

Magnetization of potassium-doped *p*-terphenyl and *p*-quaterphenyl by high-pressure synthesis

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By using the high pressure synthesis method, we fabricated the potassium-doped para-terphenyl. The temperature dependence of magnetization measured in both zero-field-cooled and field-cooled processes shows step-like transitions at about 125 K. This confirms an earlier report about the possible superconductivity-like transition in the same system. However, the magnetization hysteresis loop exhibits a weak ferromagnetic background. The estimate on the diamagnetization of this step shows that the diamagnetic volume is only about 0.04% at low temperatures, if we assume that the penetration depth is much smaller than the size of possible superconducting grains. This magnetization transition does not shift with magnetic field, but is suppressed and becomes almost invisible above 1.0 T. The resistivity measurements fail because of an extremely large resistance. By using the same method, we also fabricated the potassium-doped para-quaterphenyl. A similar step-like transition at about 125 K was also observed by using a magnetization measurement. Since there is an unknown positive background and the diamagnetic volume is too small, it is insufficient to conclude that this step is derived from superconductivity although it appears so.

DOI: [10.1103/PhysRevB.96.224501](https://doi.org/10.1103/PhysRevB.96.224501)**I. INTRODUCTION**

Organic superconductors have been extensively studied for the theoretically predicated high temperature superconductivity and exotic superconducting pairing mechanism. Usually, the organic superconductors are accompanied by low-dimensional structures, rich magnetic phase transitions, and novel ground states [1,2]. Moreover, the bandwidth of most organic superconductors is supposed to be very narrow, which inevitably leads to the strong correlation effect. In general, there are mainly two kinds of organic superconductors: organic salts such as (TMTSF)₂X, (BEDT-TTF)₂X and metal intercalated, or doped organic materials [3]. Here TMTSF means tetramethyltetraselenafulvalene (C₁₀H₁₂Se₁₄) and BEDT-TTF means *bis*(ethylenedithio)tetrathiafulvalene (C₁₀H₈S₈). In quasi-one-dimensional (TMTSF)₂X (X stands for the electron acceptor molecule), superconductivity emerges at 0.9 K under 12 kbar in the form of (TMTSF)₂PF₆, which is regarded as the first discovery of superconductivity in organic materials [4]. By replacing PF₆ with TaF₆, SbF₆, ReO₄, and so on, a series of superconductors were found [5]. Among them, the highest *T_c* at ambient pressure was found to be 1.4 K when PF₆ was replaced by ClO₄ [6]. In the quasi-two-dimensional salts (BEDT-TTF)₂X, the highest superconducting *T_c* can rise up to 14.2 K in the form of β'-(BEDT-TTF)₂ICl₂ [7]. In this system, antiferromagnetism, charge density wave, Mott insulator state and superconductivity can emerge by adjusting pressure and temperature [8]. In the area of metal intercalated organic materials, graphite intercalation compounds show superconductivity below 20 K, such as KC₈ and CaC₆ [9,10]. In the alkali-metal-doped fullerenes, the highest *T_c* can reach 40 K [11,12], which is accompanied by some characteristics of strong correlation effect, such as metal-insulating transition and antiferromagnetic spin fluctuations, and so on [13,14].

Recently, superconductors of alkali-metal-doped aromatic compounds attracted great attention as a new organic superconducting system. In 2010, superconductivity with *T_c* = 18 K was discovered in K_{3.3}picene [15], since then several new superconductors have been found, such as K₃phenanthrene with *T_c* of about 5 K [16], K-doped 1,2:8,9-dibenzopentacene with the claim of highest *T_c* of about 33 K [17]. Very recently, it was reported that high temperature superconductivity with *T_c* above 120 K might exist in potassium-doped *p*-terphenyl [18]. A superconducting-gap-like feature was then observed in the potassium-doped single crystal of *p*-terphenyl by measurements of angle-resolved photoemission spectroscopy (ARPES) [19]. This gapped feature gradually disappears with increasing temperature. The gapped feature was also observed in the potassium-doped monolayer film of *p*-terphenyl [20], however, the authors find that the gapped feature does not change with magnetic field up to 11 Tesla, suggesting a nonsuperconductive origin of this gap. In the original paper that reported the possible superconductivity, the magnetic shielding volume fraction estimated from the step-like magnetization is quite small and no resistivity data were reported [18]. As far as we know, no second group reported the observation of the phenomenon. To confirm the observation in this system, we fabricated the potassium-doped *p*-terphenyl under both ambient pressure and high pressure (2 GPa). For the samples synthesized under ambient pressure, we have not observed the step-like transitions of magnetization around 120 K. However, for high pressure synthesized samples, we can easily reproduce this step-like transition. Surprisingly, on the potassium-doped *p*-quaterphenyl we also observed this step-like magnetic transition at about 125 K. In this paper, we report the synthesis and magnetization measurements of these samples.

II. EXPERIMENTAL DETAILS

For high pressure synthesis we made the precursor sample first. Potassium metal was cut into pieces and mixed with *p*-terphenyl or *p*-quaterphenyl in a molar ratio 3:1 in the

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glove box filled with argon (both O_2 and H_2O are less than 0.1 ppm). The mixture was then put into an Al_2O_3 crucible and sealed in a quartz tube under a high vacuum. The quartz tubes were heated up to 523 K for p -terphenyl, and 623 K for p -quaterphenyl, respectively. We kept sintering the samples at these two temperatures for three days and obtained the ambient pressure synthesized samples. Unfortunately, we did not see the diamagnetic transition near 125 K on the samples made under ambient pressure. To improve the quality and compactness of the samples, we further synthesize samples under high pressure. For high pressure synthesis, the precursor made under ambient pressure was pressed into a pellet of 4 mm in diameter and 7 mm of length. The pellet was placed into a BN capsule, surrounded by a graphite sleeve resistance heater and pressure transmitting MgO rods. Afterwards, the assemblies were submitted to a pressure of 2 GPa at room temperature. Subsequently, they were heated up to 523 K for p -terphenyl, and 623 K for p -quaterphenyl, respectively. The temperatures were kept for 10 hours under 2 GPa, before being quenched to room temperature. Finally, we released the pressure. The final high pressure synthesized products are black and sensitive to air. The magnetization results were measured by a Quantum Design instrument superconducting quantum interference vibrating sample magnetometer (SQUID-VSM) with magnetic field up to 7 T. The x-ray diffraction (XRD) measurements were performed on a Bruker D8 Advanced diffractometer with the $CuK\alpha_1$ radiation at room temperature. All magnetization data reported in this paper are coming from the high pressure synthesized samples.

III. RESULTS AND DISCUSSION

Figure 1 shows the background deducted x-ray diffraction (XRD) patterns of the pure p -terphenyl, and the potassium-doped p -terphenyl synthesized under ambient and high pressure. Since potassium-doped p -terphenyl is unstable in air, the protection against air is done by covering the sample with a Kapton foil, which shows a broad hump around $2\theta \approx 20^\circ$ for the XRD data. To make the XRD curves more clear and accurate, we removed this broad hump as the background for all samples. Figure 1(a) shows the x-ray diffraction pattern for the raw material of pure p -terphenyl, which crystallizes in the space group of $P21/c$ with lattice parameters $a = 8.08 \text{ \AA}$, $b = 5.61 \text{ \AA}$, $c = 13.59 \text{ \AA}$, and $\beta = 91.55^\circ$ being consistent with previous results [21]. The inset of Fig. 1(a) illustrates the molecule structure of p -terphenyl, which consists of three benzene rings connected by the C-C bond in para position. Figure 1(b) shows the x-ray diffraction pattern for potassium-doped p -terphenyl synthesized under ambient pressure, which can be indexed well with the lattice parameters: $a = 14.24 \text{ \AA}$, $b = 3.44 \text{ \AA}$, $c = 11.17 \text{ \AA}$, and $\beta = 94.63^\circ$ with the space group of $P2/m$. The phase looks quite pure but does not show diamagnetic transition near 125 K. Figure 1(c) displays the XRD pattern of high pressure synthesized potassium-doped p -terphenyl, which can be indexed well with the lattice parameters $a = 12.97 \text{ \AA}$, $b = 16.26 \text{ \AA}$, $c = 3.71 \text{ \AA}$, and $\beta = 94.73^\circ$ with the space group of $P2/m$. As we can see, the XRD changes quite a lot after the high pressure and high temperature treatment. The space group and lattice constants are determined by the FULLPROF program with a self-consistent

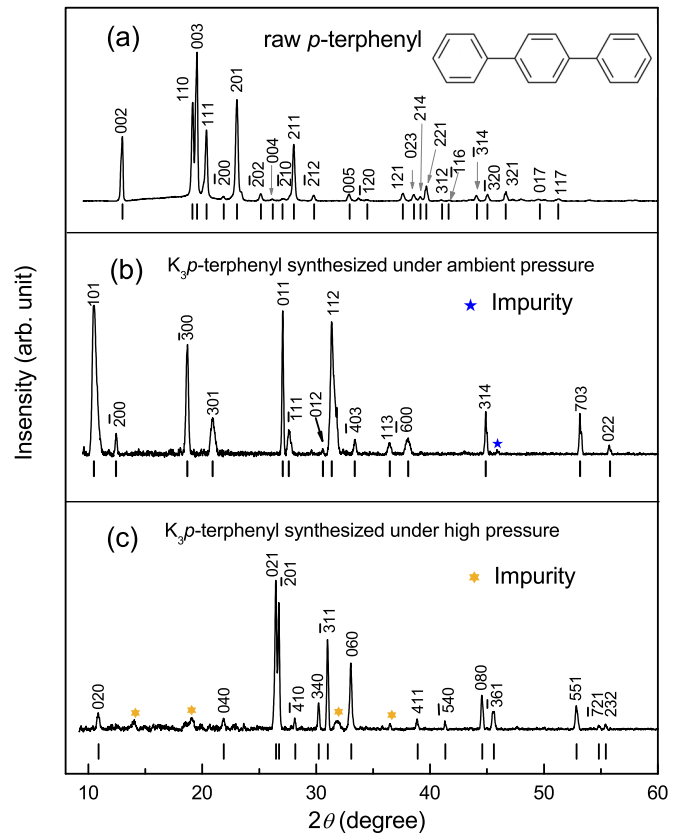


FIG. 1. (a) Powder x-ray diffraction pattern for the raw material of p -terphenyl. (b) Powder x-ray diffraction pattern for K_3p -terphenyl synthesized under ambient pressure. (c) Powder x-ray diffraction pattern for the high pressure synthesized sample K_3p -terphenyl.

fitting to the peak positions [22]. We must emphasize that, although we can figure out the possible space group of the materials, the exact structure is still difficult to resolve.

In Fig. 2, we present the temperature dependence of magnetic susceptibility measured in zero-field-cooled (ZFC) and field-cooled (FC) modes for the high pressure synthesized K_3p -terphenyl under 50 Oe and high pressure synthesized K_3p -quaterphenyl under 20 Oe, respectively. Step-like transitions can be clearly seen near 125 K in the magnetic measurements for both compounds, which confirms earlier reports about the possible superconductivity-like transition in K_3p -terphenyl [18]. However, below the temperature of the step-like transition, our data of magnetic susceptibility is positive and exhibits a strong upturn at low temperatures. To compare the shielding fraction with previous work, $\Delta\chi$ has been determined as the difference between the zero-field-cooled data and the extrapolated line of the normal state, and it is about $1.36 \times 10^{-5} \text{ emu g}^{-1} \text{ Oe}^{-1}$ at 4 K. The estimated diamagnetic signal is much larger than the previously reported value under the same magnetic field [18]. Supposing a density of about 2.5 g/cm^3 for the material, we have $4\pi\Delta\chi \approx -0.04\%$. As shown in Fig. 2(b), a similar behavior of magnetization has been observed in K_3p -quaterphenyl under 20 Oe, which possibly indicates the same origin for the transition in this compound. The upper right insets of both figures show the schematic molecular structure of potassium-doped p -terphenyl and

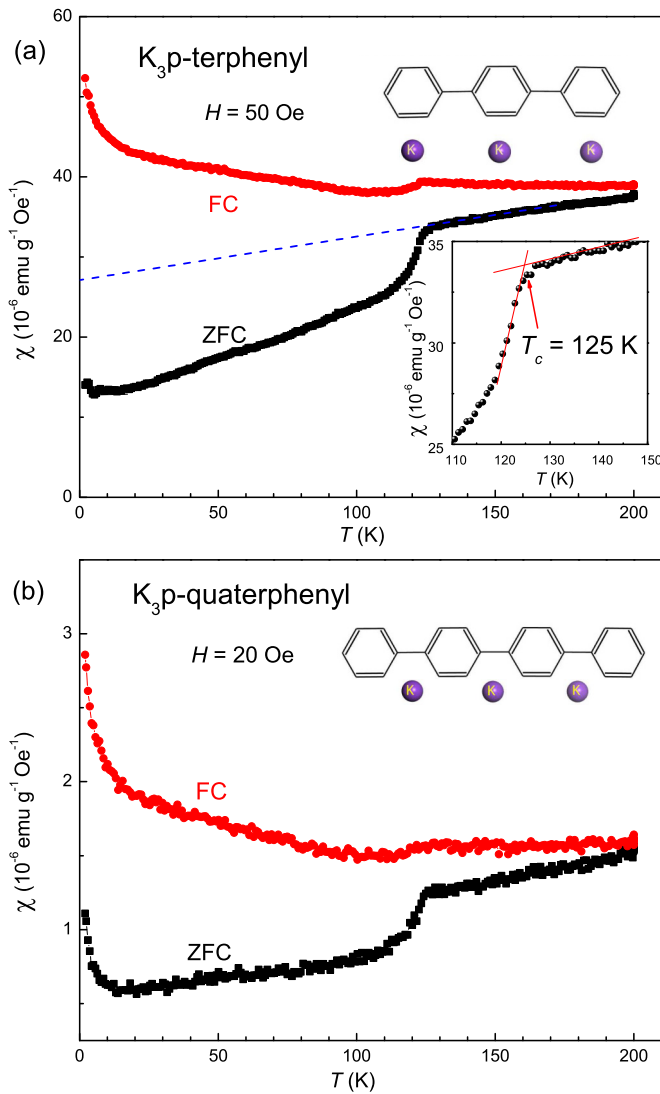


FIG. 2. Temperature dependence of magnetic susceptibility measured in both ZFC and FC modes for high pressure synthesized (a) K_3p -terphenyl (measured at 50 Oe) and (b) K_3p -quaterphenyl (measured at 20 Oe), respectively. Upper right insets in (a) and (b) present the schematic molecular structure of potassium-doped *p*-terphenyl and *p*-quaterphenyl. The bottom-right inset of (a) shows the enlarged view of magnetic susceptibility for the high pressure synthesized K_3p -terphenyl near the transition temperature. The dashed line in (a) gives an extrapolation of the magnetization above the transition temperature down to low temperatures.

p-quaterphenyl, although the real structures of the molecular crystals are still unknown. In the inset of Fig. 2(a), an enlarged view of magnetic susceptibility for K_3p -terphenyl near the step transition temperature is shown, which clearly presents the transition at about 125 K. We need to emphasize that this magnetic transition is also seen by measuring the sample with the DC mode of our magnetometer, which is the same as that in the original report. This indicates that the appearance of this step-like transition is not due to any artifact of different measuring manner.

The magnetization hysteresis loops (MHLs) of K_3p -terphenyl up to ± 4000 Oe from 60 to 150 K are shown in

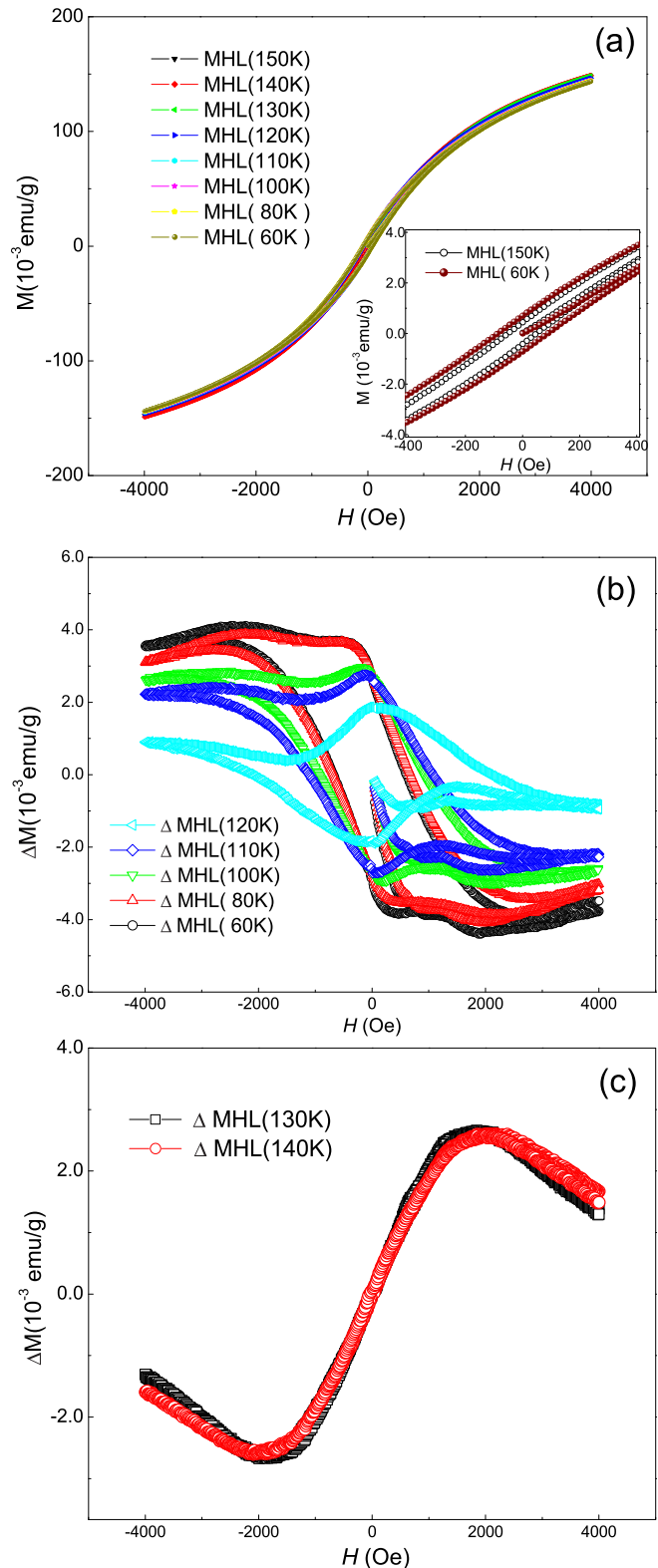


FIG. 3. (a) The magnetization hysteresis loops (MHLs) of high pressure synthesized K_3p -terphenyl from 60 to 150 K. Inset shows the enlarged view of the MHLs at 60 and 150 K. (b) Subtracted magnetization hysteresis loops measured from 60 to 120 K, where the magnetization $M(H)$ at 150 K is used as the reference: $\Delta M = M(H, T) - M(H, 150 K)$. (c) Subtracted magnetization hysteresis loops at 130 and 140 K, where the magnetization $M(H)$ at 150 K is also used as the reference.

Fig. 3(a). The inset of Fig. 3(a) presents the enlarged view of the MHLs at 60 and 150 K, respectively. Starting from the very beginning of the measurement, there is a positive curvature on the magnetization versus H curve at 60 K, which looks like a Meissner shielding effect on top of a background. Looking at the MHLs measured at 60 and 150 K, one can see that this ferromagnetic hysteresis persists above T_c , thus the diamagnetic step-like transition on the $M(T)$ curve at around 125 K has no relationship with the ferromagnetic hysteresis. This weak ferromagnetic signal may be induced by some impurities, or it is the intrinsic feature of the system. Figure 3(b) displays the difference of magnetization hysteresis loops below 125 K and that at 150 K, the latter is taken as the subtracted background, i.e., $\Delta M = M(H, T) - M(H, 150 \text{ K})$. The subtraction is done at the same magnetic field in the field sweeping process from zero to +4000 Oe, to -4000 Oe and to 4000 Oe again. After this subtraction, the Meissner effect-like shielding behaviors can be observed at low magnetic fields. These shielding behaviors can be suppressed with increasing temperature. Interestingly, the hysteresis behaviors in the ΔM versus H curves disappear at temperatures above 125 K, as shown in Fig. 3(c). This observation suggests that these diamagnetic signals of ΔM versus H curves below T_c are likely contributed by Meissner state. This is consistent with the step-like transition on the $M(T)$ curve. The hard visibility of magnetic shielding of Meissner effect on the raw data of MHLs at low temperatures may be due to the small shielding fraction compared to the weak ferromagnetic signal which appears above T_c . As we have already estimated that the maximum diamagnetic signal at 4 K for K_3p -terphenyl is only about 0.04%. This fraction is so small, comparing to the diamagnetic volume in other alkali-metal-doped aromatic hydrocarbons, which is 1.2% for K_3 picene [15], and 5.3% for K_3 phenanthrene [16]. In these two cases the shielding signal of the Meissner effect can be clearly observed both from $M(T)$ curves and MHLs.

In Fig. 4, we present the temperature dependence of magnetic susceptibilities measured in ZFC and FC modes for high pressure synthesized K_3p -terphenyl under different external fields. Since our samples absorb oxygen easily, a small hump-like feature at about 50 K always exists, which may be caused by the antiferromagnetic transition of frozen oxygen. As this anomaly is irrelevant with the physics here, we fitted the anomaly by a Gaussian function and subtract it from the experimental data. Taking the magnetic susceptibility measured under 1000 Oe in ZFC mode as an example, as shown in Figs. 4(c) and 4(d), we subtract the anomaly caused by frozen oxygen. As shown in Fig. 4(a), the magnetic susceptibility shows the step-like transition clearly near 125 K at low magnetic fields. The step-like transition is suppressed gradually with increasing magnetic field, and finally disappears above 1.0 T. However, the transition temperature remains almost unchanged. This is consistent with the previous report [18]. One possibility is that the magnetic field is insufficient to break the Cooper pairs, but suppresses the Josephson coupling or the phase coherence among the possible superconducting grains. To illustrate the transition more clearly, we show the temperature dependence of the normalized magnetic susceptibilities in ZFC mode from 90 to 150 K in Fig. 4(b). The normalization is

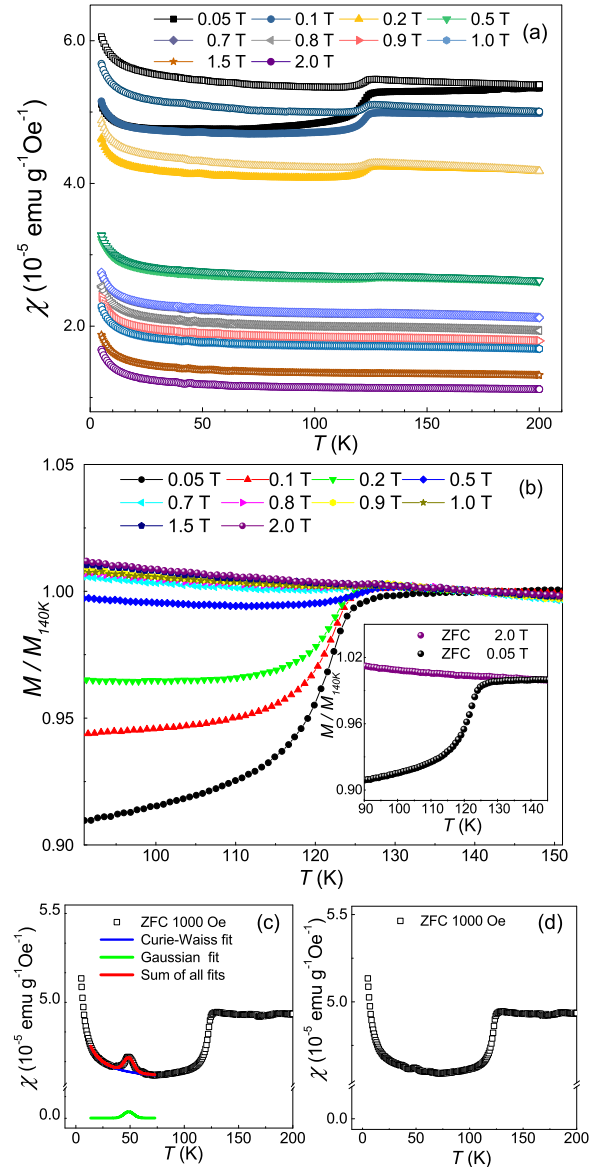


FIG. 4. (a) Temperature dependence of magnetic susceptibility measured in both ZFC (solid points) and FC (hollow points) modes for high pressure synthesized K_3p -terphenyl under different magnetic fields. (b) Temperature dependence of magnetic susceptibility divided by their own values at 140 K in ZFC mode. The inset shows the enlarged view of normalized magnetic susceptibility under 0.05 and 2.0 T near the phase transition temperature. (c) The fittings of the small hump near 50 K in the raw data of temperature dependence of magnetic susceptibility measured under 1000 Oe in the ZFC mode. (d) The hump deducted magnetic susceptibility measured under 1000 Oe in the ZFC mode.

done by dividing the magnetic susceptibilities with their own data at 140 K. As one can see, below 1.0 T, the magnetic field suppresses the transition step in a way of “filling up” gradually, while the transition temperature is almost unchanged. Above 1.0 T, the step-like transition disappears completely. The inset of Fig. 4(b) shows the normalized magnetic susceptibilities under 0.05 and 2.0 T. No step-like transition can be observed at 2.0 T. This “filling up” manner can be understood in a picture

of Josephson coupling between the superconducting grains, if the step-like transition is really induced by superconductivity.

We must emphasize that, the step-like transition of magnetic susceptibility at about 125 K and related analysis suggests that it is consistent with the picture of possible superconductivity. However, since there is a positive background of magnetic susceptibility and the magnitude of the step-like transition is still very weak, it is insufficient to conclude that the step is definitely derived from superconductivity. We also tried to measure resistivity but failed due to very large resistance. It requires more time and effort to prove that the phenomenon arises from superconductivity.

IV. CONCLUSION

In summary, we fabricated potassium-doped p -terphenyl and p -quaterphenyl by the high pressure method. The magnetic susceptibilities show the step-like transitions near 125 K for both compounds, which confirms earlier reports about the possible superconductivity-like transition in potassium-doped p -terphenyl. With increasing external magnetic field, the step

is suppressed gradually. Above 1.0 T, the transition is completely smeared out. The MHLs show a weak ferromagnetic behavior together with a small hysteresis. With the MHL at 150 K as the subtracted background, the ΔM versus H curves show type-II superconductivity-like hysteresis loops below 125 K, and this kind of hysteresis disappears above 125 K. Based on the magnetic measurements, we conclude that there might be some small fraction of superconducting phase in potassium-doped p -terphenyl and p -quaterphenyl. However, since there is a weak ferromagnetic background and the magnetic shielding volume fraction below T_c is too small, we would not conclude that this phenomenon is derived from superconductivity at this stage.

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