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# Discovery of superconductivity in K-doped 2,2'-bipyridine

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# ABSTRACT

Organic compounds are always promising candidates of superconductors with high transition temperatures. The 2,2'-bipyridine solely composed by C, H, and N atoms is examined for this proposal. The presence of Meissner effect with a transition temperature of 7.2 K in this material upon potassium doping is demonstrated by the dc magnetic susceptibility measurements. The real part of the ac susceptibility exhibits the same transition temperature as that in dc magnetization, and a sharp peak appeared in the imaginary part indicates the formation of the weakly linked superconducting vortex current. The occurrence of superconductivity is further supported by the resistance drop at the transition together with its suppression by the applied magnetic fields. The superconducting phase is identified to be  $K_3$ -2,2'-bipyridine with  $P_1$  space-group from the analysis of Raman scattering spectra and X-ray diffraction patterns as well as the first-principles calculations. This work not only opens an encouraging window for finding superconductivity from conducting polymers and their derivatives.

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## 1. Introduction

Organic materials, the important and ubiquitous substance in human beings' lives, are always composed of hydrocarbons containing only carbon and hydrogen, as well as other elements, especially nitrogen. Doping with metals in organic molecular compounds has been extensively studied for a long time. It has raised a storm of the discovery of superconductors ever since the first simple carbon-based superconductor C<sub>8</sub>A (A = K, Rb, or Cs), which exhibits a superconducting transition temperature ( $T_c$ ) of 0.02–0.55 K, found in 1965 [1]. Later, in 1980, di-(tetramethyltetraselenafulvalene)-hexafluorophosphate, (TMTSF)<sub>2</sub>PF<sub>6</sub>[2], a real organic superconductor composed by C and H

atoms, was discovered to exhibit a  $T_c$  of 0.9 K at pressure of 0.65 GPa. Interestingly, the superconductivity in  $(\text{TMTSF})_2\text{PF}_6$  occurs with the suppression of the spin-density-wave instability at high pressures [3,4]. Other materials, such as the organic charge-transfer salts based on donor molecules [5–9], the edge-shared aromatic hydrocarbons [10–12], also have been observed to superconduct. In addition, it is worth mentioning that *p*-terphenyl was found to be superconducting with  $T_c$  as high as 123 K [13], far above liquid nitrogen boiling temperature, which could be comparable to the record high  $T_c$  of about 130 K in some cuprate superconductors [14]. This discovery gives rise to great interests in finding high- $T_c$  superconductors in organic materials. Meanwhile, superconducting phases with  $T_c$  of 7.2 and 43 K were also observed in the synthetics [15,16]. The finding of the hightemperature superconductivity in this system was soon confirmed from the magnetization measurements by two independent groups [17,18]. The signature of the opening of the superconducting gap at 120 K was also detected by the ARPES measurements [19]. Most importantly, the recent observation of the resistivity dropping to zero starting from 130 K provides the evidence for the superconductivity from the resistivity measurements [20]. Along this direction, superconductivity in the other *p*-oligophenyls was found accordingly [21–23]. Superconductivity in benzene, the simplest aromatic hydrocarbon or the simplest structural unit of *p*-oligophenyls was also theoretically predicted upon dopant [24] or compression [25]. The suppression of the order-disorder transition was proposed to be the driving force for the appearance of superconductivity in p-oligophenyls [26]. It has been found [27-29] that superconductivity can always take place in organic molecules once containing phenyl. *p*-Terphenyl belongs to a poly(*para*-phenylene)

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material, which has the phenyl rings connected at the *para* positions. Previous works [30,31] reported the increasing conductivity with increasing the phenyl ring numbers. Hence, exploring superconductivity in poly(*para*-phenylene), especially in the shorter polymers, is of great importance and necessity. Once superconductivity can be realized in the shortest polymer, the other polymers with longer chain length will capture tremendous potentials to be superconductors.

Biphenyl is the shortest polymer with only two phenyl rings connected by single C-C bond. It shows a relatively simple monoclinic structure, and undergoes an incommensurate triclinic transition at about 40 K [32]. A solid isologue with biphenyl, 2,2'-bipyridine (C10H8N2), also always attracts intensive interest within the community. Comparing to biphenyl, 2,2'-bipyridine has a replacement of the two ortho-CH groups with nitrogen atoms [33]. Such a typical feature makes it a good bidentate chelating ligand. 2,2'-Bipyridine is a basis material in photoelectric applications [34]. It can form many complexes with most transition metals, such as ruthenium complexes and platinum complexes. And these complexes all exhibit intense luminescence [34-37]. Otherwise, the ligand,  $[Fe(bipyridine)_3]^{2+}$ , is often used for the colorimetric analysis of iron ions. As the versatile applications, thus, once this cheap and pervasive material, which is only composed by C, H, and N atoms, becomes a superconductor, it will be a good example to demonstrate the obtaining of organic superconductors from the pool of 2,2'-bipyridine-based materials. Moreover, it will extremely expand the applications of this material in superconductivity after optoelectronics.

In the present work, we report the realization of superconductivity in potassium-doped 2,2'-bipyridine ( $K_x C_{10} H_8 N_2$ ). Combination of the magnetic susceptibility and electrical transport measurements confirms that this material shows a superconducting transition at temperature of 7.2 K. Meanwhile, the chemical formula of  $K_3 C_{10} H_8 N_2$  for the superconducting phase is determined from the analysis of the Raman scattering spectra and X-ray diffraction (XRD) patterns. With the help of the first-principles simulations, the crystal structures and electronic properties are presented. These experimental findings in such a real organic compound composed by C, H, and N atoms open a new window to discover superconductivity from optoelectronic materials.

## 2. Experimental and computational details

## 2.1. Material synthesis

High-purity K (99%) and  $C_{10}H_8N_2$  (>99%) were purchased from Sinopharm Chemical Reagent and Alfa Aesar, respectively. The K was cut into small pieces and mixed with  $C_{10}H_8N_2$  with a mole ratio of 3:1 in a glove box with the moisture and oxygen levels less than 0.1 ppm. Then the mixture was sealed in a quartz tube under high vacuum of  $1 \times 10^{-4}$  Pa and heated at temperature of  $120 - 130^{\circ}$ C for 48 - 72 hours. The resulting  $K_x C_{10}H_8N_2$  powder sample shows uniform black color compared to the pure white color of pristine  $C_{10}H_8N_2$ .

#### 2.2. Material characterization

The *dc* and *ac* magnetization measurements were performed by Magnetic Property Measurement System (Quantum Design). The sample was loaded into a non-magnetic plastic capsule and sealed by GE-Varnish, as shown below. All preparations were performed in a glove box with the moisture and oxygen levels less than 0.1 ppm before magnetization measurements. The *dc* magnetic susceptibility measurements were performed in the temperature range of 1.8 - 300K with a magnetic field of 20 Oe, and the *ac* magnetic susceptibility measurements were conducted in the temperature range of 1.8 - 20K under an applied field with amplitude and frequency of 8 Oe and 234 Hz, respectively. The resistance measurement was carried out by Physical Property Measurement System (Quantum Design). The powder sample was put into a diamond anvil cell which can generate a quasihydrostatic condition to make the contacts between the two platinum leads and the sample work well. The two leads were stuck with four copper wires by silver conductive epoxy and then connect to the PPMS for the resistivity measurements with the imposed current of about 100 μA. Cubic boron nitride (CBN) powder was used as an insulating layer to insulate the probing platinum leads with metallic gasket. Such a compression process ensured the sample to be isolated to the external condition. Meanwhile, the pristine C10H8N2 does not denature at this pressure. Therefore, we assume that the compressed K<sub>x</sub>C<sub>10</sub>H<sub>8</sub>N<sub>2</sub> still keeps its properties at ambition condition. The whole processes were performed in the glove box. The Raman scattering experiments were measured using a 660 nm laser line with the samples sealed in quartz tubes. The excited power was less than 2 mW before a ×20 objective to avoid possible damage of samples. The XRD experiments were performed in the 2-theta range of 10-70 by an X-ray diffractometer (Empyrean, PANalytical B.V.). The samples were put on specific glasses and then covered with thin films to isolate the air.

# 2.3. Theoretical calculations

To predict the structure and electronic properties of  $K_x C_{10} H_8 N_2$ , we employed the Vienna *ab* initio simulation package (VASP) [38, 39] based on the projector augmented wave method. For the plane wave basis-set expansion, an energy cutoff of 600 eV was adopted. The Monkhorst–Pack *k*-point grids were generated according to the specified *k*-point separation of 0.02 Å<sup>-1</sup> and the convergence thresholds were set as  $10^{-6}$  eV in energy and  $10^{-3}$  eV/Åin force. The generalized gradient form (GGA) of the exchange–correlation functional (Perdew– Burke–Ernzerhof 96, PBE) was adopted [40]. And considering the non-local interaction, we have added the correction of van der Waals (vdW) in version of vdW-DF2 in the calculations [41].

### 3. Results and discussion

The temperature dependence of the *dc* magnetic susceptibility ( $\chi$ ) of  $K_{r}C_{10}H_{8}N_{2}$  (labeled as sample A) with the field cooling (FC) and zerofield cooling (ZFC) runs under the magnetic field H of 20 Oe is shown in Fig. 1(a). One can clearly see a sudden drop below 7.2 K in the ZFC and FC runs. The drastic drop of  $\chi$ , which results from the well-defined Meissner effect, indicates that a superconducting transition takes place in this sample. The temperature where the sharp drop occurred is defined as the superconducting transition temperature  $T_c$ . The calculated superconducting shielding fraction is about 0.7% at temperature of 4 K. The small shielding fraction might be not only due to the grain size being smaller than the penetration depth [10], but also because it contains non-superconducting components implied by the rising of magnetic susceptibility at low temperatures. In fact, in our synthetic more-thanfifty samples, only less than 10% of them exhibit superconductivity. Among these prepared non-superconducting samples, some show a paramagnetic phase with the representative susceptibility (marked as sample B) shown in the green curve in Fig. 1(f). To clearly demonstrate the different components of sample A, in Fig. 1(f) the superconducting phase (red dotted line) is extracted with the paramagnetic phase of B as the subtracted background. Unless explicitly stated, the following results and discussion are based on sample A.

Fig. 1(b) respectively presents the temperature dependence of the real (top) and imaginary (bottom) parts of the *ac* magnetic susceptibility of  $K_x C_{10} H_8 N_2$  at 8 Oe with a frequency of 234 Hz. The real part exhibits the almost same characteristic to the *dc* magnetic susceptibility. Meanwhile, a sharp peak appears in the imaginary part. The *ac* measurement is a more powerful signature of the occurrence of superconductivity in this material. The complex susceptibility  $\chi = \chi' + i \chi''$  is a little different from the *dc* susceptibility. The real part  $\chi'$  is a presentation of Meissner currents screening of this superconductor, and it is approximately equivalent to the ZFC susceptibility in the



**Fig. 1.** Temperature dependence of the magnetic susceptibility  $\chi$  for  $K_x C_{10}H_8 N_2$ . (a) Magnetic susceptibility of  $K_x C_{10}H_8 N_2$  (labeled as sample A) measured in the ZFC and FC runs under 20 Oe. (b) Real part and imaginary part of the *ac* susceptibility as a function of temperature. The amplitude and frequency of applied field are 8 Oe and 234 Hz, respectively. (c) Temperature dependence of the *dc* magnetic susceptibility of the sample A under various magnetic fields up to 1000 Oe in the ZFC run. (d) The isothermal hysteresis loops with scanning magnetic fields up to 1000 Oe measured at various temperatures in the superconducting state. (e) Initial part of the hysteresis loops measured at various temperatures. Inset is an example used to determine the  $H_{c1}$  value. |R|, i.e. abs(R), is the slope for the first n value at 2 K,  $n \ge 3$ . (f) Magnetic susceptibility between both samples (red dashed line) displays a purely superconducting transition. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

*dc* measurement. The imaginary part  $\chi''$  corresponds to the energy absorption in this material [42–45]. It arises from the formation of the weakly linked superconducting vortex current. Thus, *ac* susceptibility can be considered as a symbol of the appearance of superconductivity in this material. Furthermore, this parameter is used as the justification for the zero resistance [42,44]. Hence, our data further demonstrates the occurrence of a superconducting phase at 7.2 K in the K<sub>x</sub>C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>.

Magnetic susceptibility of  $K_x C_{10} H_8 N_2$  as a function of temperature in the ZFC run at different magnetic fields is also obtained. The results are depicted in Fig. 1(c). The diamagnetism of  $K_x C_{10} H_8 N_2$ , which can be clearly seen in the figure, gradually decreases with increasing magnetic field. Meanwhile, the temperature span of superconducting transition becomes significant broad as the magnetic field is increased. The estimated upper critical field  $H_{c2}$  is 800 Oe, where the almost complete loss of the diamagnetic signal is observed with cooling the temperature down to 1.8 K. However, this is just a rough estimation of  $H_{c2}$  because of the possible granular superconductivity or grain size effect in magnetic measurements. The reliable upper critical field can be obtained from the resistance measurements at magnetic fields, which will be discussed later.

The field dependent isothermal magnetization M up to 1000 Oe at various temperatures is illustrated in Fig. 1(d). The symmetric hysteresis loops demonstrate that our material exhibits a strong bulk pinning, which is a fingerprint of a type-II superconductor. In addition, the slight slope of the background indicates that the sample contains magnetic impurities. These impurities should result from the part of the compound which is not superconducting. On the other hand, one can also calculate the lower critical field from the initial part of these loops.

Fig. 1(e) presents the virgin M(H) curves at low fields measured for the temperatures from 2 to 7.2 K. The superconductivity is gradually suppressed from the initial  $T_c$  of 7.2 K. In order to determine the lower critical field  $H_{c1}$ , we calculate the regression coefficient R of a linear fitting to the data points. Then the  $H_{c1}$  is obtained where the point in R(H) starts to deviate from the linear dependence. This method is enough credible which has been examined in the previous studies [45,46]. The procedure used to determine  $H_{c1}$  for T = 2 K is shown in the inset of Fig. 1(e). Results for deduced  $H_{c1}$  are shown in Fig. 2(b), depicted by yellow points. Then we use the empirical law  $H_{c1}(T)/H_{c1}(0) = 1 - (T/T_c)^2$  to fit the lower critical field at



**Fig. 2.** (a) Temperature dependence of the resistance of  $K_x C_{10} H_8 N_2$  from 3 K to 300 K. Inset is the magneto resistance measurements under different magnetic fields. (b) The temperature dependence of the lower critical field  $H_{c1}(T)$  and upper critical field  $H_{c2}(T)$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 3. Raman scattering spectra of pristine (a), K-doped 2,2'-bipyridine (b), and biphenyl (c) at room temperature. The sticks in the upper horizontal axis give the peak positions of the vibrational modes in pristine materials.

zero-temperature  $H_{c1}(0)$ , the calculated  $H_{c1}(0)$  is 211 ± 30 Oe. The fitted results are illustrated in Fig. 2(b) with a red line, and the superconducting area is covered with violet shade.

Zero-field resistance of K<sub>x</sub>C<sub>10</sub>H<sub>8</sub>N<sub>2</sub> between 3 K to 300 K is shown in Fig. 2(a). As the very low shielding fraction of this material, the resistance measurements are very hard to be duplicated. The feature of the resistance at normal state is obviously a metallic behavior. However, due to the high content of potassium, the metallic feature also possibly comes from the redundant potassium. But the resistance in the whole temperature range is much higher than pure potassium which owns a fantastic conductivity. Thus, we assume that the resistance exhibited here has the major contribution from  $K_x C_{10} H_8 N_2$ . When enlarging the figure, one can see that the resistance exhibits a drastic drop at around 7.2 K. This phenomenon indicates a clear superconducting transition. The temperature of 7.2 K is excellently consistent with the results of both the dc and ac magnetic susceptibility measurements. As for the extremely subtle decrease of amplitude, in addition to the existence of non-superconducting component in the sample from the above magnetic analysis, the main reason is that the contact resistance has not been eliminated because the resistance is actually measured by the twoelectrode method. Due to practical difficulties such as easy oxidation of samples and poor superconducting reproducibility, better electrical transport data have not been obtained yet. The inset of Fig. 2(a) shows the resistance as a function of temperature in the dc magnetic fields

up to 3250 Oe. Due to the damage of the sample, we cannot get the magneto resistance at higher fields. From this inset one can clearly see that the superconducting transition exhibits a pronounced broadening at high fields. And the sample remains the superconductivity at 3250 Oe. The upper critical field  $H_{c2}$  is defined by using the onset  $T_c$ criteria, which is determined by the first dropped point deviated from the linear resistance curve. The results are shown in Fig. 2(b) by a blue line. We then fit the  $H_{c2}(T)$  by Werthamer–Helfand–Hohenberg phenomenological formula [47]  $H_{c2}(0) = 0.69 \times T_c \times |dH_{c2}/dT|_{T=T_c}$ , yielding the  $H_{c2}$  at zero-temperature  $H_{c2}(0) = 5731 \pm 600$  Oe. The fitted results are plotted in Fig. 2(b), and the superconducting area is covered with blue shade. Combining with  $H_{c1}(0)$ , we evaluate the London penetration depth  $\lambda_L$  and Ginzburg–Landau coherence length  $\xi_{GL}$  by using the expressions [48]  $H_{c2}(0) = \Phi_0/2\pi\xi_{GL}^2$  and  $H_{c1}(0) = (\Phi_0/4\pi\lambda_L^2)\ln(\lambda_L/\xi_{GL})$ . Here,  $\Phi_0 = h/e^* = 2.07 \times 10^{-7}$  Oe cm<sup>2</sup> is the magnetic-flux quantum. We obtained the resulting  $\lambda_L = 26 \pm 1$  nm and  $\xi_{GL} = 24 \pm 1$  nm. Thus, the Ginzburg–Landau parameter  $\kappa = \lambda_L / \xi_{GL} =$  $1.09 > 1/\sqrt{2}$  is determined for this superconductor. This result indicates that the superconductor  $K_x C_{10} H_8 N_2$  is a type-II superconductor with a transition temperature of 7.2 K.

Raman spectroscopy is a powerful tool to detect the molecular dynamics process in the organic materials. A lot of previous works [49–54] focused on the structure transition of organic materials by Raman scattering measurements. Here, we present the Raman spectra of the

 $C_{10}H_8N_2$ ,  $K_xC_{10}H_8N_2$ , and biphenyl. The introduction of biphenyl, which shares the same crystal structure with  $C_{10}H_8N_2$  and *p*-terphenyl, is to compare the vibrational modes with  $C_{10}H_8N_2$ . The Raman spectra of  $C_{10}H_8N_2$  are significantly different from those of biphenyl even though they own the same monoclinic system. The distinctions should arise from the replacement of the *N* atoms.

The clear distinction between  $C_{10}H_8N_2[55-57]$  and biphenyl [58] can be judged by the vibrational modes from 1200 to 1600 cm<sup>-1</sup> with strong intensities [Figs. 3(a) and 3(c)], especially for the additional peaks located around 1300, 1450, and 1485 cm<sup>-1</sup>. Modes with frequencies located at those ranges in alkali doped poly-*para*-phenylene are often regarded as the polarons or bipolarons [59]. And these two elementary excitations play important roles in the conductivity of these materials. They also receive great attentions because of the assumption in the new high- $T_c$  superconductors by several investigators [60–62]. Comparing the  $C_{10}H_8N_2$  and  $K_xC_{10}H_8N_2$ , several features can be drawn as follows:

- The lattice vibrational modes absolutely disappear and instead they merge to a broad hill.
- The ring breathing mode at around 1000 cm<sup>-1</sup> and the in-plane ring deforming modes at around 1600 cm<sup>-1</sup> exhibit red-shift after doping.
- The C-H bending and ring deforming modes at about 1200 cm<sup>-1</sup> to 1500 cm<sup>-1</sup> have the energy increases after doping.
- The C-H stretching bands at high frequency almost disappear after doping.

The doped K in  $C_{10}H_8N_2$  will have a significant impact on the superconducting properties. It can elongate the intralayer C–C bond length because of the intercalation of K atoms in  $C_{10}H_8N_2$ . On the other hand, K, as an electron donator, will transfer a certain amount of charges to  $C_{10}H_8N_2$ , and the number of the charges can be detected from the Raman scattering spectra [49–54]. In  $C_{10}H_8N_2$ , the modes at around 1600 cm<sup>-1</sup> are closely related to the C–C stretching. Thus, it can be chosen to calculate the amount of the charge transfer. From Figs. 3(a) and 3(b), we can see that the peak with lower frequency almost keeps its energy after doping, whereas the higher frequency exhibits 21 cm<sup>-1</sup> downshift from 1592 cm<sup>-1</sup> to 1571 cm<sup>-1</sup>. From previous works [54], each electron contributes about 7 cm<sup>-1</sup> redshift to the Raman mode. Thus, there should be three electrons transferred to  $C_{10}H_8N_2$  from K atoms. Therefore, the superconducting phase in the synthetic material is  $K_3C_{10}H_8N_2$ .

The XRD is also an effective tool to identify the fine crystal structure of the doped material. Fig. 4 shows the XRD patterns of pristine and K-doped  $C_{10}H_8N_2$ , with the comparison between experiments and the first-principles simulations. For the pristine C10H8N2 with the spacegroup  $P2_1/c$ , the crystal structure was built and optimized based on the first-principles calculations. The crystal lattice parameters are a = 5.657Å, b = 6.208 Å, c = 12.487 Å, and  $\beta = 110.87^\circ$ , respectively, which are close to experimental ones. The average error is less than 1%. As shown in Fig. 4, with the help of the optimized structure, the simulated XRD patterns are comparable with the experiments for several main peaks. The difference between simulation and experimental results is mainly due to the possible defects or some impurities in the experimental samples. In addition, the error of lattice constants between optimized and experimental ones also leads to the difference of some peaks. Within the similar procedure, we also searched for crystal structures of KxC10H8N2 and compared the simulated XRD patterns with the experiments. We found that the obtained XRD for  $K_3C_{10}H_8N_2$  with the  $P2_1$  space-group can fit the experimental data well (Fig. 4). The doping of three K atoms for per bipyridine molecule conforms the inference from Raman spectra above. As shown in Fig. 5, the formation energy of K-doped 2,2'-bipyridine depending on  $\mu_K - \mu_K(bulk)$  also exhibits the good stability of  $K_3C_{10}H_8N_2$  at K-rich condition, where  $\mu_K$  is the chemical potential of potassium, and  $\mu_K(bulk)$  can be obtained from the



Fig. 4. Comparison of XRD patterns of the pristine and doped  $C_{10}H_8N_2$  between experiments and theoretical simulations. All XRD data were collected by using the incident wavelength of  $\lambda=1.5406$  Å.



**Fig. 5.** The thermodynamic stability of  $K_x C_{10} H_8 N_2$  with formation energy versus  $\mu_K - \mu_K(bulk)$ .  $\mu_K = \mu_K(bulk)$  means that the element is so rich that the pure element phase can form. A negative of formation energy of  $K_x C_{10} H_8 N_2$  means that the doped system is stable in thermodynamics whereas the positive case is unstable.

energy per K atom in the K metal. So we predicted the superconducting phase for K-doped 2,2'-bipyridine as  $K_3C_{10}H_8N_2$ .

However, the K doping into 2,2'-bipyridine degrades the symmetry from  $P2_1/c$  to  $P2_1$ . The lattice parameters of  $P2_1$  K<sub>3</sub>C<sub>10</sub>H<sub>8</sub>N<sub>2</sub> are a = 7.468 Å, b = 7.686 Å, c = 13.681 Å, and  $\beta = 100.5^{\circ}$ , respectively. The crystal structure is exhibited in Fig. 6(a). There are two 2,2'-bipyridine molecules in unit cell. Especially, a typical twodimensional characteristic is observed in Fig. 6(a), forming the coplanar of bipyridine and potassium. The two-dimensional layer feature induced by K doping was also observed in other hydrocarbons, such as



**Fig. 6.** (a) Predicted crystal structure of  $K_3C_{10}H_8N_2$ . Brown, gray, pink, and purple balls represent C, N, H, and K atoms, respectively. (b) Calculated 3D plots of different charge density for  $K_3C_{10}H_8N_2$  with the isosurface unit of  $5 \times 10^{-3}$  e/a.u.<sup>3</sup>. The yellow and light blue areas represent the increase and the decrease of electrons in this region, respectively. (c) Band structures along highly symmetrical *k*-point paths shown in (d) and projected density of states on atomic orbitals of  $K_3C_{10}H_8N_2$ . (d) The first Brillouin zone (FBZ) and the calculated Fermi surfaces (FS) corresponding to band #1 and #2 shown in (c) as well as the total FS, respectively.

benzene [24], biphenyl [21], *p*-terphenyl [63,64], *p*-quaterphenyl [22], and *p*-quinquephenyl [23].

The different charge density  $\Delta \rho \left[ \Delta \rho = \rho (K_3 C_{10} H_8 N_2) - \rho (C_{10} H_8 N_2) \right]$  $\rho(K_3)$ ] can display the distribution of transferred charges. As shown in Fig. 6(b), the calculated different charge density indicates that the charges are transferred to C and N atoms from K atoms. The amount of the transferred charges can be obtained by calculating bader charge [65-68], and it is about 0.85e per K atom. And N atoms obtain the more electrons than C atoms. The charge transfer results in a transition from insulator to metal. So K<sub>3</sub>C<sub>10</sub>H<sub>8</sub>N<sub>2</sub> exhibits the metallic feature. Based on GGA functional, the band structure of  $K_3C_{10}H_8N_2$  has been calculated. Fig. 6(c) presents the band structures of  $K_3C_{10}H_8N_2$  along highly symmetrical k-point paths of Z(0,0,0.5) –  $\Gamma(0,0,0) - Y(0,0.5,0) - A(-0.5,0.5,0) - B(-0.5,0,0) - D(-0.5,0,0.5) -$ E(-0.5, 0.5, 0.5) - C(0, 0.5, 0.5) in the first Brillouin zone (FBZ). Two bands (band #1 and #2) cross the Fermi level, which is similar to most aromatic superconductors [24]. The Fermi surfaces (FS) corresponding to band #1 and #2 are shown in Fig. 6(d). From the projected density of states (PDOS) on atomic orbitals shown in Fig. 6(c), C-2p and N-2p mainly contribute to the energy bands near the Fermi level. The total electronic density of states is 7.56 states/eV/f.u., which is comparable with those values of the system being at low- $T_c$  phase [24]. Referring to the previous work [24],  $K_3C_{10}H_8N_2$  has the superconductivity with  $T_c$  near 7 K, which is consistent with the

predicted theoretical trend. Similar superconductivity with the low  $T_c$  was also observed in K-doped *p*-terphenyl [15], biphenyl [21], *p*-quaterphenyl [22], *p*-quinquephenyl [23], triphenylbismuth [27], tri-*p*-tolylbismuthine [28], and tri-*o*-tolylbismuthine [29], as well as in Na/K co-doped 2,2'-bipyridine [69]. Although the  $T_c$  of K-doped 2,2'-bipyridine is relatively low, the discovery of superconductivity in pyridine family is very meaningful, which expands the applications of 2,2'-bipyridine and gives more understanding of superconductivity in hydrocarbon superconductors.

The obtained crystal structure for K-doped 2,2'-bipyridine should be shared by the same compound upon doping Na/K alloy, which was reported to exhibit superconductivity at around 7 K [69]. The almost same  $T_c$  for these bipyridine and biphenyl [21] superconductors indicates the essential role of the phenyl ring and the necessity of the connected C-C bond for bearing superconductivity. However, the substitution of C by N in the phenyl ring is obviously helpful for obtaining large superconducting shielding volume because of the dual charge transfer to both C and N. Therefore, the resistance drop in the superconducting state presented here for K-doped 2,2'-bipyridine and even the zero-resistance effect in Na/K-doped 2,2'-bipyridine [69] can be observed, while the resistance for K-doped biphenyl [21] has not been detected yet. Thus, the phenyl ring is considered as the essential unit for creating superconductivity in such organic compounds [70]. The single C-C bond, which connects the phenyl rings, is the necessary unit for accepting charge carriers. These are probably the two key characteristics for superconductivity in phenyl molecules [13,15-23, 27-29,69].

### 4. Conclusions

Superconductivity with the transition temperature of 7.2 K has been found in  $K_x C_{10} H_8 N_2$ . The Meissner effect has been confirmed from the sudden drop in the *dc* magnetic susceptibility at the magnetic field cooling and zero-field cooling runs as well as the real part of the *ac* magnetic susceptibility. Meanwhile, a sharp peak in the imaginary part of the *ac* magnetic susceptibility has been detected, which indicates the existence of bulk superconductivity. This has been further supported by the drastic drop of the temperature-dependent resistance and its gradual suppression by the applied magnetic fields. A phase diagram for the upper critical field and lower critical field as a function of  $T_c$ for this new superconductor has been established. The obtained superconducting properties such as Ginzburg–Landau parameter of  $\kappa = 1.09$ classify it as a type-II superconductor. Its superconducting phase in the formula of  $K_3C_{10}H_8N_2$  has been identified from Raman spectroscopy and XRD with the comparison of the first-principles calculations.

The discovery of the superconductivity in  $K_3C_{10}H_8N_2$  is an interesting and significant achievement in the organic materials. It opens a new door for finding superconductivity in organic materials composed by C, H, and N atoms. Moreover, 2,2'-bipyridine is a basis material in photoelectric applications. This discovery extremely expands the applications of such organic materials in the superconducting field. In addition, 2,2'-bipyridine is the shortest polymer in pyridine family, the superconductivity of  $K_3C_{10}H_8N_2$  offers a potential avenue to find superconductors in the long polymers and their derivatives.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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