AIP The Journal of Chemical Physics

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Citation: J. Chem. Phys. **139**, 104302 (2013); doi: 10.1063/1.4820359 View online: http://dx.doi.org/10.1063/1.4820359 View Table of Contents: http://jcp.aip.org/resource/1/JCPSA6/v139/i10 Published by the AIP Publishing LLC.

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Structural and vibrational properties of phenanthrene under pressure

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(Received 30 May 2013; accepted 21 August 2013; published online 9 September 2013)

The structural and vibrational properties of phenanthrene are measured at high pressures up to 30.2 GPa by Raman spectroscopy and synchrotron X-ray diffraction techniques. Two phase transitions are observed in the Raman spectra at pressures of 2.3 GPa and 5.4 GPa which correspond to significant changes of intermolecular and intramolecular vibrational modes. Above 10.2 GPa, all the Raman peaks are lost within the fluorescence background; however, upon further compression above 20.0 GPa, three broad peaks are observed at 1600, 2993, and 3181 cm⁻¹, indicating that phenanthrene has transformed into amorphous phase. Using X-ray diffraction, the structures of corresponding phases observed from Raman spectra are indexed with space groups of $P2_1$ for phase I (0-2.2 GPa), P2/m for phase II (2.2-5.6 GPa), P2/m+Pmmm for phase III (5.6-11.4 GPa) which has a coexistence of structures, and above 11.4 GPa the structure is indexed with space group of Pmmm. Although phenanthrene has transformed to a hydrogenated amorphous carbon structure above 20.0 GPa, these amorphous clusters still show characteristic crystalline behavior based on our X-ray diffraction patterns. Our results suggest that the long-range periodicity and the local disorder state coexist in phenanthrene at high pressures. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4820359]

I. INTRODUCTION

Polyaromatic hydrocarbons (PAHs) have attracted a large amount of interest within various areas such as for electronic, optoelectronic, and optical applications.^{1–3} Especially the recent discovery of superconductivity in potassium doped picene⁴ has motivated extensive investigations on a series of PAHs. Other PAHs (phenanthrene,^{5,6} coronene,⁷ and de1,2:8,9-dibenzopentacene⁸) are also found to exhibit superconductivity with critical temperatures T_c 's from 5 to 33 K on doping alkali or alkali-earth metals into the crystal structure. Recent research has found that the edge structure, "armchair" or "zigzag," of the organic molecule may play an important role in the superconductivity of PAH compounds where the armchair edge is thought to be a key factor for the superconductivity showing larger electron-phonon coupling.^{4,5,8,9}

According to recent studies, the application of pressure is of paramount importance to enhance superconductivity within these organic based systems, where the T_c of K₃picene is increased about twice at 1.2 GPa from 18 K to 30 K, and the positive pressure-effect is also reported in cation doped phenanthrene.^{4–6} Due to the relatively weak intermolecular interaction of PAHs, the characteristic of these solids is very responsive to applied pressure. First-principles calculations on tripotassium doped picene revealed that the magnetism is sensitive to the variation of volume or pressure in this organic compound.¹⁰ Both ferromagnetic and antiferromagnetic spin orderings are strongly suppressed as pressure is increased. Previous investigations revealed that pentancene, which has the same number of benzene rings as picene and a different C-C edge structure (zigzag), can be transformed into a metallic state at 27 GPa.¹¹ Additionally, the investigation into the high-pressure behaviors of these compounds is of great use to understand their physical and chemical properties which are related to electronic, vibrational, and crystal structure. In particular, high-pressure optical spectroscopy is extensively applied to examine and understand the effects of polymorphic transitions and chemical transformations in PAHs.¹²⁻¹⁴ However, most high-pressure investigations of PAHs are focused on acene (with zigzag edge) instead of phenacene (with armchair edge), and the previous studies are limited to the relative low pressure due to the large fluorescence background. For phenacene family, the high-pressure studies of picene were recently reported,^{15,16} giving a deep insight into the pressure dependence of the electronic properties and intermolecular interaction of this compound.

Phenanthrene is the simplest molecule with an armchair configuration that consists of three benzene rings where a larger superconducting volume fraction was reported in cation doped phenanthrene than for the other PAH based

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superconductors. According to the study of fluorescence of phenanthrene under applied pressure, an abrupt change in total intensity of the spectra occurred at approximately 2.5 GPa, which may be associated with a structural phase-transition.¹⁷ However, from these findings one cannot gain more information on this phase change at the low pressure range. The behavior of the sample at higher pressures is still lacking and thus requires more investigations.

Within this manuscript we present a high-pressure investigation of phenanthrene by combining Raman scattering and synchrotron X-ray diffraction (XRD) up to 30.8 GPa. Our studies provide an investigation of the pressure-related changes in molecular vibrations and the corresponding responses of the crystal structure in phenanthrene. From our studies three possible phases are shown to exist in phenanthrene up to 30.8 GPa, where the corresponding unit cell of each phase is determined based on the XRD data obtained. Our results also suggest that under further compression to 20 GPa, phenanthrene transforms into hydrogenated amorphous carbon based on the Raman spectra; however, the XRD data suggest that crystalline regions exist up to 30.8 GPa leading to a local disordered state.

II. EXPERIMENTAL DETAILS

Phenanthrene of 98% purity, colorless crystal, was purchased from TCI Co.18 and used without any further purification. High-pressure Raman measurements were carried out in symmetric diamond anvil cells (DACs) with the culets of 300 μ m. A 100 μ m hole which was drilled in the center of stainless-steel gasket served as the sample chamber. One small piece of the sample was placed in the chamber and small ruby grains were put on one of the diamond culets that served as the pressure calibration. The pressure acting on the sample can be determined by the shift of the ruby wave number by the well-established ruby fluorescence method.¹⁹ No pressure transmitting medium was used for the measurements. Renishaw Invia Raman system with a spectrometer (1800 lines/mm grating) was used for the measurement, giving a resolution of 1 cm⁻¹. The Raman spectra were measured in backscattering geometry with visible laser excitation (532 nm) with power less than 50 mW. The spectra were collected from 100 to 3300 cm^{-1} .

High-pressure synchrotron XRD experiments were performed with the same DAC at room temperature, using synchrotron radiation at the Beijing Synchrotron Radiation Facility (BSRF). The wavelength of the X-ray is 0.6199 Å. The sample-to-detector distance and the image plate orientation angles were calibrated using CeO₂ standard. No pressure transmitting medium was used for the measurements. The two-dimensional diffraction images were converted to 2θ versus intensity data plots using the FIT2D software.

III. RESULTS AND DISCUSSION

A. Evolution of vibrational properties with pressure

The crystal structure and molecular structure of phenanthrene are shown in Fig. 1. The crystal belongs to the space



FIG. 1. Molecular structure and crystal structure of phenanthrene at ambient pressure.

group $P2_1$ with two molecules in the unit cell. The phenanthrene molecule contains 24 atoms, the spectrum possesses 66 intramolecular modes,²⁰ spanning irreducible representations as $23A_1+22B_2+11A_2+10B_1$.²¹ The vibrational modes can be divided into two different types in Raman spectra: intermolecular modes and intramolecular modes.²² The intermolecular modes, representing the motions of rigid molecules under whole molecular interaction, are in the low frequency region of the Raman spectra, while the intramolecular modes in the high frequency region represent the vibration of atoms in a molecule. For phenanthrene, the assignment of intramolecular modes are available from previous works.^{23,24} The force field effect has been taken into account in their calculational works, reaching a good agreement between computed and observed frequencies.²⁴ Table I lists the most intense peaks in spectra and the assignments of their vibration types²³ within the phenanthrene molecule.

Raman spectra of phenanthrene are collected from ambient pressure to high pressure (30.2 GPa) followed by decompression, and the selected spectra in the frequency region of 100-3300 cm⁻¹ are shown in Fig. 2. Additionally, the intensities of the Raman peaks drop with increasing pressure, and above 10.2 GPa all the Raman peaks within the spectra are lost within the luminescence background. With increasing pressure, all the Raman peaks shift to higher frequencies except a peak originally at 1144 cm⁻¹. Upon further compression, several peaks become weak and vanished at different pressures and the other Raman peaks cannot be observed due to the increasing luminescence background above 10.2 GPa. When pressure is further increased above 20.0 GPa, the luminescence background vanishes but no original Raman peaks reappear. However, three new broad peaks were observed, respectively, around 1600, 2993, and 3181 cm⁻¹ above 20.0 GPa. Then, the broad peaks shift sluggishly to higher frequencies upon further compression, and these peaks still remained upon the release of pressure while the original Raman modes were not recovered.

According to the previous vibrational assignments,²³ the intermolecular modes of phenanthrene occupies up to 200 cm^{-1} , but only one peak L₁ can be observed within this region at ambient pressure in our measurement. Another intermolecular mode L₂ at 143 cm⁻¹ appears at 2.3 GPa, which moves from the frequency range below 100 cm⁻¹ (outside of our measurement range). Additionally, a new peak appears as

TABLE I. Intramolecular vibrations of phenanthrene: Vibrational assignment, symmetries, and observed frequencies.

Modes	Assignment ^{a,b}	Symmetry	Obs (cm ⁻¹)
v ₁	α (CCC)	B ₂	236
ν_2	$\delta(\text{CCCC})$	A_1	251
<i>v</i> ₃	$\delta(\text{CCCC})$	A_1	401
v_4	$\alpha(\text{CCC})$	B ₂	412
v_5	$\delta(\text{CCCC})$	B_1	443
v_6	$\alpha(\text{CCC})$	B ₂	498
v_7		B_1	537
ν_8	$\alpha(\text{CCC})$	A_1	549
<i>v</i> 9	γ (HCCC)	A_1	710
v_{10}	$\alpha(\text{CCC})$	B_1	713
v_{11}	t(CC)	A_1	1039
v_{12}	$t(CC) + \beta(HCC)$	A_1	1144
v ₁₃	$t(CC) + \beta(HCC)$	A_1	1166
v_{14}	$\delta(\text{CCCC})$	A_1	1173
V15	$\delta(\text{CCCC})$	A_1	1204
v_{16}	1348b - 115b = 1233b	B_1	1228
v_{17}	β (HCC)	B_1	1248
v_{18}	$t(CC) + \beta(HCC)$	A ₁	1353
V19	$710a \times 2 = 1420a$	A_1	1422
v_{20}	$t(CC) + \beta(HCC)$	A_1	1432
v_{21}	$t(CC) + \beta(HCC)$	A_1	1443
v_{22}	t(CC)	A_1	1526
v_{23}	t(CC)	B ₁	1573
v_{24}	t(CC)	A_1	1596
v_{25}	t(CC)	B_1	1617
v_{26}	t(CC)	A_1	1626
v_{27}	s(CH)	B_1	3044
v_{28}	s(CH)	A_1	3071
v_{29}	s(CH)	A_1	3086
v ₃₀	s(CH)	B1	3099

^aInternal coordinates are defined as follows: *t* is C-C stretching, α is CCC bending, β is HCC bending, γ is HCCC out-of-plane bending, and δ is CCCC torsion. ^bFrom Ref. 27.

a shoulder on the intermolecular mode of L₁ at 2.3 GPa, and as pressure increases the peaks are splitted into two distinct modes, which is due to a structural transformation caused by application of external pressure. Furthermore, one C-H stretching mode v_{30} originally at 3088 cm⁻¹ disappeared at 2.3 GPa (see Fig. 2). With increasing pressure to 5.4 GPa, some changes occurred in the Raman spectra, indicating possible substantial changes in the crystal and/or molecular structures, where there is a loss of degeneracy or splitting of the v_4 (C-C-C-C bending) and v_{11} (C-C stretching) modes. These changes are also coupled to a loss of several intramolecular modes: v_{13} , v_{14} , v_{19} , and v_{20} . Compressing continually, all the peaks gradually become broad and disappear in the increasing luminescence background around 10.2 GPa. In frequencies range from 1500 to 1700 cm^{-1} , no apparent discontinuity, disappearance, or splitting was observed in the C-C stretching vibration modes under pressure, implying the stability of carbon bonding below 10.2 GPa.

The selected pressure dependencies of the Raman peaks are depicted in Fig. 3 to illustrate any possible phase transitions occurring within the sample under applied pressure. From these data one can identify three phases: the first between 0 and 2.3 GPa, the second between 2.3 and 5.4 GPa,



FIG. 2. Raman spectra up to 30.2 GPa. (a) Representative Raman spectra of phenanthrene in the frequency range of 100-800 cm⁻¹. (b) Selective Raman spectra of phenanthrene in the frequency range of 1000-3200 cm⁻¹. The arrows indicate the changes of the Raman spectra.

and the third between 5.4 and 10.2 GPa. The first phase transition at 2.3 GPa is identifiable from the splitting of the intermolecular mode L₁, also associated with a change in slope from 27.7 to 6.6 cm⁻¹/GPa, along with discontinuities associated with the $v_{19,20}$ peaks and a disappearance of the v_7 and v_{30} peaks. This first phase transition (transformation to phase II) is due to a molecular rearrangement whereby the phenanthrene molecules must change to a more tightly packed structure. This structural change is consistent with the fluorescence spectra of phenanthrene previously reported by Jones and Nicol,¹⁷ where a decrease in total intensity of fluorescence spectra was observed above 2.5 GPa.

Compression above 5.4 GPa shows a transformation to phase III where there is a loss of intramolecular modes which is shown in Fig. 3. There may also be a change in the slope at the phase boundary for the lattice modes thus also showing that these changes may have consequences on not only the



FIG. 3. Pressure dependence of the frequencies of phenanthrene for the observed modes in all regions at room temperature. The vertical dashed lines at near 2.3 and 5.4 GPa indicate the proposed phase boundaries.

molecular structure but also the crystal structure. Above 10.2 GPa, most peaks in the spectra disappear within the luminescence background.

Although no Raman peaks are observed above 10.2 GPa, the Raman spectra measurement was continued to be performed upon compression up to 30.2 GPa because there was no direct observation of metallization in phenanthrene (i.e., visible darkening of the sample in DAC) below 10.2 GPa. Upon further compression, diamond luminescence background gets weaker, but no original Raman peaks recover. However, three broad peaks were observed in the range of 1500-1700 cm⁻¹ above 20.0 GPa. This broad peak corresponds to the stretching motion of sp^2 carbon pairs in the rings or chains, which is an important characteristic of disordered, nanocrystalline, and amorphous carbon,^{25,26} suggesting that phenanthrene has changed to an amorphous material at high pressures. Additionally, we also observed another two broad peaks around 2993 and 3181 cm^{-1} above 20.0 GPa. These two bands could be assigned, respectively, to the C-H stretching vibration and the second order mode of sp^2 carbon pairs stretching mode observed at 1600 cm⁻¹.^{25,26} The C-H characteristic indicated the fact that the phenanthrene compound transformed to amorphous hydrogenated carbon instead of carbonization which was observed in the high pres-



FIG. 4. Photos of phenanthrene under back illumination at pressures of 5.3, 17, and 27.6 GPa. The sample gradually changed from colorless to darken but still keeps visible upon compression.

sure studies of shock waves on phenanthrene.²⁷ This chemical reaction to amorphous hydrogenated carbon is consistent with the high pressure studies of other aromatic compound such as benzene,^{28–30} pyrene,¹⁴ and picene.¹⁵ Upon decompression the broad peaks move back to lower wave numbers. However, no other original Raman modes are recovered. This illustrates that an irreversible change has taken place.

In addition, we recorded the changes of colors of phenanthrene with increasing pressure (as shown in Fig. 4). The sample gradually changed from colorless to yellow and finally to dark red. This color change can be explained by a redshift of the absorption peaks as a function of pressure which was already experimentally observed³¹ as well as theoretically considered.³² Upon compression up to 30.0 GPa, light is still able to pass through the sample under illumination. It indicated that phenanthrene does not metallize or carbonize under pressure.

B. Analysis of structural evolution with pressure

The XRD data were collected from ambient pressure to 30.8 GPa (Fig. 5). On compression the Bragg peaks shift to higher angles indicating the shrinkage of the phenanthrene lattice. Within the Raman data there was evidence of a phase transition at 2.3 GPa and within the XRD data there is a change in the diffraction data also suggesting/supporting the phase transition observed around 2.3 GPa. Upon further compression, a new reflection peak appears around the peak at $4^{\circ} 2\theta$ (110) at 5.6 GPa, and the intensity of this peak gradually strengthens accompanied with the decreasing intensity of the (110) peak upon further compression. The corresponding changes were also observed in the Raman spectra at 5.4 GPa, strongly indicating a structural phase transitions in phenanthrene. With increasing pressure, another transition is observed at 8.8 GPa where the 12° peak is split where the higher angle out of these two reflections decreases in intensity under further compression. A new peak appears at $18.6^{\circ} 2\theta$ above 11.4 GPa and as the pressure is further increased, although the overall intensity decreases, the peaks remain up to 30.8 GPa.

The profile fitting of the patterns was performed in terms of the Le Bail method by using the GSAS program³³ to investigate the crystal structure under applied pressure. The data and results from the fits at selected pressures can be seen in Fig. 6. At 0.3 GPa, the data could be fitted using the space group $P2_1$ determined from single crystal diffraction data of phenanthrene at ambient pressure. As previously stated, the



FIG. 5. Synchrotron X-ray ($\lambda = 0.6199$ Å) diffraction patterns of phenanthrene at various pressures up to 30.0 GPa.

first phase transition is observed at 2.2 GPa but the structure of these high pressure phases is unknown and thus Dicvol06³⁴ and Peakfit v4³⁵ were used to determine the possible space group and its lattice parameters. For phase II, all the diffraction peaks were resolved at 2.2 GPa and indexed mainly to the monoclinic system or orthorhombic system. Compared with other organic compound such as coronene,³⁶ investigations revealed that coronene transformed to the body centered orthorhombic structure from monoclinic phase below 2.0 GPa. However, the orthorhombic phase group is not suitable in our cases because of the bad fitting results. The monoclinic space group of P2/m is selected as the candidate for refinement of phase II due to reasonable figures of merit (M,F) and/or volume of the cell. As shown in Fig. 6(b), the lattice parameters, which are determined from a fit with P2/m space group at 4.3 GPa, are a = 20.465(1) Å, b = 9.834(7) Å, c= 8.337(1) Å, and β = 93.94° where, based on the refinements, the predicted volume per formula unit of phenanthrene is 211.85 Å³ assuming Z = 8. From 5.6 to 11.4 GPa, the majority of the diffraction peaks could be fitted using the P2/m space group except for the emerging new peaks at 5.6 GPa where the sample is entering a mixed phase state or becoming increasingly more complex. Thus, a new high pressure phase must be introduced into the refinement of the phase from 5.6 to 11.4 GPa. From the higher pressure data above 11.4 GPa, the double peaks at approximately 4° and $12^{\circ} 2\theta$ become a single peak due to a further phase change. This high pressure phase was determined to belong to the space group *Pmmm*, which is orthorhombic, and the refinement at 14.4 GPa is shown in Fig. 6(d). Therefore, the mixed phase between 5.6 and 11.4 GPa could be fit using a superposition of both P2/m and Pmmm space groups, where the refinement is shown in Figure 6(c) for 8.8 GPa. Therefore, where these



FIG. 6. X-ray diffraction patterns of phenanthrene at pressures of 0.3 GPa (a), 4.3 GPa (b), 8.8 GPa (c), and 14.4 GPa (d). The open circles represent the measured intensities and the red lines the results of profile refinements by the best Le Bail-fit with each space group. The positions of the Bragg reflections are marked by vertical lines and the difference profiles are shown at the bottoms (blue lines). The *R* values are Rp = 0.29%, Rwp = 0.52% for the fitting at 0.3 GPa, Rp = 0.22%, Rwp = 0.46% at 4.3 GPa, Rp = 0.15%, Rwp = 0.28% at 8.8 GPa, and Rp = 0.22%, Rwp = 0.34% at 14.4 GPa. Insets: Enlarged X-ray patterns and their fittings at low angles.

new peaks emerge at 5.6 GPa, clusters within the sample are changing to orthorhombic symmetry.

Using the GSAS software, it has been possible to determine the lattice parameters for the sample at each applied pressure where the unit cell volume can be easily calculated. The pressure dependence of the volume per formula unit is shown in Fig. 7, and the dependence can be decided systematically by an appropriate equation of state (EoS). For phenanthrene, the Birch-Murnaghan equation of state (BM3 EoS)³⁷ was used to obtain the bulk modulus and its derivative. The Birch-Murnaghan equation of state is defined as

$$P = 3K_0 f_E (1 + 2f_E)^{\frac{5}{2}} \left[1 + \frac{3}{2} (K'_0 - 4) f_E \right], \qquad (1)$$

where $f_E = [(\frac{v_0}{v})^{\frac{2}{3}} - 1]$, V_0 is the volume per formula unit at ambient pressure, V is the volume at pressure P given in



FIG. 7. Volume per formula unit change of phenanthrene with pressure. The solid lines demonstrate the fitting data of phases to the Birch-Murnaghan equation of state and vertical dashed lines denote the phase boundaries.

GPa, K_0 is the bulk modulus at ambient pressure, and K'_0 is the value of the first pressure derivative of bulk modulus at ambient pressure. K_0 and K'_0 are two independent parameters. The first phase could not be fitted by the equation of state due to the limited amount of data, however in Fig. 7 the two solid lines represent the fit to each serrate phase (P2/m)and *Pmmm*). It should be noted that the unit cell volume of mixed phase (5.6-11.4 GPa) is impossible to be determined due to the existence of two phases. But we still can observe the changes of each phase (P2/m and Pmmm) in mixed phase through their respective unit cell volume. The bulk modulus of phase P2/m is 16.16 GPa with $K'_0 = 28.43$, $V_0 = 235.57$ Å³ and that of phase *Pmmm* is 19.45 GPa with $K'_0 = 19.91$, $V_0 = 237.1684 \text{ Å}^3$. The bulk moduli of phenanthrene above 2.2 GPa are almost twice more than the ambient bulk modulus of anthracene^{38,39} which is the isomer of phenanthrene. The increasing bulk moduli infer an enhancement of bond strength during phase transitions and indicate the intrinsic higher compressibility of phenanthrene under high pressure.

At high pressures (>20 GPa) the Raman spectroscopy data show that the material enters an amorphous phase where all the Raman active vibrational modes are lost; however, from the XRD data there is still a periodic structure as diffraction peaks are observed. Although the sample undergoes a chemical reaction to hydrogenated amorphous carbon, some carbon atoms or molecules may still remain on lattice sites. These remained atoms or molecules yield observable periodicity. However, the weak intensity and increased broadness suggest that small crystalline clusters are being observed and there is a coexisting ordered and disordered phase. The similar observation is also made in solvated C₆₀ systems at high pressure reported by Wang et al.⁴⁰ The C₆₀ molecules from the crystalline solvated fullerene phase $C_{60} \cdot m$ -xylene undergo an order-to-disorder transition under compression at approximately 35 GPa but they keep their translational symmetry. However, for pure C₆₀ without m-xylene solvent, the face-centered cubic periodicity of the C60 molecular units disappears when it amorphizes above 30 GPa. Therefore, they suggest that the m-xylene solvent molecules play a crucial role in maintaining the long-range periodicity in the ordered amorphous structure by acting as a spacer between the C_{60} molecules leading to a more rigid structure. In our experiments, coexistence of an ordered and disordered state is obtained in the pure phenanthrene without spacer molecules in contrast to C_{60} · m-xylene. The certain strong interaction must be existed in such system maintaining the long-range order at high pressures. This is important to develop the potential physical properties in this system, such like that the potentially higher T_c of superconductivity could be existed in doped phenanthrene upon heavy compression due to the stability of crystalline characteristic under pressure. Understanding the mechanism of this phenomenon remains an interesting project for future research.

IV. CONCLUSIONS

We performed high pressure measurements of Raman scattering and synchrotron X-ray diffraction of phenanthrene up to 30.8 GPa at room temperature. We determined three phases existed in phenanthrene up to 30.8 GPa. The space groups for the phases were identified to be as follows: $P2_1$ at 0-2.2 GPa, P2/m at 2.2-5.6 GPa, and Pmmm at 11.4–30.8 GPa. At high pressures (>20 GPa) phenanthrene transforms to hydrogenated amorphous carbon where small crystalline clusters exist but the overall bulk structure is destroyed.

ACKNOWLEDGMENTS

This work was supported as part of EFree, an Energy Frontier Research Center funded by the U.S. Department of Energy (DOE), Office of Science under DE-SC0001057. The work done in China was supported by the Cultivation Fund of the Key Scientific and Technical Innovation Project, Ministry of Education of China (No. 708070), the Shenzhen Basic Research Grant (No. JC201105190880A), the National Natural Science Foundation of China (No. 11274335), Guangdong Natural Science Foundation (No. S2012040007929), and the Fundamental Research Funds for the Central Universities SCUT (No. 2012zz0078).

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