



Superconductivity above 30 K in alkali-metal-doped hydrocarbon

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The recent discovery of superconductivity with a transition temperature (T_c) at 18 K in K_x picene has extended the possibility of high- T_c superconductors in organic materials. Previous experience based on similar hydrocarbons, like alkali-metal doped phenanthrene, suggested that even higher transition temperatures might be achieved in alkali-metals or alkali-earth-metals doped such polycyclic-aromatic-hydrocarbons (PAHs), a large family of molecules composed of fused benzene rings. Here we report the discovery of high- T_c superconductivity at 33 K in K-doped 1,2:8,9-dibenzopentacene ($C_{30}H_{18}$). To our best knowledge, it is higher than any T_c reported previously for an organic superconductor under ambient pressure. This finding provides an indication that superconductivity at much higher temperature may be possible in such PAHs system and is worthy of further exploration.

The discovery of high-temperature superconductivity in iron pnictides has greatly renewed the interest in searching for other new high- T_c materials^{1–4}. Organic metals and superconductors share many features with iron pnictides and cuprates - a quasi-two-dimensional band structure, the proximity to antiferromagnetism, unconventional superconductivity, etc. It becomes more and more evident that organic metals and superconductors serve as a fascinating field for materials science and solid state physics. More than one hundred molecular-based superconductors have been found since the discovery of first organic superconductor (TMTSF)₂PF₆ in 1979 [ref.⁵]. The highest transition temperature ($T_c \approx 13$ K) was reported for the κ -(ET)₂Cu[N(CN)₂]Cl salt under applied pressure⁶. The discovery of Carbon-60 (C_{60} , composed of fused benzene rings), has led to the discovery of a new subclass of organic superconductors, alkali-metal doped fullerides, A_3C_{60} [ref.^{7–9}], with the transition temperature up to 38 K under applied pressure⁹. In their chemical nature, all these compounds are either cation radical salts based on TTF-derivatives or anion radical salts based on the M(dmit)₂ complexes and fullerene complexes. Their novel electronic properties are attributed to the delocalized π -electrons due to orbital overlap. Furthermore, superconductivity in graphite intercalation compounds (GICs) has been extensively studied for several decades, where T_c ranges from below 1 K for KC_8 ($T_c = 0.39$ K) up to 11.5 K for CaC_6 [ref.^{10,11}]. Graphite is an extreme of the polycyclic condensed aromatic hydrocarbon, consisting of an infinite network of benzene rings. Thus, doping of such materials with π -electron networks might bring out novel physical properties, such as superconductivity. Indeed, very recently, Mitsuhashi *et al.* reported that superconductivity with T_c of 18 K could be induced by doping potassium into picene ($C_{22}H_{14}$)¹², a hydrocarbon molecular with five benzene rings condensed in an armchair manner^{13–16}. Here we report the superconductivity with transition temperature up to 33.1 K in potassium doped hydrocarbon with seven benzene rings, 1,2:8,9-dibenzopentacene. It is reasonable to expect that, through carrier doping, higher T_c superconductivity may be realized in other PAHs, a large family of molecules based on fused benzene rings.

Results

The temperature dependence of the magnetization measured in a field of 10 Oe for $K_{3,17}$ -dibenzopentacene is given in Fig. 1. The zero-field-cooling (ZFC) and field-cooling (FC) susceptibility shows a sharp drop at around 28.2 K which also can be seen from the ac susceptibility as shown in the left inset in Fig. 1a. Such diamagnetic behavior is characteristic of superconductivity. The distinct magnetic signatures of ZFC and FC below the superconducting critical temperature originate from the screening supercurrent (ZFC regime) and the Meissner-Ochsenfeld effect of magnetic flux expulsion (FC regime). The diamagnetic signal onset temperature is described as superconductivity temperature T_c^{onset} . As seen from Fig. 1a, T_c^{onset} was defined to be 28.2 K for

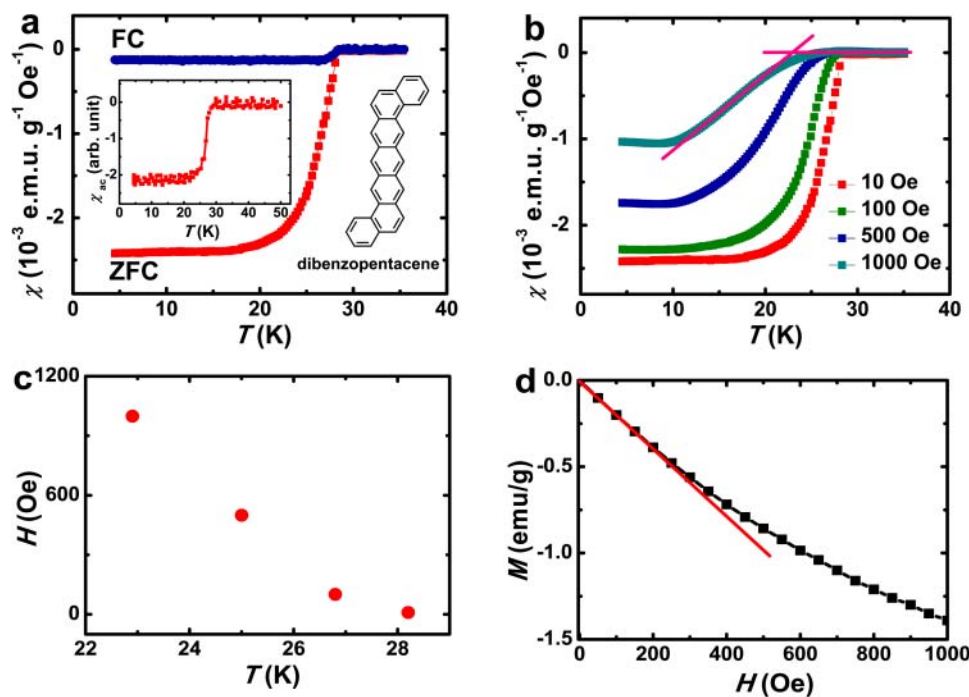


Figure 1 | Magnetization data for $K_{3,17}$ -dibenzopentacene. (a) χ versus T plots for $K_{3,17}$ -dibenzopentacene with $T_c^{\text{onset}} = 28.2$ K at $H = 10$ Oe (main panel). The left inset shows the ac susceptibility at $H = 5$ Oe, and the right inset shows the molecular structure of dibenzopentacene; unfortunately, to our knowledge, no report on the crystal structure of 1,2:8,9-dibenzopentacene has been published. (b) χ versus T plots for the sample in the ZFC measurements under different magnetic field H . The solid lines indicate the determination of the transition temperature as described in the text. (c) The H versus T_c plot. (d) Field dependence of the magnetization isotherm for the sample measured at 4.5 K. The solid line gives the linear fit to the low field $M(H)$ curve.

$K_{3,17}$ -dibenzopentacene. The shielding volume fraction at 5 K is estimated to be 5.5% (assuming a density of 1.8 g/cm³), which is comparable to the value reported for superconducting K_x picene¹², K_x phenanthrene¹⁷, and is about the same as that initially reported for K-doped C_{60} and for Rb-doped C_{60} [ref.^{8,18}], although following works have dramatically increased the superconducting fraction for alkaline-earth-metal doped phenanthrene¹⁹ and alkali-metal doped C_{60} [ref.^{20,21}]. The small superconducting fraction may be due to the smaller sizes of the obtained crystallites than the London penetration depths¹². Further investigations of the dependence of the superconducting fraction on temperature, initial composition and reaction time will undoubtedly lead to high yields of superconducting phase.

Figure 1b shows temperature dependence of measured χ for various applied fields H in the ZFC measurements. There was an obvious drop of χ at 23 K even at 1000 Oe, indicating that the superconducting phase is not completely destroyed at weak applied field. The fact that T_c is suppressed slowly by applying the magnetic fields indicates the observed superconductivity in this material is intrinsic. The corresponding upper critical field H versus T_c is plotted in Fig. 1c. T_c was determined through a linear extrapolation of the slopes before and after the point at which the sample began superconducting, as shown in Fig. 1b. At the present stage, it is difficult to determine the upper critical field $H_{c2}(0)$ at 0 K from H - T_c curve. Figure 1d depicts the $M(H)$ versus H plot at 4.5 K measured by sweeping the magnetic field at a constant rate of 10 Oe/sec, which indicates that $K_{3,17}$ -dibenzopentacene is a type-II superconductor with a strong vortex pinning. In the Meissner state, $M(H)$ curve is linear and the lower critical field H_{c1} is defined as the field in which $M(H)$ deviates from linearity. Here H_{c1} was estimated to be 200 Oe at 4.5 K, which is higher than that of the potassium doped picene with $T_c = 18$ K [ref. 12] ($H_{c1} \sim 100$ Oe; however, the authors gave the value of 380 Oe determined from the minimum position of the M - H plot).

Superconductivity with higher temperature can also be observed for high K-content sample, $K_{3,45}$ -dibenzopentacene. The onset

temperature of diamagnetism is $T_c^{\text{onset}} = 33.1$ K as seen in ZFC experiment (see Fig. 2a), where the critical temperature is the highest to date among the organic superconductors under ambient pressure. The magnitude of the shielding signal at 25 K corresponds roughly to 3.2% of perfect diamagnetism. Additional features are seen at 20 K and 5 K, which might be ascribed to different superconducting phases with lower transition temperatures. One should note that the latter two characteristic temperatures are similar to the reported values for the superconducting K_x picene and K_x phenanthrene^{12,17}. It is reasonable to suspect that these two superconducting phases come from the breakdown of PAH chains during the reaction process. Interestingly, the T_c obtained for twice annealed sample of K_3 -dibenzopentacene was 7.4 K, with superconducting shielding fraction of 3.6%, as shown in Fig. 2b. Similar phenomenon has been observed in K_x picene¹², where two superconducting phases ($T_c = 7$ or 18 K) were occasionally obtained under the same experimental conditions, but did not coexist with each other. Further efforts should be made to clarify this issue in the near future.

Discussion

1,2:8,9-dibenzopentacene is a condensed aromatic hydrocarbon with both linear and angular fusion of the benzene rings, which can be viewed as two phenanthrene segments bridged through two $-\text{CH}=\text{group}$ (see right inset of Fig. 1a). Regardless of the influence of the structural/geometric difference among picene, phenanthrene and dibenzopentacene (one should note that superconductivity with T_c up to 15 K was also observed for K-doped coronene, which is composed of six peri-fused benzene rings. It is still not clear whether the perfect W-shaped configurations of benzene rings are the key role to achieve superconductivity in doped PAHs^{13–16}, although there is no superconductivity found for petancene, the isomer of picene¹²), it can be seen that with increasing the length of PAH chain, the superconducting transition temperature increases dramatically (see Fig. 3): T_c increases from 5 K for K_x phenanthrene¹⁷ with three

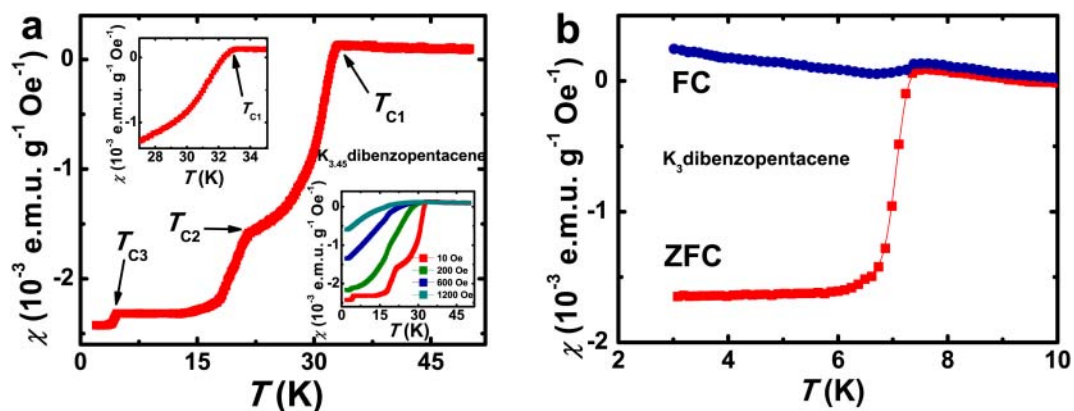


Figure 2 | Temperature dependence of magnetization for $K_{3,45}$ dibenzopentacene and K_3 dibenzopentacene. (a) χ versus T plots for superconducting $K_{3,45}$ dibenzopentacene at $H = 10$ Oe (main panel). The ZFC curve indicates the presence of three different superconducting phases. The left inset shows an expanded scale, the region around T_C , revealing a critical temperature of 33.1 K. The right inset shows χ versus T plots for the sample $K_{3,45}$ dibenzopentacene in the ZFC measurements under different magnetic field H . It clearly shows that all the three superconducting transitions are suppressed slowly by applying the magnetic fields. (b) χ versus T plots for the twice annealed K_3 dibenzopentacene sample with $T_C = 7.4$ K at $H = 10$ Oe.

benzene rings to 18 K for K_x picene¹² with five benzene rings, and up to 33.1 K for K_x dibenzopentacene with seven benzene rings, which is in contrast to the theoretical predication^{22,23}. In general, the dimensionless electron-phonon coupling constant $\lambda = N(\epsilon_F)V$ is directly related to V and $N(\epsilon_F)$. Here, the interaction matrix element V dominated by intramolecular vibrational modes is inversely proportional to the number of atoms in the molecule that donates π -electrons. Assuming a conventional Bardeen-Cooper-Schrieffer (BCS) mechanism with electron-phonon interaction, and the same density of states $N(\epsilon_F)$ at the Fermi level, the doped phenanthrene should have the highest T_C in all the aromatic hydrocarbons^{22,23}. However, in a molecular crystal, the crystal structure, molecular overlaps, and phonon modes are important factors for determining the strength of pairing interaction.

Usually, increasing the length of the PAH chain would increase the extent of its interactions with neighboring chains, while the density of states at the Fermi level, is mainly dominated by intermolecular interactions. One can speculate that an increase in $N(\epsilon_F)$ overcomes any decreases in V on going from K_3 phenanthrene to K_3 dibenzopentacene. Further studies are needed, however, to shed more light on the microscopic aspects of pairing. It is believed that

organic materials with higher superconducting transition temperature could be produced in the near future.

Methods

Samples were prepared by direct heating potassium metal with 1,2,8,9-dibenzopentacene in an evacuated tube at 300–350 °C for 7–20 days. To improve the homogeneity of products, a second anneal is sometimes performed. An alternative method for sample synthesis was also developed. The starting materials were loaded into liquid ammonia solution and stirred for 6 hours. The resulting products were then dried under vacuum for several hours to remove the solvent, and subsequently sealed in an evacuated tube and annealed at 250–300 °C for 7–20 days. The latter synthetic route allows for a reduction of annealing temperature and improvement of homogeneity of the products, but it does not allow precise control of the potassium content of the resulting samples. All the obtained powder samples are uniform dark black in color, which is totally different from the red color of pure dibenzopentacene. Superconductivity was observed for the samples with compositions of the form K_x dibenzopentacene, for $3.0 \leq x \leq 3.5$. It seems to be the fact that the superconducting shielding fraction could be improved by increasing the annealing temperature. Magnetization measurements have been performed in a commercial SQUID-VSM magnetometer (Quantum Design). For the zero-field-cooled (ZFC) magnetization measurements, the samples were first cooled down to 2.5 K in zero field, then the magnetic field was applied and the temperature raised to 50 K with 1 K/min. Thereafter, temperature was reduced to 2.5 K without changing the applied field. The field-cooled (FC) magnetization was then measured with increasing temperature. Hysteresis loop measurements were carried out at 4.5 K, after cooling in zero field from room temperature.

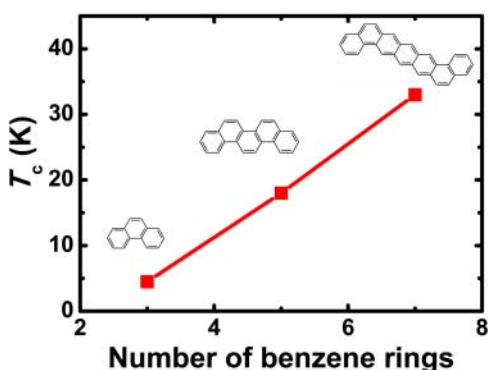


Figure 3 | Dependence of the superconducting transition temperature on the number of benzene rings. T_C increases from 5 K for K_x phenanthrene with three benzene rings to 18 K for K_x picene with five benzene rings, and up to 33.1 K for K_x dibenzopentacene with seven benzene rings, shows linear relativity to the number of benzene rings.

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Author contributions

M. Q. X. conceived the experiments, prepared the samples, carried out the magnetic susceptibility measurements and XRD measurements. Y. W., H. X. Y., X. L. D. provided assistance with the magnetic susceptibility measurements and XRD measurements. D. M. W., J. B. H. and F. W. L. provided assistance with sample synthesis. T. B. C. initiated the project. G. F. C. initiated the project, conceived and supervised the experiments, analyzed the data and wrote the paper.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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