} \exp\left[-\frac{1.04(1 + \lambda_x)}{\lambda_x - \mu^*(1 + 0.62\lambda_x)} \right] \\
&= \frac{\nu_{\ln,x}}{1.2} \exp\left[-\frac{1.04[1 + N(\varepsilon_F)l_x]}{N(\varepsilon_F)l_x - \mu^*[1 + 0.62N(\varepsilon_F)l_x]} \right], \quad (1)
\end{aligned}
$$

where μ^* is the Coulomb pseudopotential describing the
electron-electron repulsion. The subscript x put on all
parameters refers to the electron charge in the molecule.

l_x is the total electron-phonon coupling constant for the
molecule, which is defined as

$$
l_x = \sum_m l_{x,m} = \sum_m g_{x,m}^2 h\nu_m. \quad (2)
$$

$g_{x,m}$ is the dimensionless vibronic coupling constant
[7–9] for the mth vibrational mode. $\nu_{\ln,x}$ is the logarithmi-
cally averaged phonon frequency and is defined as

$$
\nu_{\ln,x} = \exp\left\{ \sum_m \frac{l_{x,m} \ln\nu_m}{l_x} \right\}. \quad (3)
$$

The term $\nu_{\ln,x}$ denotes the frequency characteristic of the
electron-phonon interaction. The dimensionless electron-
phonon coupling constant λ_x [$= N(\varepsilon_F)l_x$] is directly
related to l_x and $N(\varepsilon_F)$. l_x is mainly dominated by intra-
molecular vibrational modes, while $N(\varepsilon_F)$ is mainly domi-
nated by intermolecular interactions.

Let us examine the electron-phonon interactions in
$22ph^{3-}$. In earlier work [7–9,13–16], we analyzed the
vibronic interactions and estimated the possible T_c's in
the monoanions ($x = -1$) and monocations ($x = +1$) of
polyacenes and polyphenacenes. Our predicted $\nu_{\ln,x}$, $l_{x,m}$,
and l_x for the monocations of polyacenes [7–9] were
in excellent agreement with those obtained by high-
resolution gas-phase photoelectron spectroscopy [17,18].
In the mono- and trianions, the carriers partially occupy the
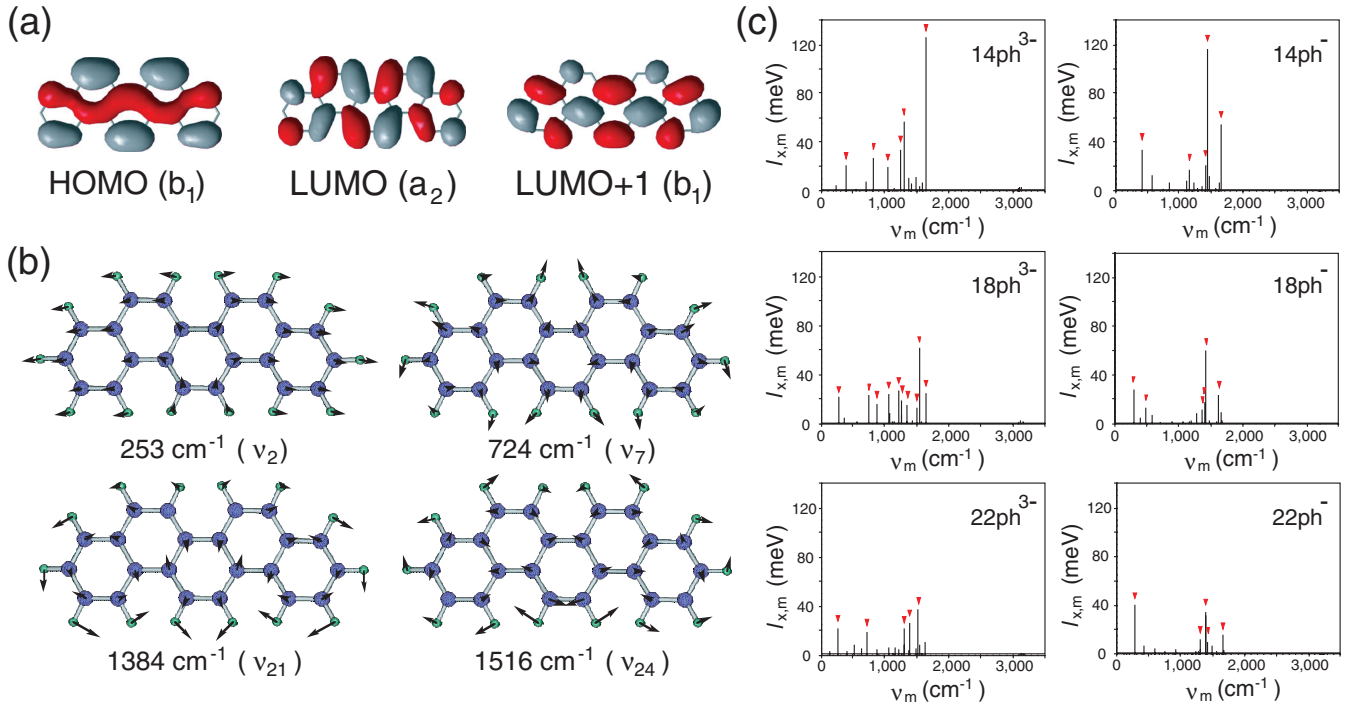lowest unoccupied molecular orbital (LUMO) and the

FIG. 2 (color).   (a) Phase patterns of the frontier orbitals and (b) selected vibronically active modes in $22ph^{2-}$; the normal coordinate
analyses are performed for $22ph^{2-}$ to determine the electron-phonon coupling interaction of $22ph^{3-}$, as fully described in text and
the Supplemental Material [19]. (c) Plots of $l_{x,m}$-ν_m for the tri- and monoanions of 14ph, 18ph, and 22ph. The inverse triangles refer to
the $l_{x,m}$ peaks contributing mainly to l_x.

second lowest unoccupied molecular orbital (LUMO + 1), respectively. Therefore, $g_{-1,m}$ and $g_{-3,m}$ can be defined as orbital vibronic coupling constants for the LUMO ($g_{LUMO,m}$) and LUMO + 1 ($g_{LUMO+1,m}$), respectively (see Figs. SI1–SI2 in the Supplemental Material [19]). The phase patterns of the LUMO and LUMO + 1 wave functions and the selected vibronically active modes in 22ph are shown in Fig. 2(a).

The electron-phonon coupling constants versus frequency in the mono- and trianions of 22ph are shown in Fig. 2(b). The C-C stretching A_1 modes of 1384 (ν_{21}) and 1516 cm^{-1} (ν_{24}) strongly couple to the LUMO + 1 in 22ph [20]. The low-frequency A_1 mode of 253 cm^{-1} (ν_2) also strongly couples to the LUMO + 1 in 22ph. That is, the low-frequency mode ν_2 (as well as the C-C stretching modes ν_{21} and ν_{24}) plays an essential role in the electron-phonon interactions in 22ph^{3-}. This can be understood from the symmetry of the LUMO + 1 wave functions and the vibronically active modes shown in Figs. 2(a) and 2(b). For example, when 22ph^{2-} is distorted along the A_1 mode of 1516 cm^{-1} ν_{24}, the bonding and antibonding interactions between two neighboring carbon atoms in the LUMO + 1 become stronger and weaker, respectively, and thus the LUMO + 1 is significantly stabilized in energy by such a distortion. This is the reason why the C-C stretching ν_{24} mode couples most strongly to the LUMO + 1 in 22ph. Similar considerations apply to the ν_2 and ν_{21} modes.

Let us next discuss the total electron-phonon coupling constants in the trianion (l_{-3}) and monoanion (l_{-1}) of 22ph molecular crystals. The coupling constants l_{-3} and l_{-1} for 22ph are estimated to be 0.206 and 0.179 eV, respectively (Fig. 3), so l_{-3} is slightly larger than l_{-1} in 22ph. By using Eq. (3), we estimated $\nu_{ln,-3}$ and $\nu_{ln,-1}$ for 22ph from l_{-3}, l_{-1}, $l_{-3,m}$, $l_{-1,m}$, and ν_m (theoretical background in Supplemental Material [19]). Thus $\nu_{ln,-3}$ and $\nu_{ln,-1}$ for 22ph are estimated to be 1001 and 899 cm^{-1}, respectively.

Let us look into the possible T_c's for aromatic hydrocarbons (tables in [19]). The T_c's for K$_3$22ph are reported to be 7 and 18 K [10]. Here, we estimate the $N(\varepsilon_F)$ values so as to reproduce the observed T_c's according to Eq. (1) by using the theoretical values of $\nu_{ln,-3}$ and l_{-3} described above. In this calculation, μ^* is varied from 0.0 to 0.3. It is generally known that μ^* ranges from 0.10 to 0.20 [21–28]. The $N(\varepsilon_F)$ calculated for 22ph^{3-} and 22ph$^-$ are listed in Table I. The T_c of 18 K for 22ph^{3-} is reproduced by using $N(\varepsilon_F) = 2.44$ for $\mu^* = 0.10$, $N(\varepsilon_F) = 2.93$ for $\mu^* = 0.15$, and $N(\varepsilon_F) = 3.46$ for $\mu^* = 0.20$. Therefore, the estimated values of $N(\varepsilon_F)$ for 22ph^{3-} ($T_c = 18$ K) range from 2.44 to 3.46 for $\mu^* = 0.10$–0.20. Mitsuhashi et al. reported an experimental estimate for $N(\varepsilon_F)$ of K$_3$22ph ($T_c = 18$ K) to be 1.2 states per (eV molecule spin) [10]. Thus, this theoretical $N(\varepsilon_F)$ reproduces the experimental value, indicating that our theoretical approach is
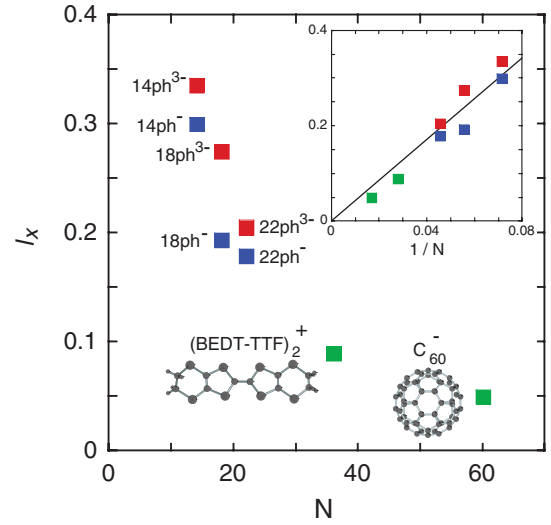

FIG. 3 (color). Plots of l_x-N for tri- and monoanions of polyphenacenes (14ph, 18ph, and 22ph), (BEDT-TTF)$_2^+$, and C$_{60}^{3-}$. The red and blue squares denote the l_x values for the tri- and monoanions of polyphenacenes, respectively. The green squares denote those for (BEDT-TTF)$_2^+$ (Ref. [5]) and C$_{60}^{3-}$ (Refs. [21–25]). In the inset, the l_x values are plotted as a function of $1/N$.

reliable, and that electron-phonon interaction is a dominant factor in the superconductivity of K$_3$22ph.

Let us approach the key factors underlying high-temperature superconductivity by comparing superconductivity in aromatic K$_3$22ph with that in superconducting molecular systems such as alkali-metal-doped C$_{60}$ and BEDT-TTF. The BEDT-TTF family exhibits superconducting transitions below $\sim$10 K [4–6]. The estimated l_{+1} for (BEDT-TTF)$_2$ is 0.090 eV and the $N(\varepsilon_F)$ is 2–5 states per (eV molecule spin) [4–6], showing that the l_{+1} for (BEDT-TTF)$_2$ is much smaller than the l_{-3}, 0.206 eV, for 22ph. As shown in the inset in Fig. 3, l_x is approximately proportional to N^{-1},

$$l_x \propto \frac{1}{N}, \qquad (4)$$

where N is the number of atoms in the molecule that donate π electrons. Thus the electron-phonon interaction is strong if N is small [21–28]. The total number of carbon and sulfur atoms in 22ph^{3-} and (BEDT-TTF)$_2^+$ is 22 and 36, respectively. This is the reason why l_{-3} for 22ph^{3-} is larger than l_{+1} for (BEDT-TTF)$_2^+$. The $N(\varepsilon_F)$ in (BEDT-TTF)$_2^+$, 2–5 states per (eV molecule spin), is almost the same as the 2.4–3.5 states per (eV molecule spin) in 22ph^{3-}. Therefore, the larger l_{-3} (0.206 eV) of 22ph as compared with the l_{+1} of 0.090 eV for (BEDT-TTF)$_2$ is the main reason why the T_c for 22ph^{3-} is higher than that for (BEDT-TTF)$_2^+$.

The l_{-3} for C$_{60}$ is 0.050 eV, and the $N(\varepsilon_F)$ is 10–14 states per (eV molecule spin) [1–3,21–25]. The l_{-3} for C$_{60}$ is smaller than that for 22ph. This is because the

TABLE I. Calculated $N(\varepsilon_F)$ (per eV molecule spin) as a function of μ^*.

μ^*	0.00	0.05	0.10	0.15	0.20	0.25	0.30	0.35
$22ph^{3-}$ ($T_c = 18$ K)	1.60	2.00	2.44	2.93	3.46	4.03	4.69	5.41
$22ph^-$ ($T_c = 18$ K)	1.90	2.37	2.90	3.46	4.08	4.76	5.52	6.38
$22ph^{3-}$ ($T_c = 7$ K)	1.22	1.59	1.99	2.43	2.90	3.42	3.98	4.62
$22ph^-$ ($T_c = 7$ K)	1.45	1.88	2.35	2.84	3.39	3.99	4.66	5.39

number of carbon atoms, 60, in C_{60}^{3-} is larger than the 22 in $22ph^{3-}$. Therefore, $22ph^{3-}$ might be expected to exhibit a higher T_c than C_{60}^{3-}. However, the frontier orbitals in a C_{60} molecule that form the conduction band are threefold degenerate. This degeneracy of the frontier orbitals would be expected to produce the high $N(\varepsilon_F)$; such a high degeneracy for the C_{60} molecule originates in the high geometrical symmetry I_h. Actually, the $N(\varepsilon_F)$ of 10–14 states per (eV molecule spin) estimated for C_{60}^{3-} is higher than that of $22ph^{3-}$, which has no degeneracy in the frontier orbitals. Regardless of the fact that l_{-3} for C_{60}^{3-} is smaller than that for $22ph^{3-}$, the observed T_c in C_{60}^{3-}, 18–33 K [1–3], may be explained by the fact that the $N(\varepsilon_F)$ of C_{60}^{3-} is higher than that of $22ph^{3-}$.

It is worth noting that intramolecular electron-phonon interaction in $22ph^{3-}$ is stronger than those in $(BEDT\text{-}TTF)_2^+$ and C_{60}^{3-}. The l_x is dominated by the intramolecular vibration modes and cannot easily be changed by physical means such as pressure, thermal perturbation, magnetic, or electric fields, in contrast to the $N(\varepsilon_F)$, which is mainly dominated by intermolecular interactions. However, we can synthesize new aromatic molecules that have larger l_x and $\nu_{\ln,x}$ than $22ph^{3-}$; i.e., the l_x can be changed by chemical means. Let us discuss a candidate molecule that may exhibit a higher T_c than $22ph^{3-}$. The l_x increases with decreasing molecular size, as shown in Figs. 2 and 3. Therefore, the high l_x for smaller polyphenacenes such as phenanthrene ($14ph^{3-}$ and $14ph^-$) and chrysene ($18ph^{3-}$ and $18ph^-$) (Fig. 1) may give them higher T_c's than $22ph^{3-}$ if the $N(\varepsilon_F)$ is kept the same as that for $22ph^{3-}$. The lattice constants a and b, which are related to the ab plane forming the π-conduction network, remain almost unchanged even when the molecular size changes; $a = 8.4744$ Å, $b = 6.1720$ Å, $c = 9.4805$ Å, $\beta = 98.01°$, for $14ph$ [29], and $a = 8.472$ Å, $b = 6.170$ Å, $c = 13.538$ Å, $\beta = 90.81°$, for $22ph$. This may provide almost the same $N(\varepsilon_F)$ in these hydrocarbon solids. Consequently, using smaller molecules is a key factor for improving T_c in such a strongly electron-phonon coupling aromatic hydrocarbon superconductors.

We have predicted the possible T_c's for various organic molecular crystals within the framework of the BCS theory. Here, the possible limitation for the prediction of T_c based on BCS theory should be discussed. The T_c observed actually for $K_3 22ph$ is 18 K, which may be reasonably explained by a phonon-mediated mechanism; i.e., the T_c was exactly understood based on the electron-phonon coupling and McMillan's formula. Further, we stress that applying a phonon-mediated mechanism to discuss the T_c of polyphenacenes ($22ph$, $18ph$, and $14ph$) is substantially reasonable, but the T_c higher than ~ 40 K may not actually be realized [30]. This may be the possible limitation to increase T_c by using smaller molecules, or the limitation of our approach. Furthermore, we suggest a possible incompleteness of the BCS theory, especially its inability to absolutely predict the occurrence of superconductivity, even if nonvanishing T_c is predicted for any material [30–33]. It is also suggested that the present understanding of superconductivity based on BCS theory has to be reconstructed at the very fundamental level [30]. Nevertheless, predicting T_c for hydrocarbons is significant and reliable since a series of materials, hydrocarbons, actually exhibited superconductivity [10,34].

Many researchers have tried to increase the $N(\varepsilon_F)$ by doping large metal ions or spacer molecule(s) and spacer atom(s) into the intermolecular spaces in superconducting solids. However, the extremely large l_{-3} found in $K_3 22ph$ may present another way to raise T_c in molecular superconductors, in that increasing the electron-phonon coupling in the molecules leads to an improved T_c. Specifically, the diversity of aromatic hydrocarbons provides a fertile field in the search for increased electron-phonon interaction.

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[20]　The LUMO + 1 in 22ph corresponds to the LUMO in $22ph^{2-}$. Actual calculation is performed for $22ph^{2-}$ and the vibrational frequencies refer to those of $22ph^{2-}$. See Supplemental Material [19].

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