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Negative isotope effect for charge transport in acenes and derivatives

– A theoretical conclusion

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Abstract: The isotope effect (IE) on charge transport in polyacenes had been proposed in 1970 to judge transport mechanism. However, there had not been definitive answer for more than 40 years as whether such IE is positive or negative, both theoretically and experimentally, because either theory was too approximate or experimental estimate was too rough to make judgment. Employing the quantum nuclear tunneling model for organic semiconductor, we investigate the IE on both hole and electron transport for acenes and their derivatives. We show that both ¹³C-substitution and deuteration lead to negative IE. By introducing phenyl, chlorine, or alkyl side-chains into acenes, IE become 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 IE.

Introduction

Organic semiconductors have long attracted considerable interests because of their unique properties in molecular electronics and photonics, such as organic field effect transistors (OFET), organic light emitting diodes (OLED) and organic solar cells (OSC).¹⁻⁴ Charge carrier mobility, as the crucial factor on the performance of electronic devices has been widely studied by experimentalists and theorists. Acenes and derivatives are generally regarded as the prototypical organic molecular semiconductors in OFET.⁵⁻¹¹ The hole mobility of pentacene single crystal based OFET can reach $40 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature,¹² while that in naphthalene, anthracene and tetracene single crystals can only be about $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ 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 $16 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ⁷ and $2 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ^{10, 17}, respectively. While there have been tremendous progresses achieved in materials synthesis and device fabrication for acenes and derivatives, our understanding on 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 shows that the transport in tetracene is actually governed by the hopping mechanism rather than band model.³⁶ Moreover, in situ charge modulation spectroscopy on OFET with TIPS-pentacene as the active layer also indicates 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 hopping³⁷ was suggested to account for such paradoxical phenomena for TIPS-pentacene.³⁸ Such nuclear tunneling effect has been adopted in several charge transport models³⁹⁻⁴⁴ to well elucidate the transport mechanism in organic semiconductors and polymers.

To illustrate the role of electron-phonon interaction on charge transport, Munn *et al.* have proposed to use isotope effect (IE) for charge mobility in anthracene single crystal in 1970.⁴⁵ Within the Holstein model with one or two oscillators, and under first-order perturbation and quasi-localized electron limit, the IE on mobility was found to be positive in the “slow-electron” end and negative in “slow-phonon” end. Their subsequent measurements for electron mobility in *c'* direction for the all-deuterated anthracene crystals exhibited a positive IE (11%), which seemed to demonstrate “slow-electron” picture.²³ In 1971, Morel and Hermann observed a much stronger positive IE (> 300%) in *c'* direction's also for electron mobility in all-deuterated anthracene.⁴⁶ However, in 1973, they overturned this result and reported a 10% negative IE in the *c'* direction and zero effect in *a* and *b* directions.¹⁸ Later, Schein and McGhie observed unnoticeable IE on electron mobility in *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 IE effect to probe quantum nuclear tunneling effect in organic semiconductors such as NDI and PDI.⁴⁷ Our calculation results indicated that both deuteration and ¹³C-substitution would decrease electron mobility for both NDI and PDI, since heavier atoms could weaken the quantum nuclear tunneling effect, approaching the semiclassical end where there is no IE. In addition, we found 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 c' direction, which is much lower than that in a , b directions due to the herringbone crystal packing structure, can still be considered to behave in 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 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, ^{13}C -substitution effect on hole and electron transport as well as deuteration effect on electron transport will become weaker as conjugated length increasing 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 deeply understood via normal mode analysis. For the systems with similar reorganization energy distribution, the larger total reorganization energy, the stronger IE is. If only C=C stretching vibration makes major contribution to reorganization energy, deuteration effect will be slight. If in-plane bending vibration of aromatic ring also considerably contributes to reorganization energy, both ^{13}C -substitution and deuteration can lead to 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 Fermi Golden Rule which can be expressed as

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

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

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

Under the displaced harmonic oscillator approximation,^{37, 48} eqn (1) can be translated into

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

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 of 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 charged state and 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 neutral (λ_1) or charged molecule (λ_2) is the sum over all modes at each state as

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

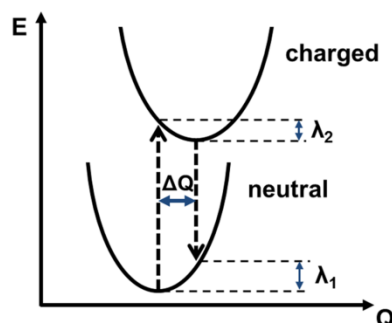


Fig. 1 Schematic representation of the potential energy surface of the neutral and charged molecules.

ΔQ is the normal mode displacement. λ_1 and λ_2 are reorganization energies for neutral and charged

molecules respectively.

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

$$\frac{k_H - k_L}{k_L} = \frac{\int_{-\infty}^{\infty} dt \exp \left\{ -\sum_j S_j^H \left[(2\bar{n}_j^H + 1) - \bar{n}_j^H e^{-i\omega_j^H t} - (\bar{n}_j^H + 1) e^{i\omega_j^H t} \right] \right\}}{\int_{-\infty}^{\infty} dt \exp \left\{ -\sum_j S_j^L \left[(2\bar{n}_j^L + 1) - \bar{n}_j^L e^{-i\omega_j^L t} - (\bar{n}_j^L + 1) e^{i\omega_j^L t} \right] \right\}} - 1 \quad (7)$$

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 molecular parameters appeared in eqn (3) with Gaussian 09 package.⁴⁹ The neutral and charged geometries of all acenes are optimized with B3LYP functional^{50, 51} and 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 DUSHIN program,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 isotopic systems are also totally the same for the reason of 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 $e^{-\Gamma|t|}$ factor with a very small broadening $\Gamma = 10 \text{ cm}^{-1}$ for all systems to guarantee the convergence, which can be regarded as dissipation broadening from the environments.

Results and Discussion

According to eqn (7), we calculate the IE by 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 here calculate both the IE of hole

transport and 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 isotopic substitution on acenes will reduce the hole and electron mobility. It is understood that both reorganization energy and intermolecular transfer integral are independent on 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 in *c* direction's electron mobility for all-deuterated anthracene, indicating the importance of nuclear tunneling effect. It should be noted that they also found no IE in *a* and *b* directions for anthracene, which can be understood by the band-like theory with acoustic phonon dominance as our previous calculation.⁴⁷

We find that there is nearly no IE on hole transport for all-deuterated acenes. To the contrary, there exists 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 stronger IE on both electron and hole mobility than deuteration, and the effect on electron transport (8%~9%) is onefold increased compared to hole transport (4%~5%). IE also decreases with the conjugation length. According to our previous study,⁴⁷ the necessary condition for 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.

Table 1 IE (in %) by 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 method (AP) and normal mode analysis (NM).

compounds	hole	electron
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	$^{12}\text{C}\rightarrow^{13}\text{C}$ IE	H \rightarrow D IE	λ_{NM}	λ_{AP}	$^{12}\text{C}\rightarrow^{13}\text{C}$ IE	H \rightarrow 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

The total hole/electron reorganization energies achieved by eqn (6) show good coincidence with those obtained from 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 have been presented in Fig. 2. Selected vibration modes with most significant contribution 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**) contributed to the reorganization energy which are mainly C=C stretching vibration accompanied with C-C-H bending vibration around 1400 cm^{-1} and 1600 cm^{-1} . Thus, replacing all backbone ^{12}C by ^{13}C can lead to large decreases on frequencies of those modes, while changing all H to D causes little impact on them (Table 2). Therefore for hole transport, ^{13}C -substitution can lead to much larger IE than deuteration. For electron transport, in 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 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 observable IE on electron transport, with the former stronger than the latter. Note that such a difference in reorganization energy of **Mode 1** between hole and electron transport is directly attributed to the difference in equilibrium geometry displacement from neutral to cation/anion state as well as in the electronic distribution of HOMO/LUMO, which has

been fully analyzed in Supporting Information.

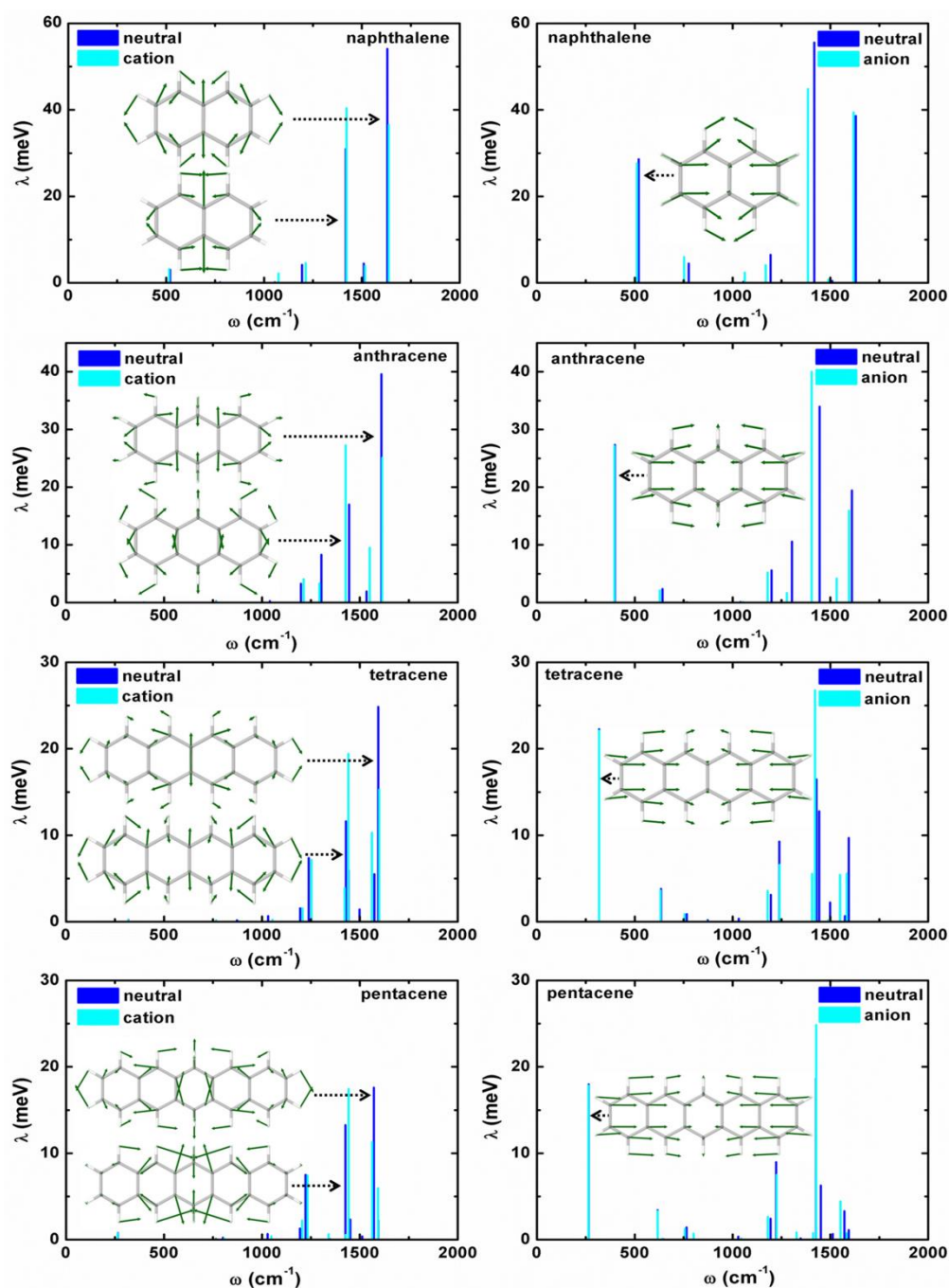


Fig. 2 The reorganization energy projected into normal modes for pristine acenes. *Neutral* (*cation*, *anion*) represents the reorganization energy caused by the geometry modification at neutral (*cation*, *anion*) state. Selected vibration modes are also depicted inside.

Table 2 Frequencies (in cm^{-1}) of three vibration modes presented in Fig. 2 for all isotopic acenes at 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	500.52	398.90	384.27	384.41	318.52	306.78	307.93	264.13	254.35	255.97
		(-3.66%)	(-3.86%)		(-3.66%)	(-3.66%)		(-3.68%)	(-3.32%)		(-3.70%)	(-3.09%)
Mode 2	1417.37	1363.41	1421.82	1444.70	1389.05	1430.47	1428.24	1373.81	1428.09	1426.21	1373.33	1420.86
		(-3.81%)	(0.31%)		(-3.85%)	(-0.98%)		(-3.81%)	(-0.01%)		(-3.70%)	(-0.38%)
Mode 3	1630.48	1571.21	1602.37	1609.66	1550.54	1584.38	1593.89	1535.36	1569.56	1572.08	1515.87	1563.76
		(-3.63%)	(-1.72%)		(-3.67%)	(-1.57%)		(-3.67%)	(-1.53%)		(-3.58%)	(-0.53%)

^aThe relative changes of frequencies for all ¹³C-substituted or all-deuterated acenes compared to pristine acenes are labeled in parentheses.

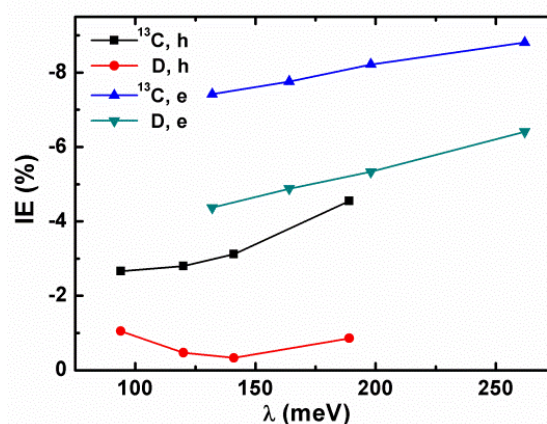


Fig. 3 The relationship between reorganization energy and IE on hole (h) and electron (e) transport for acenes by all ¹³C-substitution (¹³C) or all-deuteration (D).

As the conjugation length increases, the reorganization energy decreases. The vibrations involved by carbon contribute most to hole/electron reorganization energy, and vibrations involved by hydrogen contribute significantly to electron reorganization energy while contribute little to hole reorganization energy. Thus, the ¹³C-substitution effect on hole and electron transport as well as the deuteration effect on electron transport show positive correlations with the reorganization energy for acenes, while deuteration effect on hole transport has no relation to reorganization energy, seeing 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 its relation to IE which can be expressed as⁵⁵

$$\omega_{\text{eff}} = \sqrt{\sum_i \omega_i^2 \lambda_i / \sum_i \lambda_i} \quad (8)$$

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 ¹³C-substituting (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 ¹³C-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 with frequency larger than 1000 cm⁻¹, acenes with larger reorganization energy will lead to less CT rate. Considering that acenes possess smaller effective frequency and larger reorganization energy in electron transport than hole transport, the similar frequency reduction after ¹³C-substitution will lead to larger increase on Huang-Rhys factor and stronger IE on electron transport; while much larger frequency reduction in electron transport after deuteration can result to much stronger deuteration effect compared to hole transport.

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	1509.07	1521.02	1461.98	1515.85	1488.71	1430.91	1483.68	1452.36	1396.16	1446.55
		(-3.89%)	(-0.25%)		(-3.88%)	(-0.34%)		(-3.88%)	(-0.34%)		(-3.87%)	(-0.40%)
electron	1336.05	1288.16	1306.54	1263.93	1218.55	1236.47	1218.58	1174.63	1193.56	1182.47	1139.77	1158.246
		(-3.58%)	(-2.21%)		(-3.59%)	(-2.17%)		(-3.61%)	(-2.05%)		(-3.61%)	(-2.05%)

^aThe relative changes of frequencies for all ¹³C-substituted or all-deuterated acenes compared to pristine acenes are labeled in parentheses.

We next extend 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 ^{12}C atoms with ^{13}C or all H atoms with D have been computed as shown in Table 4. It is seen that IE is generally stronger than that of acenes. Especially for hole transport, most ^{13}C -substitution effects are 2-3 times increase and the deuteration effects are one order of magnitude increase. All deuteration on TIPS-pentacene can reduce hole and electron mobility by ca. 15%.

For **1** and **2**, the contribution from aromatic ring in-plane bending vibration to hole/electron reorganization energy are significantly increased after phenylvinyl or phenylethynyl substitution, seeing Table S2 (ESI[†]), especially for hole transport, thus all ^{13}C -substitution or deuteration can lead to dramatic IE on both hole and electron mobility. For dichlorotetracene (**3**), introducing two chlorines into tetracene causes little change on vibration type and reorganization energy of normal modes compared to tetracene, so that IE is similar to those in tetracene. While for tetrachlorotetracene (**4**), four chlorines replaced can break down the planarity of tetracene, so that ring in-/out-plane bending vibration make important contribution to hole/electron reorganization energy. Thus, there are remarkable IEs on hole/electron transport by all ^{13}C -substitution or deuteration. For TIPS-pentacene (**5**), the in-plane bending vibration of pentacene and the rocking/wagging vibrations of alkyl side-chain all make significant contribution to hole/electron reorganization energy. Since all-deuteration can dramatically reduce the frequencies of those vibrations, deuteration effect on both hole and electron transport are as strong as ca. -15%. Therefore, introducing phenyl, chlorine, or alkyl side-chains into acenes for **1**, **2**, **4**, and **5** has changed reorganization energy distribution dramatically, and the contribution made by the vibrations that isotopic substitution positions involved is increasing, thus IE is naturally strengthened compared to their parents.

Fig. 4 Molecular structures of the common acene derivatives considered in this work.

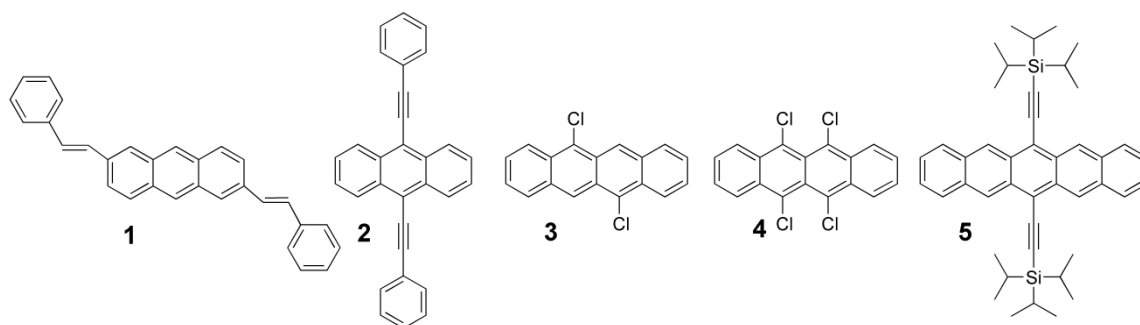


Table 4 IE (in %) on both hole and electron transport for acene derivatives shown in Fig. 4 by all/backbone ^{13}C -substitution ($^{12}\text{C}\rightarrow^{13}\text{C}$) or deuteration ($\text{H}\rightarrow\text{D}$) and corresponding reorganization energy (λ , in meV) obtained by normal mode analysis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

Compd.	hole				electron			
	$^{12}\text{C}\rightarrow^{13}\text{C}$ IE	$\text{H}\rightarrow\text{D}$ IE	λ_{NM}	λ_{AP}	$^{12}\text{C}\rightarrow^{13}\text{C}$ IE	$\text{H}\rightarrow\text{D}$ 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

Conclusions

We employ 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 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 nearly no impact on hole transport, while 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 vibration is the major contribution to reorganization energy

in hole transfer process, ^{13}C -substitution can lead to remarkable effect on hole transport, while deuteration causes little effect. However in electron transfer process, in addition to C=C stretching, the in-plane bending of ring also make considerable contribution to the reorganization energy, which leads to much stronger deuteration effect as well as ^{13}C -substitution effect. Moreover, introducing phenyl, chlorine, or alkyl side-chains into acenes can cause more pronounced IE for both hole and electron transports.

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Notes

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