PAPER

Negative isotope effect for charge transport in acenes and derivatives – a theoretical conclusion†

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The isotope effect (IE) on charge transport in polyacenes was proposed in 1970 to judge the transport mechanism. However, there had not been a definitive answer for more than 40 years as to whether such an IE is positive or negative, both theoretically and experimentally, because either theory was too approximate or the experimental estimate was too rough to make a judgment. Employing the quantum nuclear tunneling model for organic semiconductors, we investigate the IE on both hole and electron transport for acenes and their derivatives. We show that both ^{13}C-substitution and deuteration lead to a negative IE. By introducing phenyl, chlorine, or alkyl side-chains into acenes, the IE becomes more remarkable, especially for hole transport. The vibrational relaxation processes involving in-plane bending of ring or alkyl side-chain motions are found to be responsible for the IE.

Introduction

Organic semiconductors have long attracted considerable interest because of their unique properties in molecular electronics and photonics, such as organic field effect transistors (OFETs), organic light emitting diodes (OLEDs) and organic solar cells (OSCs).[1–4] Charge carrier mobility, as the crucial factor in the performance of electronic devices, has been widely studied by experimentalists and theorists. Acenes and their derivatives are generally regarded as the prototypical organic molecular semiconductors in OFETs.[5–11] The hole mobility of pentacene single crystal-based OFETs can reach 40 cm^2 V^{-1} s^{-1} at room temperature,[12] whilst that in naphthalene, anthracene and tetracene single crystals can only be about 1 cm^2 V^{-1} s^{-1} or less.[13–16] With the help of chemical substitutions, both the mobility and stability of acene derivatives can be improved. For example, the hole mobilities of the derivatives of tetracene and pentacene, rubrene and 6,13-bis-(triisopropylsilylethynyl) (TIPS)-pentacene are 16 cm^2 V^{-1} s^{-1} (ref. 7) and 2 cm^2 V^{-1} s^{-1},[10,17] respectively. While there has been tremendous progress achieved in materials synthesis and device fabrication for acenes and derivatives, our understanding of the charge transport mechanism is still very limited and under controversy. The measured

temperature-dependent mobility below 100 K normally presents a band-like transport behavior for acenes.[16,18,19] As temperature increases, a band to hopping transition has been reported at room temperature.[13,14,16,18–24] Semiclassical hopping,[25–28] band-like,[27,29,30] and polaron models[31–35] for acenes have been proposed to characterize the transport mechanisms, and one recent experiment showed that the transport in tetracene is actually governed by the hopping mechanism rather than the band model.[36] Moreover, *in situ* charge modulation spectroscopy on an OFET with TIPS-pentacene as the active layer also indicated that the transporting carriers come from localized charges, even at very low temperature, while the mobility decreases with temperature.[10] For understanding such exotic transport behavior, quantum nuclear tunneling of localized charge hopping[37] was suggested to account for such paradoxical phenomena for TIPS-pentacene.[38] Such a nuclear tunneling effect has been adopted in several charge transport models[39–44] to elucidate the transport mechanism in organic semiconductors and polymers well.

To illustrate the role of electron–phonon interactions on charge transport, Munn *et al.* proposed to use the isotope effect (IE) on charge mobility in an anthracene single crystal in 1970.[45] Within the Holstein model with one or two oscillators, and under first-order perturbation and a quasi-localized electron limit, the IE on mobility was found to be positive in the "slow-electron" limit and negative in the "slow-phonon" limit. Their subsequent measurements for electron mobility in the c' direction for the all-deuterated anthracene crystals exhibited a positive IE (11%), which seemed to demonstrate the "slow-electron" picture.[23] In 1971, Morel and Hermann observed a much stronger positive IE (>300%) in the c' direction on electron mobility in all-deuterated anthracene.[46] However, in 1973, they

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overturned this result and reported a 10% negative IE in the c' direction and zero effect in the a and b directions.[18] Later, Schein and McGhie observed an unnoticeable IE on electron mobility in the c' direction in naphthalene.[19] Very recently, Frisbie *et al.* reported a negligible IE for hole transport in all-deuterated rubrene.[7] We recently proposed using the IE effect to probe the quantum nuclear tunneling effect in organic semiconductors such as *N,N'*-n-bis(n-hexyl)-naphthalene diimide (NDI) and *N,N'*-n-bis(n-octyl)-perylene diimide (PDI).[47] Our calculation results indicated that both deuteration and ^{13}C-substitution would decrease electron mobility for both NDI and PDI, since heavier atoms could weaken the quantum nuclear tunneling effect, approaching the semiclassical limit where there is no IE. In addition, we found that no isotope effect should exist in a band-like transport process when acoustic phonon scattering dominates.

In this work, we intend to look at the IE on charge transport in acenes and their derivatives in order to clarify the historical controversy. Although acenes and their derivatives are widely regarded as band-like transport materials, the mobility in the c' direction, which is much lower than that in the a, b directions due to the herringbone crystal packing structure, can still be considered to behave in a hopping mechanism. Here, we focus on the ^{13}C-substitution and deuteration effects on both electron and hole transport in naphthalene, anthracene, tetracene, pentacene and their derivatives. For all acenes and their derivatives, our results show negative effects on both hole and electron mobility by all ^{13}C-substitution or all-deuteration, which is opposite to the conclusions of Munn *et al.*,[23,45] but in agreement with Morel's.[18] For acenes, all-deuteration has little impact on hole mobility, but can reduce electron mobility by *ca.* 5%. All ^{13}C-substitution can reduce hole and electron mobility by *ca.* 5% and 8%, respectively. Moreover, the ^{13}C-substitution effect on hole and electron transport as well as the deuteration effect on electron transport will become weaker as the conjugated length increases for acenes. After substituting with phenyl, chlorine, or alkyl side-chains, the IE of acene derivatives can be strengthened. All of these isotope effects have been investigated in detail *via* normal mode analysis. For the systems with similar reorganization of the energy distribution, the larger the total reorganization energy, the stronger the IE is. If only C=C stretching vibrations make a major contribution to the reorganization energy, the deuteration effect will be slight. If in-plane bending vibrations of aromatic rings also considerably contribute to the reorganization energy, both ^{13}C-substitution and deuteration can lead to a stronger IE on transport for acenes and their derivatives.

Theoretical methodology

The quantum charge transfer (CT) rate from one molecule to another can be derived from the Fermi Golden Rule which can be expressed as

$$W_{i \to f} = \frac{2\pi}{\hbar^2} \left| \langle \Phi_f | H' | \Phi_i \rangle \right|^2 \sum_\upsilon \sum_{\upsilon'} P_{i\upsilon} \left| \langle \Theta_{f\upsilon'} | \Theta_{i\upsilon} \rangle \right|^2 \delta(\omega_{f\upsilon', i\upsilon}), \quad (1)$$

where $\Phi_{i(f)}$ and $\Theta_{i(f)}$ represent the electronic and vibrational wave functions separately, and $P_{i\upsilon}$ denotes the Boltzmann distribution function

$$P_{i\upsilon} = \left[\sum_\upsilon \exp\left(\frac{-E_{i\upsilon}}{kT} \right) \right]^{-1} \exp\left(\frac{-E_{i\upsilon}}{kT} \right). \quad (2)$$

Under the displaced harmonic oscillator approximation,[37,48] eqn (1) can be translated into

$$k^{QM} = \frac{|V|^2}{\hbar^2} \int_{-\infty}^{\infty} dt$$
$$\times \exp\left\{ -\sum_j S_j \left[(2\bar{n}_j + 1) - \bar{n}_j e^{-i\omega_j t} - (\bar{n}_j + 1) e^{i\omega_j t} \right] \right\}. \quad (3)$$

Here, $V = |\langle \Phi_f | H' | \Phi_i \rangle|$ is the intermolecular transfer integral, $\bar{n}_j = 1/[\exp(\hbar\omega_j/k_B T) - 1]$ is the occupation number for the *j*-th vibrational mode with frequency ω_j, and S_j is the Huang–Rhys factor relating to the *j*-th mode:

$$S_i = \frac{\omega_i}{2\hbar} (\Delta Q_i)^2, \quad (4)$$

where ΔQ_i represents the displacement along the *i*-th normal mode coordinate between the equilibrium positions of the charged state and the neutral state (Fig. 1). The reorganization energy in geometry between the neutral and charged states through the *k*th intramolecular vibrational mode is determined by

$$\lambda_k = S_k \hbar \omega_k, \quad (5)$$

and the total reorganization energy for the neutral (λ_1) or the charged molecule (λ_2) is the sum over all modes at each state as

$$\lambda_{1(2)} = \sum_j \lambda_j^{1(2)} = \sum_j S_j^{1(2)} \hbar \omega_j^{1(2)}. \quad (6)$$

We assume the same crystal structures for different isotopes since the molecules have the same equilibrium geometries, and the IE does not modify the intermolecular integral V.
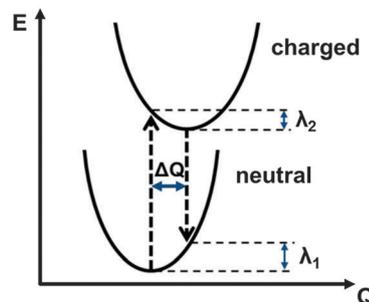
Fig. 1 Schematic representation of the potential energy surfaces of the neutral and charged molecules. ΔQ is the normal mode displacement. λ_1 and λ_2 are reorganization energies for the neutral and charged molecules, respectively.

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Therefore, the IE on the CT rate between two molecules can be expressed as:

$$
\frac{k_{\mathrm{H}} - k_{\mathrm{L}}}{k_{\mathrm{L}}} = \frac{\int_{-\infty}^{\infty} \mathrm{d}t \, \exp\left\{ -\sum_j S_j^{\mathrm{H}} \left[\left(2\bar{n}_j^{\mathrm{H}} + 1 \right) - \bar{n}_j^{\mathrm{H}} \mathrm{e}^{-i\omega_j^{\mathrm{H}} t} - \left(\bar{n}_j^{\mathrm{H}} + 1 \right) \mathrm{e}^{i\omega_j^{\mathrm{H}} t} \right] \right\}}{\int_{-\infty}^{\infty} \mathrm{d}t \, \exp\left\{ -\sum_j S_j^{\mathrm{L}} \left[\left(2\bar{n}_j^{\mathrm{L}} + 1 \right) - \bar{n}_j^{\mathrm{L}} \mathrm{e}^{-i\omega_j^{\mathrm{L}} t} - \left(\bar{n}_j^{\mathrm{L}} + 1 \right) \mathrm{e}^{i\omega_j^{\mathrm{L}} t} \right] \right\}} - 1
\tag{7}
$$

where k_{L} and k_{H} are the CT rates of the light and heavy isotopically substituted systems. Density functional theory (DFT) is applied to calculate the molecular parameters appearing in eqn (3) with the Gaussian 09 package.[49] The neutral and charged geometries of all acenes are optimized with the B3LYP functional[50,51] and the 6-31G(d) basis set. According to previous work, the effect of diffuse functions is negligible, even for reorganization energies of electron-transporting processes.[52] With the help of the program DUSHIN,[53] the corresponding Huang–Rhys factors and the reorganization energies are obtained for each normal mode under the displaced harmonic oscillator approximation. The total reorganization energies of the isotopic systems are also totally the same for the reason of having the same electronic structure. For the rigid systems, the integral part in eqn (3) or (7) is hard to converge without a decay factor. Thus we add a Lorentzian $\mathrm{e}^{-\Gamma|t|}$ factor with a very small broadening $\Gamma = 10 \ \mathrm{cm}^{-1}$ for all systems to guarantee the convergence, which can be regarded as dissipation broadening from the environment.

Results and discussion

According to eqn (7), we calculated the IE from all ^{13}C-substitution and all-deuteration for naphthalene, anthracene, tetracene and pentacene. Even though acenes are typical p-type transport materials, for the sake of comparing with the existing results, we calculate here both the IE on hole transport and on electron transport, as presented in Table 1. Our theoretical results indicate that the IE on both hole and electron transport by ^{13}C-substitution or deuteration are all negative, namely that isotopic substitution on acenes will reduce the hole and electron mobilities. It is understood that both the reorganization energy and the intermolecular transfer integral are independent of isotopic substitution, while lowering frequencies of normal modes implies enhanced scattering with charge carrier (Huang–Rhys factor) and weakened nuclear tunneling ability, thus reducing the CT rate or mobility. The deuteration effect on

electron mobility for anthracene is in contrast to that in ref. 45 but in agreement with Morel's experimental discovery about electron mobility in the c direction for all-deuterated anthracene, indicating the importance of the nuclear tunneling effect. It should be noted that they also found no IE in the a and b directions for anthracene, which can be understood by the band-like theory with acoustic phonon dominance as in our previous calculation.[47]

We find that there is nearly no IE on hole transport for all-deuterated acenes. In contrast, there exists a noticeable deuteration effect (ca. 5%) on electron transport which is one order of magnitude higher than that on hole transport. All ^{13}C-substitution leads to a stronger IE on both electron and hole mobility than deuteration, and the effect on electron transport (8–9%) is onefold increased compared to the effect on hole transport (4–5%). The IE also decreases with the conjugation length. According to our previous study,[47] the necessary condition for a large IE on transport is that the isotopic substitution position should be involved actively in the relevant vibration with appreciable contribution to the reorganization energy and electron–phonon coupling.

The total hole/electron reorganization energies achieved by eqn (6) coincide well with those obtained from the adiabatic potential method (Table 1), and also agree well with previous theoretical and experimental results.[28,54] The reorganization energies projected into normal modes for pristine acenes are presented in Fig. 2. Selected vibration modes with the most significant contributions to the reorganization energy have also been depicted in Fig. 2, and their corresponding frequencies before and after isotopic substitutions are listed in Table 2. For hole transport, there are two most significant modes (modes 2 and 3) contributing to the reorganization energy, which are mainly C=C stretching vibrations accompanied by C–C–H bending vibrations at around 1400 cm^{-1} and 1600 cm^{-1}. Thus, replacing all the backbone ^{12}C atoms by ^{13}C can lead to large decreases in the frequencies of those modes, while changing all the H atoms to D causes little impact on them (Table 2). Therefore, for hole transport, ^{13}C-substitution can lead to a much larger IE than deuteration. For electron transport, in

Table 1 The IE (in %) from all ^{13}C-substitution and all deuteration for four acenes, as well as the corresponding total reorganization energy (λ, in meV) obtained from the adiabatic potential (AP) method and normal mode (NM) analysis

Compounds	Hole				Electron			
	^{12}C → ^{13}C IE	H → D IE	λ_{NM}	λ_{AP}	^{12}C → ^{13}C IE	H → D IE	λ_{NM}	λ_{AP}
Naphthalene	−4.55	−0.86	189	187	−8.81	−6.41	262	261
Anthracene	−3.12	−0.33	141	139	−8.22	−5.33	198	198
Tetracene	−2.80	−0.47	120	116	−7.76	−4.88	164	162
Pentacene	−2.66	−1.05	94	94	−7.42	−4.37	132	132
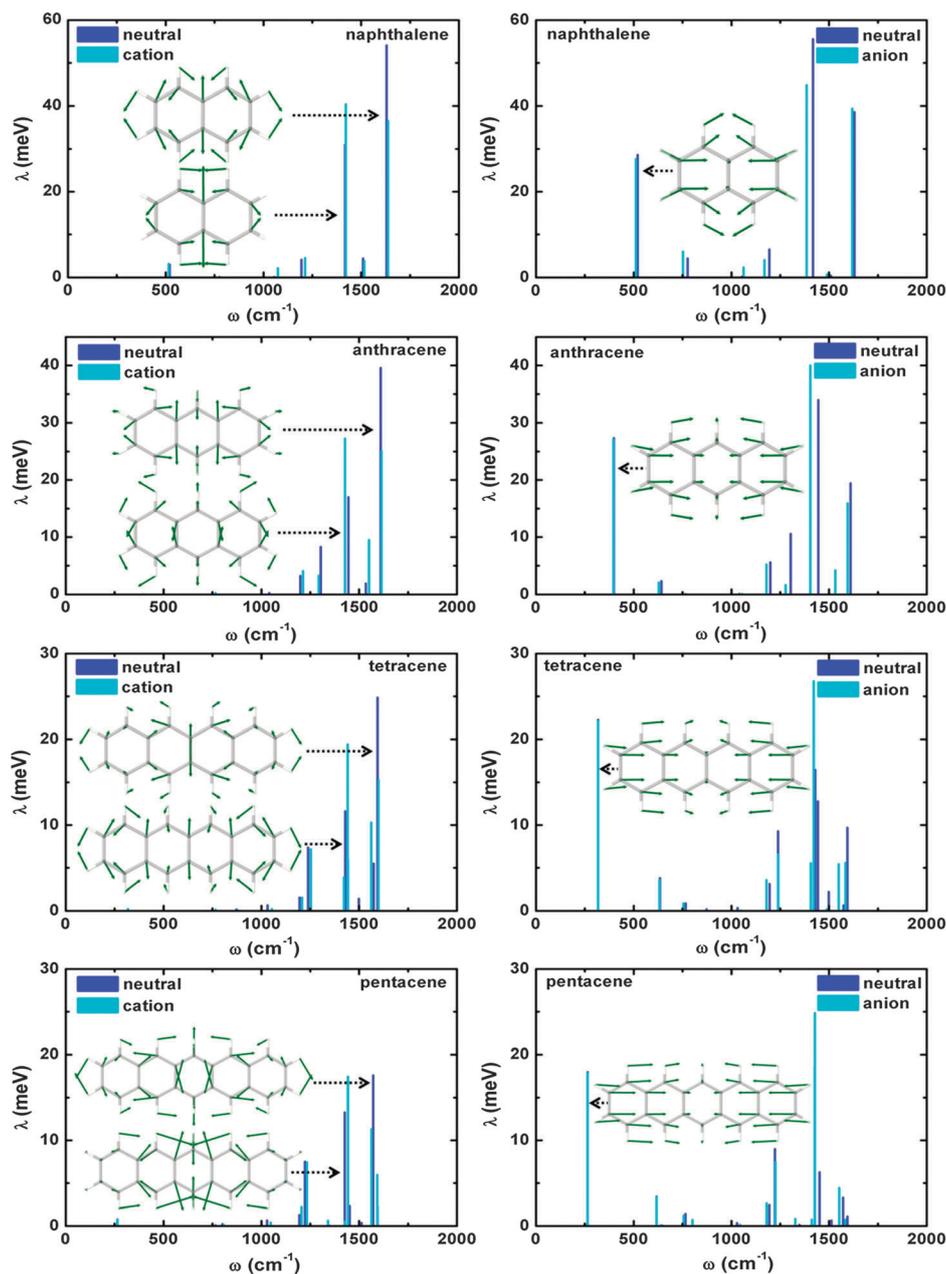
Fig. 2 The reorganization energy projected into normal modes for several pristine acenes. Neutral (cation, anion) represents the reorganization energy caused by the geometry modification at a neutral (cationic, anionic) state. Selected vibration modes are also depicted inside.

addition to the high frequency modes with C=C stretching (modes 2 and 3), another low frequency mode (mode 1) with in-plane bending vibration of the aromatic ring also contributes significantly to the reorganization energy, which leads to a larger reorganization energy than that in hole transport. Both ^{13}C-substitution and deuteration can noticeably reduce the frequency of mode 1, and the frequencies of modes 2 and 3 are also reduced by ^{13}C-substitution (Table 2). Therefore, both ^{13}C-substitution and deuteration cause an observable IE on electron transport, with the former stronger than the latter. Note that such a difference in the reorganization energy of mode 1 between hole and electron transport is directly attributed to the

difference in equilibrium geometry displacement from the neutral to the cationic/anionic state as well as in the electronic distribution of the HOMO/LUMO, which has been fully analyzed in the ESI.†

As the conjugation length increases, the reorganization energy decreases. The vibrations involving carbon atoms contribute most to the hole/electron reorganization energies, and vibrations involving hydrogen atoms contribute significantly to the electron reorganization energy whilst contributing little to the hole reorganization energy. Thus, the ^{13}C-subsitution effect on hole and electron transport as well as the deuteration effect on electron transport show positive correlations with the reorganization

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Table 2 Frequencies (in cm^{-1}) of the three vibrational modes presented in Fig. 2 for all the isotopic acenes in their neutral states[a]

	Naphthalene			Anthracene			Tetracene			Pentacene		
	$C_{10}H_8$	$^{13}C_{10}H_8$	$C_{10}D_8$	$C_{14}H_{10}$	$^{13}C_{14}H_{10}$	$C_{14}D_{10}$	$C_{18}H_{12}$	$^{13}C_{18}H_{12}$	$C_{18}D_{12}$	$C_{22}H_{14}$	$^{13}C_{22}H_{14}$	$C_{22}D_{14}$
Mode 1	520.61	501.56 (−3.66%)	500.52 (−3.86%)	398.90	384.27 (−3.66%)	384.41 (−3.66%)	318.52	306.78 (−3.68%)	307.93 (−3.32%)	264.13	254.35 (−3.70%)	255.97 (−3.09%)
Mode 2	1417.37	1363.41 (−3.81%)	1421.82 (0.31%)	1444.70	1389.05 (−3.85%)	1430.47 (−0.98%)	1428.24	1373.81 (−3.81%)	1428.09 (−0.01%)	1426.21	1373.33 (−3.70%)	1420.86 (−0.38%)
Mode 3	1630.48	1571.21 (−3.63%)	1602.37 (−1.72%)	1609.66	1550.54 (−3.67%)	1584.38 (−1.57%)	1593.89	1535.36 (−3.67%)	1569.56 (−1.53%)	1572.08	1515.87 (−3.58%)	1563.76 (−0.53%)

[a] The relative changes of frequencies for all ^{13}C-substituted or all-deuterated acenes compared to those of pristine acenes are labeled in parentheses.
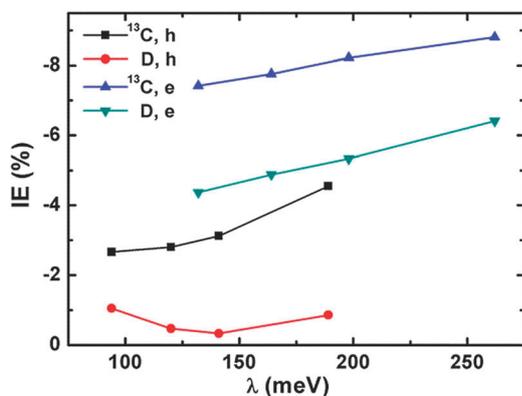
Fig. 3 The relationship between reorganization energy and IE on hole (h) and electron (e) transport for acenes by all ^{13}C-substitution (^{13}C) or all-deuteration (D).

energy for acenes, while the deuteration effect on hole transport has no relation to reorganization energy, as shown in Fig. 3. From Fig. 2, the hole/electron reorganization energy distributions on normal modes for all acenes are similar to each other. We can use the effective frequency to interpret the relationship to the IE which can be expressed as[55]

$$\omega_{\text{eff}} = \sqrt{\sum_i \omega_i^2 \lambda_i \Big/ \sum_i \lambda_i}. \tag{8}$$

The effective frequencies of acenes for hole transport are in the range of 1400–1500 cm^{-1}, and for electron transport are in the range of 1100–1300 cm^{-1} (see Table 3). Furthermore, the relative reductions of effective frequency by all ^{13}C-substitution (all-deuteration) are similar for all acenes for hole (electron) transport.

Since the effective frequencies in acenes are all similar for hole (electron) transport, the frequency reductions upon ^{13}C-substitution and deuteration are also similar. According to eqn (6), the larger the reorganization energy, the larger is the Huang–Rhys factor. Since the occupation number $\bar{n}$ is close to zero for frequencies larger than 1000 cm^{-1}, acenes with larger reorganization energies will lead to lower CT rates. Considering that acenes possess a smaller effective frequency and a larger reorganization energy in electron transport than in hole transport, the similar frequency reduction after ^{13}C-substitution will lead to a larger increase of the Huang–Rhys factor and a stronger IE on electron transport; while the much larger frequency reduction in electron transport after deuteration can result in a much stronger deuteration effect compared to that for hole transport.

We next extended the calculation for several acene derivatives as shown in Fig. 4, bis(phenylvinyl)-anthracene (**1**), bis(phenylethynyl)-anthracene (**2**), dichlorotetracene (**3**), tetrachlorotetracene (**4**), and TIPS-pentacene (**5**). The IE caused by replacing all the ^{12}C atoms with ^{13}C or all the H atoms with D have been computed as shown in Table 4. It is seen that the IE is generally stronger than that of acenes. Especially for hole transport, most ^{13}C-substitution effects are 2–3 times greater and the deuteration effects increase by one order of magnitude. All deuteration on TIPS-pentacene can reduce hole and electron mobility by *ca.* 15%.

For structures **1** and **2**, the contributions from the aromatic ring in-plane bending vibration to the hole/electron reorganization energies are significantly increased after phenylvinyl or phenylethynyl substitution, as shown in Table S2 (ESI†), especially for hole transport, thus all ^{13}C-substitution or deuteration can lead to a dramatic IE on both hole and electron mobilities. For dichlorotetracene (**3**), introducing two chlorines

Table 3 The effective frequencies (in cm^{-1}) of acenes and their isotopic substitutions for hole and electron transport[a]

	Naphthalene			Anthracene			Tetracene			Pentacene		
	$C_{10}H_8$	$^{13}C_{10}H_8$	$C_{10}D_8$	$C_{14}H_{10}$	$^{13}C_{14}H_{10}$	$C_{14}D_{10}$	$C_{18}H_{12}$	$^{13}C_{18}H_{12}$	$C_{18}D_{12}$	$C_{22}H_{14}$	$^{13}C_{22}H_{14}$	$C_{22}D_{14}$
Hole	1512.88	1453.99 (−3.89%)	1509.07 (−0.25%)	1521.02	1461.98 (−3.88%)	1515.85 (−0.34%)	1488.71	1430.91 (−3.88%)	1483.68 (−0.34%)	1452.36	1396.16 (−3.87%)	1446.55 (−0.40%)
Electron	1336.05	1288.16 (−3.58%)	1306.54 (−2.21%)	1263.93	1218.55 (−3.59%)	1236.47 (−2.17%)	1218.58	1174.63 (−3.61%)	1193.56 (−2.05%)	1182.47	1139.77 (−3.61%)	1158.246 (−2.05%)

[a] The relative changes of frequencies for all ^{13}C-substituted or all-deuterated acenes compared to those of pristine acenes are labeled in parentheses.
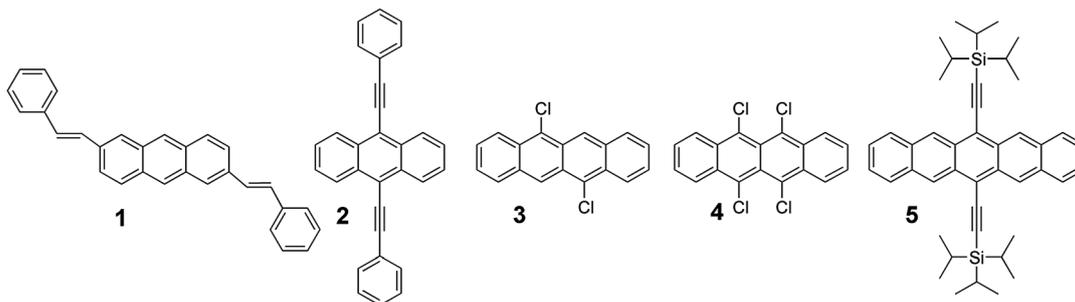
Fig. 4 Molecular structures of the common acene derivatives considered in this work.

Table 4 The IE (in %) on both hole and electron transport for the acene derivatives shown in Fig. 4 by all/backbone ^{13}C-substitution (^{12}C → ^{13}C) or deuteration (H → D) and the corresponding reorganization energy (λ, in meV) obtained by normal mode (NM) analysis and the adiabatic potential (AP) method

	Hole				Electron			
Compound	^{12}C → ^{13}C IE	H → D IE	λ_{NM}	λ_{AP}	^{12}C → ^{13}C IE	H → D IE	λ_{NM}	λ_{AP}
1	−9.75	−6.46	160	158	−10.56	−10.60	199	197
2	−7.84	−4.35	141	140	−8.05	−4.45	184	183
3	−3.09	−0.28	139	138	−7.63	−4.90	174	174
4	−8.61	−5.19	159	167	−9.59	−5.96	176	174
5	−7.03	−14.76	137	134	−9.59	−16.11	199	197

into tetracene causes little change on the vibration type and reorganization energy of normal modes compared to tetracene, so that the IE is similar to that in tetracene. For tetrachlorotetracene (**4**), four chlorine substituents can break down the planarity of tetracene, so that ring in-/out-plane bending vibrations make an important contribution to the hole/electron reorganization energy. Thus, there are remarkable IEs on hole/electron transport from all ^{13}C-substitution or from deuteration. For TIPS-pentacene (**5**), the in-plane bending vibration of pentacene and the rocking/wagging vibrations of the alkyl side-chains all make significant contributions to the hole/electron reorganization energy. Since all-deuteration can dramatically reduce the frequencies of those vibrations, the deuteration effects on both hole and electron transport are as strong as *ca.* −15%. Therefore, introducing phenyl, chlorine, or alkyl side-chains into acenes as in structures **1**, **2**, **4**, and **5** has changed reorganization energy distributions dramatically, and the contribution made by the vibrations which involve isotopic substitution positions is increased, thus the IE is naturally strengthened in comparison to that for the parent acenes.

Conclusions

We employed the quantum nuclear tunneling model to systematically investigate the IE on both hole and electron transport for acenes and their derivatives. Historically, both positive and negative IEs have been proposed both theoretically and experimentally for acenes. This work shows that both ^{13}C-substitution and deuteration always lead to a negative IE for both hole and electron mobility, which is in agreement with Mey *et al.*,[18] but in contrast to Munn *et al.*[23] For naphthalene, anthracene, tetracene and pentacene, deuteration has almost no impact on hole transport, whilst its effect on electron transport is about one order of magnitude higher, reaching *ca.* −5% for all acenes. The ^{13}C-substitution effect is usually less than −5% for hole transport, while it reaches *ca.* −8% for electron transport. Since C=C stretching vibrations are the major contribution to the reorganization energy in the hole transfer process, ^{13}C-substitution can lead to a remarkable effect on hole transport, while deuteration causes little effect. However in the electron transfer process, in addition to C=C stretching, the in-plane ring bending also makes a considerable contribution to the reorganization energy, which leads to a much stronger deuteration and ^{13}C-substitution effects. Moreover, introducing phenyl, chlorine, or alkyl side-chains into acenes can cause a more pronounced IE for both hole and electron transports.

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