# PCCP



# PAPER

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# 1 Introduction

Benzene and its derivatives are always attractive materials because of their novel and excellent physical and chemical properties benefitting from the delocalized cyclic continuous  $\pi$ bonds between the carbon atoms. Among the benzene derivatives, poly(para-phenylene) (PPP) materials draw extensive attention. These materials all have a structure with a certain number of phenyl rings connected at the para positions. The short *p*-oligophenyls (POPs) are named with the prefixes of bi-, ter-, quater-, quinque-, and sexi-, before the phenyl for the two to six phenyl ring compounds, respectively. Early studies revealed that these materials all show insulating or semiconducting behavior in the normal state, whereas their conductivities increase by several orders of magnitude due to the formation of polarons and bipolarons after alkali or alkali earth metal doping.<sup>1-3</sup> The molecular structure in the doped compounds changes from a benzene structure to a quinoid

# Order-disorder transition in *p*-oligophenyls

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Poly(para-phenylene) has been recognized as one important family of conducting polymers upon doping with donors or acceptors. This system possesses a chain-like structure with infinite benzene rings linked with a single C-C bond. Oligophenyls as models of poly(para-phenylene) with short chains in the para position were found to exhibit superconductivity at transition temperatures ranging from 3 K to 123 K upon doping. Structural studies have revealed that there exist order-disorder transitions in many p-oligophenyls with almost doubled lattice constants in the b and c directions at low temperatures. Such a transition is of relevance to the understanding of the emergence of novel quantum functionality where unconventional polaronic interactions are relevant for the new emerging theory of superconductivity in this system. However, the accurate temperatures for the order-disorder transitions amongst these p-oligophenyls are still needed to be determined. The chain length effects on the order-disorder transitions in this system remain unknown. Here we report the systematic investigation of the evolution of the vibrational properties of the crystalline p-oligophenyls over a wide temperature range. The order-disorder transition is identified by three indicators, the lowest energy peak together with the intensity ratios between the 1280 cm<sup>-1</sup> and 1220 cm<sup>-1</sup> modes and between the two modes at around 1600 cm<sup>-1</sup>. A phase diagram of the order-disorder transition temperature and the melting curve for p-oligophenyls are thus established. The former is found to increase with the chain length and saturates at around 350 K for poly(para-phenylene).

> structure; this structure is available to the conduction electrons so that the localized electrons in one molecule, especially the  $\pi$ -electrons, can transfer to the next molecules by combining to the doped atoms.<sup>4,5</sup> In addition, the conductivities of the doped PPP materials show an increasing tendency with increasing molecular chain length.<sup>1,3</sup> Such versatile properties of PPP materials enable them to be extensively applied in scientific research and applications. For example, biphenyl (P2P) can be a starting material of a host of organic compounds, *p*-terphenyl (P3P) is often used as an ultraviolet laser dye,<sup>6</sup> *p*-quaterphenyl (P4P) and its derivatives are always extensively applied in organic thin film transistors and organic light emitting diodes,<sup>7-10</sup> and so on. Now, the PPP materials are back in the spotlight because of the recent discoveries of the superconducting phases with the transition temperatures of 3.4 K and 7.2 K.<sup>11-16</sup> These are significant findings after the prediction of the superconductivity in solid benzene molecular crystals.<sup>17</sup> And the 7.2 K phase is seemingly considered as a common phase in PPP materials. These findings reveal PPP materials to be good candidates for finding superconductors with high transition temperatures.

> The herringbone type structure also generates two adverse forces,  $^{18-20}$  one is the steric repulsive force resulting from the four hydrogen atoms of the neighboring two phenyl rings, and the other is the attractions among the delocalized  $\pi$ -electrons, they tend to be parallel to each ring in one molecule. Due to the

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two competing forces, the two neighboring rings in one individual molecule, such as in the gas state or in solutions, will exhibit a stable angle. As in the case of liquid biphenyl, the tilt angle in the individual molecule is confirmed to be  $44^{\circ}$ .<sup>21</sup> However, after crystallizing, the twist angles turn into zero on average despite the strong thermal librations of the phenyl rings around the long molecular axes.<sup>22-25</sup> Interestingly, it seems as if the shaky molecules of PPP materials freeze up at certain temperatures, and the interring tilt angles between rings simultaneously reemerge.<sup>20,22-29</sup> Furthermore, the angles of the adjacent molecules have opposite orientations. As a result, the structure of PPP materials transforms from monoclinic to triclinic with the remaining four molecules in one-unit cell. Such a structural transition can be confirmed by broad humps in the specific heat measurements.<sup>30–35</sup> These transitions are divided into two categories: "displacive" and "order-disorder" types. Biphenyl is the unique "displacive"-type material in PPPs.<sup>25,36</sup> This material has two incommensurate structural transitions occurring at 40 K and 21 K with the reciprocal lattice vectors  $q_{\delta} = \delta_{a}a^{*} + 1/2(1 - \delta_{b})b^{*}$  and  $q_{\delta} = 1/2(1 - \delta_{b})b^{*}$ , respectively.<sup>30,34,35,37-39</sup> The other PPP materials all belong to the "order-disorder" type with the transition temperatures ranging from 193 K to 295 K for *p*-terphenyl to *p*-sexiphenyl.<sup>27,40,41</sup> Raman spectroscopy as a convenient and effective tool is broadly applied to study the vibrational properties of PPP materials. The chain length effects of POPs have been investigated by Raman scattering.<sup>42</sup> And the Raman spectra of biphenyl, p-terphenyl, and p-quaterphenyl under extreme conditions, such as low temperature and high pressure, are also recorded to understand the internal vibrational properties.<sup>27,39,43-52</sup> The peaks of these materials all exhibit drastic splits at low temperature due to the decreases of the full width at half maximum (FWHM) below the transition temperatures. The FWHMs of the lowest energy peak and the intensity ratios of the modes at around 1220, 1280, and 1600  $\text{cm}^{-1}$  all show anomalous tendencies at around the transition temperatures. These indicate that this structural transition significantly impacts the vibrational properties of PPP materials. However, the low-temperature Raman spectra of *p*-quinquephenyl (P5P) and *p*-sexiphenyl (P6P) are rarely recorded. Whether these remarkable indicators are applicable to the PPP materials with long chain length remains shrouded in mystery. Detailed analyses of the similarity and difference among benzene and these PPP materials are still needed. Since the common superconducting phase was found in PPP materials, their fundamental properties are becoming increasingly essential and important.

Here, we present the Raman spectra of benzene, *p*-quinquephenyl, and *p*-sexiphenyl in the temperature range from 5 K to the temperature above the ambient condition. The temperature effects on the vibrational properties of the modes ranging from the lattice vibrations to the high-energy C–H vibrations, especially the lowest energy peak and the modes at around 1220, 1280, and 1600 cm<sup>-1</sup>, are studied in detail. The results are then compared with previous works focused on biphenyl, *p*-terphenyl, and *p*-quaterphenyl.<sup>43,44,47</sup> Our work provides the basis for the understanding of the vibrational properties of PPP

materials, and it is also of great significance for the further study on PPP materials. In addition, our work also contributes to exploring the properties of other materials which have the similar molecular conformations to PPP materials.

### 2 Experimental details

In the experiments all the high-purity samples were purchased from Sinopharm Chemical Reagent and Alfa Aesar. They were all sealed in quartz tubes with high transmittances for Ramanscattering experiments in a glove box with the moisture and oxygen levels less than 0.1 ppm. The tubes were stuck on the heater by using glue with high thermal conductivity to reduce the error of the internal temperature. Then the heater was put in a cryogenic vacuum chamber for cooling down to low temperature. Due to the different melting points, benzene was measured from 5 K to 300 K, p-quinquephenyl was measured from 5 K to 350 K, and *p*-sexiphenyl was measured from 5 K to 360 K. The applied wavelength of the exciting laser was 660 nm. The power was less than 1 mW before an  $a \times 20$ objective to avoid possible damage to samples. The integration time is 20 s. A 1024-pixel Charge Coupled Device designed by Princeton was used to record the Raman spectra.

### 3 Results and discussion

Fig. 1 presents the Raman spectra of benzene and POPs from biphenyl to p-sexiphenyl at 300 K and 10 K excited by a 660 nm laser. Some areas are zoomed in for clarification, and the classifications of the vibrational modes are presented in Fig. 1(b).<sup>53</sup> All the scattering intensities have been normalized by  $I(\omega) = I_0(\omega)/[n(\omega,T) + 1]$ . Here,  $n(\omega,T)$  is the Bose-Einstein distribution function evaluated at mode energy  $\omega$  and temperature T, and  $I_0(\omega)$  is the observed intensity.<sup>47</sup> The internal normal modes can be approximately separated into the interand intramolecular terms. The former stems from the relative rotation and translation motions of the phenyl groups, and are always located below about 200 cm<sup>-1</sup>. The latter is associated with the in-plane and out-of-plane vibrations in the individual molecule, and always has high energies. Due to the liquid state of benzene under ambient conditions, the spectrum of benzene is very weak at 300 K and the librational modes are submerged in the strong background signal. The liquid benzene crystallizes to an orthorhombic phase at around 280 K, and the spectrum intensity becomes stronger. The five POPs belong to the monoclinic system under ambient conditions, and all exhibit structural transitions with the structural transformation to triclinic at low temperatures. The transition temperatures are 40, 193, 233, 264, and 295 K confirmed by heat capacity measurements respectively for P2P, P3P, P4P, P5P, and P6P.<sup>33</sup> As seen in Fig. 1, the spectra of each material at 10 K show significant differences as compared with those at 300 K. The major features are summarized as follows:

• No distinguishable peaks can be observed in the lattice motion range of liquid benzene, whereas some peaks appear in the high energy range. This indicates that the latter peaks are



**Fig. 1** Raman spectra of benzene, biphenyl, *p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl and *p*-sexiphenyl measured at 300 K (a) and 10 K (b) excited by a 660 nm laser. Each spectrum is plotted in the same scale. The molecular graphs of each POP material are painted in (a). Classifications of the vibration modes are depicted above the spectrum of benzene at 10 K. The partial spectra are zoomed in for clear distinction.

associated with the vibrations among the inner atoms of the benzene ring. In addition, some new peaks appeared in the spectra of POPs, such as the peaks located at around 800 cm<sup>-1</sup>, 1220 cm<sup>-1</sup>, 1280 cm<sup>-1</sup>, 1500 cm<sup>-1</sup>, and so on. These peaks should result from the interaction of the phenyl rings.

• Nearly all the modes show drastic splits at 10 K, especially the librational motions. The anomalous splits were confirmed by previous Raman scattering measurements and found to have resulted from the drastic decreases of the peak widths below the structure transition temperatures.<sup>43,44,47</sup>

• The tendencies of the intensities of the two ring breathing modes almost remain the same at low temperature, their intensities decrease with increasing phenyl numbers.

• The modes around 1220 and 1280  $\text{cm}^{-1}$  are associated with the C-H in-plane bending modes and the interring C-C stretching modes, they stem from the interaction of the neighboring rings, thus they disappear in the spectra of benzene. The 1220  $\text{cm}^{-1}$  mode gradually decreases the intensity with decreasing chain length and this mode absolutely vanishes in

P2P, whereas 1280 cm<sup>-1</sup> shows less changes. This scenario agrees with a previous work,<sup>54</sup> in which it was concluded that the former mode is more sensitive to the chain length and planarity than the latter. The modes around 1600 cm<sup>-1</sup> are associated with the C-C stretching modes, and the intensities of these modes increase with increasing phenyl numbers. They all exhibit severe splits at low temperatures.

• The backgrounds of all the materials are nearly straight under ambient conditions, however they raise as a broad hill. In addition, peaks located at around 500 cm<sup>-1</sup> with the width more than 100 cm<sup>-1</sup> appear at low temperatures in the six materials. They have been excluded from the external dirty signals. These anomalous phenomena should result from the increase of the fluorescence effect.<sup>43,44,47</sup>

• The intensities of the high-energy C–H stretching modes decrease as the phenyl ring number is increased, and they also dramatically split at low temperatures. This behavior implies that these peaks are associated with the terminal rings. Otherwise, this behavior can also be occurred due to the monotonous decrease of the H and C ratios with increasing chain length.<sup>42</sup>

The detailed Raman spectra with respect to the lattice motions of each material are presented in Fig. 2, and the spectra of P2P, P3P, and P4P are cited from the published references.<sup>43,44,47</sup> The most significant feature is the drastic splits of the librational modes with decreasing temperature. The splits have been confirmed to have resulted from the decrease of the FWHMs at low temperatures.<sup>43,44,47</sup> Otherwise, all the peaks have blue-shifts, and the intensities simultaneously increase. For benzene, the lattice librational peaks suddenly appear after crystallizing, and then blueshift upon cooling. The POPs show entirely different Raman spectra from benzene due to the different crystal structures. Meanwhile, among the five POPs, the spectra of P2P also show a little distinction. First, due to the incommensurate lattice modulation in P2P, several new peaks appear below the transition temperature, whereas no new peaks can be observed in the spectra of other POPs without any modulations on the lattice. All the sharp peaks stem from the splits of the broad peaks above the transition temperature. Second, the wavenumbers of the peaks in P2P, as well as the peak numbers at low temperatures, are different compared to other POPs even though they belong to the same crystal structure (monoclinic in the normal state and triclinic after the structural transition). Such phenomena should have resulted from the strong intermolecular forces which are comparable to some intramolecular forces.<sup>55</sup> The strong forces are also the reason why the unique displacive transition of P2P comes from. Otherwise, the free molecules of the longer polymers have more complex librations around the long axis than P2P. This can also impact the vibrational properties. The number of librational modes for P2P is reduced accordingly. In addition, one can also see that the intensities of these peaks at 5 K decrease with increasing phenyl ring numbers from 3 to 6 despite a gradual increase in the transition temperatures. This should result from the gradual increase of the lattice parameters, and the interaction forces among molecules decrease as the chain length is increased.





Fig. 2 Raman spectra of benzene, biphenyl, *p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl and *p*-sexiphenyl measured at different temperatures. All the spectra are displaced vertically for clarification.

Among the lattice modes, the lowest frequency mode draws a lot of attention. This mode can be a good indicator of the chain length at normal state because that the frequency of this mode regularly changes with increasing molecular chain length. Here, we fit the lowest frequency peaks of each material by a Lorentz function, and the temperature dependent FWHMs are shown in Fig. 3. Indeed, the frequency of this peak monotonously decreases with increasing chain length. This tendency is also retained at low temperatures even though all the lowest energy peaks of the POPs blueshift with decreasing temperature (see Fig. 3(a)). Thus, the lowest energy peak is adequate to be a good indicator of the molecule length in PPP materials at



Fig. 3 (a) Frequencies of the lowest energy peaks of the POPs as a function of temperature. (b)–(f) FWHMs of biphenyl, p-terphenyl, p-quaterphenyl, p-quinquephenyl, and p-sexiphenyl as a function of temperature. The structural transition temperatures are pointed out by the vertical dashed lines, and the shaded parts indicate the error ranges.

different temperatures. The temperature dependent FWHMs of the POPs are presented in Fig. 3(b)-(f). Previous Raman scattering works discovered that the drastic peak splits at low temperatures mainly result from the abrupt reduction of the peak widths at around the structural transition temperature, and the lowest energy peak is a typical example.<sup>42-44,47</sup> As seen in Fig. 3, all the POPs are in accord with this scenario, including the "displacive" type biphenyl; this material also exhibits a width decrease at around the transition temperature. However, the frequencies of these modes show little anomalies at around the transition temperature (see ref. 51, 52 and 55). This indicates that the molecular geometry distortion has limited impact on the crystal packing energy. More interestingly, for the "order-disorder"-type POPs, the magnitudes of the FWHM gradually decrease with increasing chain length, the magnitude almost vanishes for *p*-sexiphenyl. Such a tendency should result from the increasing chain length. With increasing chain length, the thermal dynamics among the phenyl rings become stable. Thus, the twist angles between the neighboring phenyl rings reduce with increasing molecular length, and the infinite long polymer is believed to be planar under various conditions. Consequently, the influence of the reconstructed angle below the transition temperature gradually fades away. In addition, the transition temperatures confirmed by Raman scattering are all higher than those determined by heat capacity measurements.

Such a condition results from the entrance of the thermal anomalous state; this state has been discovered by thermodynamic studies.<sup>30–35</sup> This also indicates that the internal vibrational properties are very sensitive to the structure changes.

The C-H in-plane bending modes and the interring C-C stretching modes located at around 1220 and 1280 cm<sup>-1</sup> are common indicators to identify the molecular conjugations (chain length and planarity) and the structural transition. 42-44,47,54,56-62 Fig. 4(b)–(f) present the temperature evolutionary Raman spectra of these two modes; the transition temperature of each material has been pointed out by dashed lines. These two peaks exhibit stable frequencies in the normal state, as well as broad widths. However, they show fierce splits below the transition temperatures. The splits primarily result from the drastic decreases of the FWHMs of each mode, which can be clearly seen in the maps. Interestingly, the 1220 cm<sup>-1</sup> modes of the four POPs all red-shift with decreasing temperature, whereas the 1280  $\text{cm}^{-1}$  modes blueshift, except that for P2P, the 1280 cm<sup>-1</sup> mode red-shifts upon cooling and is almost stable below transition and the 1220 cm<sup>-1</sup> mode disappears. It is seemingly likely that the vibrational mode in P2P at around 1280 cm<sup>-1</sup> is in connection with the 1220 cm<sup>-1</sup> mode when compared to the other POPs. The atomic displacement patterns of these two modes are presented in Fig. 4(a). In this figure, the 1220 cm<sup>-1</sup> mode more closely resembles the distortion of the interring C–C bonds, and the 1280 cm<sup>-1</sup> mode shows more



**Fig. 4** (a) The displacement patterns of the 1220 and 1280 cm<sup>-1</sup> modes. (b)–(f) Temperature dependent intensity maps of the biphenyl, *p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl and *p*-sexiphenyl. Raman spectra at 5 K and 300 K of each POPs are depicted for clarification. The transition temperatures are pointed out by the horizontal dashed lines.

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similarity to the C-H bending. Meanwhile, theoretical calculation has been performed on these two modes.<sup>54</sup> The former mode (see Fig. 4(a)) is rationalized to be associated with the delocalized band which stems largely from the C atoms on the para positions, and the latter mode is more determined by the localized band resulting from the off-axis C atoms. With decreasing temperature, the POP molecules always remain planar even though the molecular thermal disturbance gradually decreases, only the interring C-C bond becomes little shorter and the benzene rings have little distortions.<sup>63,64</sup> Thus, the energy of the 1220 cm<sup>-1</sup> mode slightly decreases and the 1280 cm<sup>-1</sup> mode shows the opposite change. Below the transition temperature, the twist angles appear. Consequently, the energy of the delocalized band is significantly suppressed, and that of the localized band is enhanced. The anomalous behavior in P2P is also analysed in the theoretical work. Due to the strong crystal packing forces, the crystalline torsional potential in biphenyl is smaller than in other POPs.<sup>20</sup> This scenario should be the major reason for the anomalous behaviors in P2P.

These modes were fitted by Lorentz function, and the frequency difference and the intensity ratio of the two modes of each material are presented in Fig. 5. At room temperature, as can be seen in Fig. 5(a), the energy separation of these two modes increases with increasing phenyl ring number in one molecule and looks like non-convergence for the infinite long polymer. The intensity ratio of the POPs monotonously decreases, but the pace of the decrease slows, and the ratio almost converges to zero for the infinite long polymer. The intensity ratio of the two modes is indeed suitable to estimate the molecular conjugation. Meanwhile, the

energy separation of these two modes can also be used to indicate the molecular chain length. Below transition temperature, however, these two peaks exhibit severe splits; this anomalous change makes the selects of the frequencies of these two peaks more difficult. Here, we fitted the two peaks with the strongest intensities at around 1220 and 1280  $\text{cm}^{-1}$ . The results are compared with the published data of P2P, P3P, and P4P. For P2P, the intensity ratio of the 1280  $\text{cm}^{-1}$  and 1000 cm<sup>-1</sup> modes was chosen because the 1220 cm<sup>-1</sup> mode almost disappears and the intensity of the 1000 cm<sup>-1</sup> mode shows almost no change as the temperature changes.43 All the ratios show anomalous changes at around the structural transition temperatures, but the amplitudes of the anomalies gradually decrease with increasing chain length. In P6P, any anomalous signs are hardly seen to identify the transition temperature. The vanishing tendency shares the same feature with the FWHM of the lowest energy peak. On the other hand, the energy separations of these materials also show small changes. All the curves exist inflection points at around the structural transition temperatures, and it is still obvious in the longer polymers. Thus, the energy separation between the 1220 and 1280  $\text{cm}^{-1}$ modes is applicable to estimate the molecular conjugation. All these phenomena should also result from the reappearance of the interring distortion angles and the decrease of the inter-ring torsion angles of the longer polymers.<sup>20,43,44,47</sup>

The temperature evolutionary intensity maps of the modes at around 1600  $\text{cm}^{-1}$  of benzene and POPs are presented in Fig. 6. Two strong peaks appear at room temperature, whereas they split into several peaks at low temperatures. These splits result from the reduction of the intensities and the FWHMs



**Fig. 5** (a) Intensity ratios and the energy separations at room temperature of the 1220 and 1280 cm<sup>-1</sup> modes as a function of the phenyl number. The intensity ratio of biphenyl is an estimated value due to the weak intensity of the 1220 cm<sup>-1</sup> mode, and is thus plotted by a violet solid ball. (b)–(f) Intensity ratios and energy separations of the 1220 and 1280 cm<sup>-1</sup> modes as a function of temperature of POP materials.

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with decreasing temperature, and thus the weak peaks appear at low temperature. In the maps of benzene, the two peaks exhibit broad widths and weak intensities. After crystallizing, there are abrupt decreases in the widths of these two peaks, as well as the frequencies. The intensities also show sudden increases below the crystallization temperature. In addition, these anomalies occur almost at all the vibrational modes. All the changes should have resulted from the crystallization of benzene into an orthorhombic structure from a disordered state. The anharmonic effect is significantly reduced due to the ordered arrangement of the molecules after crystallization. Meanwhile, because of the greater molecular force field surrounding the benzene molecules, the benzene rings swell. This distortion effectively reduces the vibrational energies among the atoms, *i.e.*, the peaks in the spectra will red shift. Such a phenomenon makes Raman spectroscopy a powerful tool to estimate the melting point of benzene; this method is also applicable to other materials. For the spectra of the POPs, these two peaks blue-shift upon cooling and show few anomalies at around the transition temperatures except for P2P. The frequencies, widths, and intensities of these two modes in P2P all exhibit unusual tendencies below 45 K, the lower energy peak even shows a redshift behavior. This anomalous change should also result from the smaller crystalline torsional potential in P2P than in other POPs because of the strong crystal packing forces.<sup>20</sup>

The intensity ratio of these two modes are also always used to estimate the molecular conjugation.<sup>42,56,65</sup> However, like the modes at around 1220 and 1280 cm<sup>-1</sup>, due to the drastic splits of these peaks, it becomes more difficult to distinguish these peaks. Here we choose two peaks located at around 1600 cm<sup>-1</sup> with the strongest intensities; the temperature dependent intensity ratios between the lower energy peaks and the higher energy peaks of POPs are presented in Fig. 6(e) and (f), and compared with P2P, P3P, and P4P.<sup>43,44,47</sup> All the ratios show anomalous variations below the transition temperatures. However, the anomalies become increasingly obscure with increasing chain length. One can see clear anomalies in P2P and P3P, whereas the other materials show few anomalies, which should have also resulted from the gradually decreased torsion angles of the longer polymers.

The theoretical calculation of these two peaks suggested that they stem from the "resonance split" of one peak.<sup>65–68</sup> The lower energy peak A is a fundamental band, and the higher energy peak B ( $\nu_8$ ) is a combination tone of the two fundamental bands  $\nu_1$ and  $\nu_6$  respectively at around 992 and 606 cm<sup>-1</sup>. In addition, the energy separation between  $\nu_8$  and  $\nu_6 + \nu_1$  is an indicator of the mode mixing level. This value also responds to both the inter-ring twist and chain length, and thus can be used to estimate the molecular conjugation.<sup>43,44,47,65</sup> The calculated ( $\nu_6 + \nu_1$ ) –  $\nu_8$  of benzene and POPs are shown in Fig. 7. The energy separation of



Fig. 6 Temperature dependent intensity maps of benzene, biphenyl, *p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl and *p*-sexiphenyl. Raman spectra at 5 K and 300 K of each POP are depicted for clarification. The transition temperatures are pointed out by the horizontal dashed lines.



Fig. 7 Left: Intensity ratios of the higher energy peak (B) and the lower energy peak (A) as a function of temperature. Right: Temperature dependent frequency difference between  $\nu_6 + \nu_1$  and  $\nu_8$ .

benzene shows different features: it suddenly drops below the crystallization temperature, and then increases with decreasing temperature. All the energy separations of POPs show descending tendencies upon cooling. This phenomenon indicates that the mixing levels between the fundamental and combination bands decrease at low temperatures. In addition, they also show anomalous changes at around the transition temperatures. This implies that the mixing is also sensitive to the ring twist. However, the anomalous amplitude of the mixing level, as well as the intensity ratio of these two peaks, is very weak in the longer polymers. Only in P2P and P3P obvious anomalies can be observed. Consequently, these two indicators are not applicable under the low temperature conditions.



**Fig. 8** Phase diagram of the melting point and the structural transition temperature of benzene, biphenyl, *p*-terphenyl, *p*-quaterphenyl, *p*-quinquephenyl, and *p*-sexiphenyl.  $T_{\rm st}$ : the structural transition temperature.

In the end, a corresponding phase diagram of the melting point and structural transition temperature is plotted in Fig. 8. The rhombuses represent the transition temperatures of benzene and POPs from the literature.33,40 This diagram is used as a guide to predict the physicochemical properties of the polymer with long chain length. In this figure, the melting point monotonously increases from benzene to *p*-sexiphenyl, and the extrapolated temperature of the infinite long polymer is more than 1000 K. This is identical to previous works which suggests that the infinite long PPP is almost an infusible material.<sup>40</sup> The structural transition temperature also increases with increasing chain length, whereas the growth rate gradually decreases. Benzene is suggested to have no structural transition at low temperatures, *i.e.*, in the crystalline benzene, all the benzene rings should be parallel to each other. The extrapolated structural transition temperature of the infinite long polymer is about 350 K.

### 4 Conclusions

In conclusion, Raman scattering spectra of benzene, p-quinquephenyl, and p-sexiphenyl were recorded at different temperatures. The vibrational properties of these materials were comprehensively analyzed, and the results were compared with previous works focused on biphenyl, p-terphenyl, and p-quaterphenyl. All these three indicators of the molecular conjugation, including the lowest energy peak and the intensity ratios between the 1280 cm<sup>-1</sup> and 1220 cm<sup>-1</sup> modes and between the two modes at around 1600 cm<sup>-1</sup>, were examined under low temperature conditions. The frequency of the lowest energy peak shows a decreasing tendency with increasing chain length. Meanwhile, all the p-oligophenyls exhibit drastic

decreases in the peak widths of the lowest energy peaks, and thus can be used to estimate the molecular conjugation at low temperatures. The other two indicators also show anomalous changes at around the structural transition temperatures and are also applicable under the low temperature conditions. However, the drastic splits of these modes make the calculations of the intensity ratios more difficult. In addition, due to the gradual decrease of the inter-ring twist with increasing molecular chain length, the amplitudes of the anomalies gradually vanish. The anomaly is almost indistinguishable in the *p*-sexiphenyl and the longer polymers. In the end, a phase diagram of the melting point and the structural transition temperature was estabilished. They all increase with increasing chain length, and the extrapolated melting point and transition temperature for the polymer with infinite chain length are above 1000 K and 350 K, respectively.

# Conflicts of interest

There are no conflicts to declare.

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