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Theoretical study of substitution effects on molecular reorganization energy in organic semiconductors

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Chemical substitutions are powerful molecular design tools to enhance the performance of organic semiconductors, for instance, to improve solubility, intermolecular stacking, or film quality. However, at the microscopic level, substitutions in general tend to increase the molecular reorganization energy and thus decrease the intrinsic charge-carrier mobility. Through density functional theory calculations, we elucidate strategies that could be followed to reduce the reorganization energy upon chemical substitution. Specific examples are given here for hole-transport materials including indolocarbazoles and several triarylamine derivatives. Through decomposition of the total reorganization energy into the internal coordinate space, we are able to identify the molecular segment that provides the most important contributions to the reorganization energy. It is found that when substitution reduces (enhances) the amplitude of the relevant frontier molecular orbital in that segment, the total reorganization energy decreases (increases). In particular, chlorination at appropriate positions can significantly reduce the reorganization energy. Several other substituents are shown to play a similar role, to a greater or lesser extent. © *2011 American Institute of Physics*. [doi:10.1063/1.3632105]

I. INTRODUCTION

Organic semiconductors have attracted considerable attention in recent years because of the growing interest in low-cost, light-weight, and flexible opto-electronic device applications.[1,2] In these applications, the efficiency of charge transport within the organic layers plays a key role. Therefore, the mechanism of charge transport, especially its evolution as a function of temperature, has attracted much attention recently.[3–6] Transport models have been proposed in two extreme regimes: the band regime for delocalized electrons and the hopping regime for localized charges. Depending on the relative magnitude of the parameters in the Hamiltonian, the regime of charge transport can be predicted.[4] There has been experimental evidence for band-like transport in organic single crystals, where the mobility decreases with temperature. Interestingly, however, Nan *et al.* have presented a study[5] indicating that, even within a localized charge picture, when the molecule is coupled to high-frequency intramolecular vibration modes and the quantum nature of such vibrations is taken into account, a "band-like" charge diffusion behavior can result; in this instance, the charge mobility is calculated to decrease with temperature, in contrast to the thermal activation behavior obtained in the context of the semi-classical Marcus theory where phonons are assumed to be classical. Thus, this model provides a bridge between the two limiting behaviors.

Regardless of the exact nature of the transport mechanism, the carrier mobility increases with the intermolecular electronic coupling (V) and decreases with the local electron-phonon coupling (λ, reorganization energy). Therefore, these two parameters have been evaluated for many systems.[7,8] Designing functional organic materials with large mobility has been a central challenge in the field of organic electronics. Many attempts have been made to improve the charge-transport properties of well-known organic semiconductors via substitution or functionalization.[9,10] For example, halogen substitutions have been used to promote molecular stacking,[11,12] or to alter the carrier type.[13,14] However, the reorganization energies, and consequently the activation barriers for electron transfer, have been found to increase significantly in the case of many substitutions.[15,16] In particular, perfluorination was found to more than double the reorganization energy of tetracene and pentacene;[17,18] partial fluorination and alkoxy substitution of tetracene have also led to larger reorganization energies, while alkyl substitution has been found to produce a lesser impact.[19] Heterocyclic oligomers including thiophenes, furans, and pyrroles have also been subjected to various substitutions with, for instance, fluoro, isobenzo, ethylenedioxy, cyano, trifluoromethyl, or amino groups; here as well, the substitutions were found to increase the reorganization energies significantly.[20] To the best of our knowledge, the only exceptions correspond to cyano and isobenzo groups that have been shown to reduce the internal reorganization energy for pentacene, tetracene, and heterocyclic oligomers.[20,21] It would thus be useful to gain a better understanding of the

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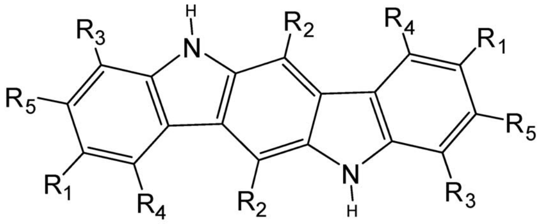


1: R1=R2=R3=R4=R5=H ; **1a**: R1=Cl; R2=R3=R4=R5=H ;

1b: R5=Cl; R1=R3=R4=R5=H; **c**: R2=Cl; R1=R2=R4=R5=H;

d : R3=Cl; R1=R2=R3=R5=H; **e** : R4=Cl; R1=R2=R3=R4=H

FIG. 1. Molecular structures of 1, 1a, 1b, c, d, and e.

impact of chemical substitution on the molecular reorganization energy through quantum-mechanics calculations.

Indolo[3,2-b]carbazole derivatives, see Fig. 1, represent a class of hole-transport materials for which the effect of various substitution groups on the transport properties has been experimentally investigated.[22] Ong *et al*. have found that the parent indolocarbazole compound exhibits a low mobility, on the order of 5∼6 × 10^{-3} cm^2 V^{-1} s^{-1} at low temperature (25 K). The 3,9-dichloro derivative (**1b**) also gives a low mobility of 1.2 × 10^{-4} at 25 K and 2∼3.5 × 10^{-3} cm^2 V^{-1} s^{-1} at 70 K. However, the 2,8-dichloro derivative (**1a**) exhibits higher mobility of 2∼3 × 10^{-2} cm^2 V^{-1} s^{-1} at 25 K and 0.85–1.4 × 10^{-1} cm^2 V^{-1} s^{-1} at 70 K. It was assumed that the higher mobility of (**1a**) is due to differences in molecular packing with respect to (**1**) or (**1b**).[22(d)]

Here, we use density functional theory (DFT) to investigate the effects of substitution on the reorganization energy in **1**. Our results show that the reorganization energy in indolo [3,2-b]carbazole derivatives can be substantially reduced by substitution at appropriate positions. Our analysis is based on an internal-coordinate decomposition, which highlights the chemical nature of the charge-relaxation process. This analysis can improve molecular design by describing which functional groups should be added in which positions in order to reduce the molecular reorganization energy.

II. THEORETICAL METHODOLOGY

The total reorganization energy is usually evaluated based on adiabatic potential energy surfaces (AP), see Fig. 2:

$$\lambda^{(1)} = E^{(1)}(M) - E^{(0)}(M), \quad \lambda^{(2)} = E^{(1)}(M^{\bullet +}) - E^{(0)}(M^{\bullet +}). \tag{1}$$

Here, $E^{(0)}(M)$ and $E^{(0)}(M^{\bullet +})$ denote the ground-state energies of the neutral state and of the charged state, respectively; $E^{(1)}(M)$ is the energy of the neutral molecule in the optimized geometry of the ion state, and $E^{(1)}(M^{\bullet +})$ is the energy of the charged state at the optimized geometry of the neutral molecule. The total reorganization energy consists of two terms corresponding to the geometry relaxation energies ($\lambda^{(1)}$and $\lambda^{(2)}$) when going from the neutral-state geometry to the charged-state geometry and vice versa.[23,24]

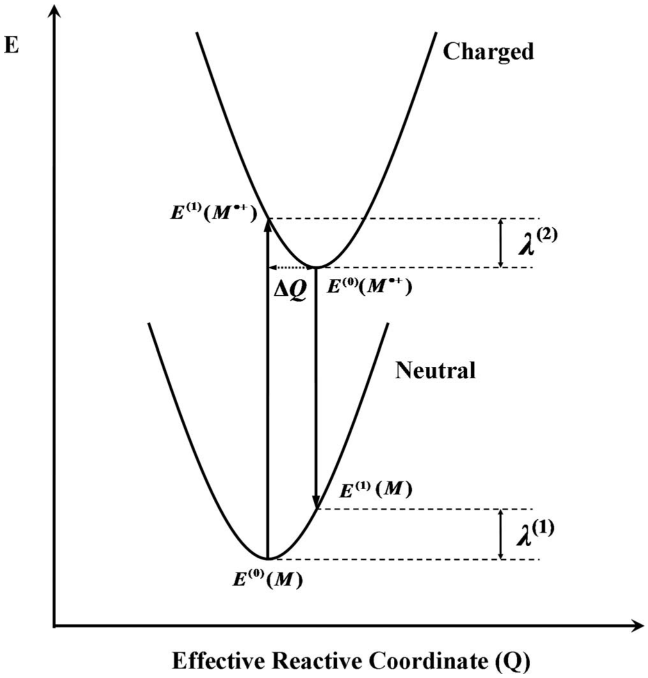


FIG. 2. Sketch of the potential energy surfaces for neutral and cationic molecules, illustrating the normal-mode displacement (ΔQ) and the relaxation energies ($\lambda^{(1)}$ and $\lambda^{(2)}$).

An alternative way to evaluate the reorganization energy is to rely on a normal-mode (NM) analysis. The total reorganization energy (λ) obtained from both AP and NM approaches are in excellent agreement.[27,29] The NM analysis has been exploited to simulate the shape of the first ionization peak in gas-phase UPS spectra; the agreement between simulated and experimental spectra validates the use of DFT to estimate the reorganization energy;[28,29] therefore, the normal-mode analysis based on DFT calculations has been adopted to evaluate the total reorganization energy throughout this work. Within the harmonic approximation, the total reorganization energy reads[25]

$$\lambda = \sum_i \lambda_i = \sum_i \frac{1}{2}\omega_i^2 \Delta Q_i^2. \tag{2}$$

Here, λ_i is the reorganization energy due to mode i with frequencyω_i. ΔQ_i represents the displacement along the ith normal mode coordinate between the equilibrium positions of charge state and neutral state, see Fig. 2. The total reorganization energy is obtained by summation over all vibrational modes. The normal displacements ΔQ_i between the neutral state and the charged state are evaluated with the DUSHIN program.[25] The molecular geometries and normal modes for the ground and charged states were calculated using the B3LYP hybrid density functional in conjunction with the 6–31g(d) basis set as implemented in the GAUSSIAN09 package.[26] In order to better understand the contribution of the local structure to the total reorganization energy, the displacements along normal modes can be represented via rectilinear displacements in Cartesian coordinates

(R) as

$$\Delta \mathbf{Q} = \mathbf{C}^T \mathbf{m}^{1/2} (\mathbf{R} - \mathbf{R}_0). \tag{3}$$

Here, the columns of **C** represent the n_v eigenvectors of the normal modes; **m** is a (3n × 3n) diagonal matrix whose nonzero elements correspond to the masses associated with the Cartesian coordinates.

Equations (2) and (3) have been widely employed in the literature.[27] However, since normal modes represent a linear combination of all atomic molecular coordinates, it is difficult to visualize the variations in reorganization energy due to local structural modifications. We show here that the use of internal coordinates, that provide a direct link to the chemical structure, can be very useful in such instances. Following Reimers,[25] we express the normal-mode coordinates as linear combinations of internal coordinates:

$$\Delta Q_i = \sum_j \alpha_{ij} \Delta S_j, \tag{4}$$

$$\Delta S'' = \mathbf{B}''(\mathbf{R} - \mathbf{R}_0), \quad \Delta S''_i = T_{ij} \Delta S_j, \quad \mathbf{B}'' = \mathbf{TB}. \tag{5}$$

Here, **B** is the Wilson matrix. The non-orthogonal and orthogonal non-redundant rectilinear internal displacements $\Delta S'(B')$ and $\Delta S''(\mathbf{B}'')$ can be obtained through linear transformation **T**.[25]

By substituting Eq. (4) into Eq. (2), we obtain the reorganization energy in terms of internal coordinates,

$$\begin{aligned} \lambda &= \sum_j \lambda(S_j) \\ &= \sum_j \sum_i \frac{1}{2\omega_i} \left(\alpha_{ij}^2 \Delta S_j^2 + \sum_{m(\neq j)} \alpha_{ij} \alpha_{im} \Delta S_j \Delta S_m \right). \end{aligned} \tag{6}$$

Here, $\lambda_j = \sum_i (1/2\omega_i) \alpha_{ij}^2 \Delta S_j^2$represent the diagonal terms and $\lambda_{jm} = \sum_i (1/2\omega_i) \sum_{m(\neq j)} \alpha_{ij} \alpha_{im} \Delta S_j \Delta S_m$, the non-diagonal terms. The reorganization energy can be alternatively expressed via the vibronic coupling constants.[28] Assuming that there is no Duschinsky mixing and thus that the molecular charged state involved in electron transfer is characterized by the same force constants as the neutral state, the two terms (λ_1 and λ_2) contributing to the total reorganization energy will be nearly identical; this is the case indeed for many rigid molecules[28,29] and the minor differences seen in the derivatives shown in Table S5 suggest that the assumption is appropriate for our investigated systems.

The reorganization energy can now be written as a sum of normal-mode contributions,

$$\lambda = \sum_i \lambda_i = \sum_i \frac{V_i^2}{2\omega_i^2}, \tag{7}$$

where V_i is the vibronic coupling constant for mode i:

$$V_i = \left\langle \Psi^+ (\mathbf{r}, \mathbf{R}_0) \left| \left(\frac{\partial H(\mathbf{r}, \mathbf{R})}{\partial Q_i} \right)_{\mathbf{R}_0} \right| \Psi^+ (\mathbf{r}, \mathbf{R}_0) \right\rangle. \tag{8}$$

Here, $\Psi^+ (\mathbf{r}, \mathbf{R}_0)$ is the wavefunction of the charged molecular state at the optimal geometry (R_0) of the neutral state. By means of Eq (4), we can also define the coupling constants in terms of internal coordinates and express the reorganization energy as a function of these constants

$$\begin{aligned} V_i &= \sum_j \alpha_{ij} \left\langle \Psi^+ (\mathbf{r}, \mathbf{R}_0) \left| \left(\frac{\partial H(\mathbf{r}, \mathbf{R})}{\partial S_j} \right)_{\mathbf{R}_0} \right| \Psi^+ (\mathbf{r}, \mathbf{R}_0) \right\rangle \\ &= \sum_j \alpha_{ij} \tilde{V}_j, \end{aligned} \tag{9}$$

$$\tilde{V}_j = \left\langle \Psi^+ (\mathbf{r}, \mathbf{R}_0) \left| \left(\frac{\partial H(\mathbf{r}, \mathbf{R})}{\partial S_j} \right)_{\mathbf{R}_0} \right| \Psi^+ (\mathbf{r}, \mathbf{R}_0) \right\rangle, \tag{10}$$

$$\lambda = \sum_j \lambda(\tilde{V}_j) = \sum_j \sum_i \frac{1}{2\omega_i} \left(\alpha_{ij}^2 \tilde{V}_j^2 + \sum_{m(\neq j)} \alpha_{ij} \alpha_{im} \tilde{V}_j \tilde{V}_m \right). \tag{11}$$

It is important to note that, while providing a more direct link to the local molecular properties, expressions (6) and (11) for the reorganization energies, in contrast to expressions based on normal coordinates and related couplings, also contain non-diagonal contributions from the internal coordinates (and the related coupling constants).

The application of the approaches based on direct calculations of the linear coupling constants can be simplified by making use of Koopmans' theorem approximation, i.e., by replacing in Eqs. (9) and (10) the total energy of the charged molecule with the energy of the relevant frontier molecular orbital. For instance, the hole vibronic coupling constant can be expressed as

$$V_i = \frac{\partial E_{\mathrm{HOMO}}}{\partial Q_i}. \tag{12}$$

In addition, by expressing the molecular orbital energy in the tight-binding model, the change in the vibronic coupling constants upon substitution can be related to the change in atomic densities:

$$E_{\mathrm{HOMO}} = C_1^2 \beta_{1,1} + C_1^2 \beta_{2,2} + 2C_1 C_2 \beta_{12} + 2C_1 C_3 \beta_{13} + ..., \tag{13}$$

$$\tilde{V}_i = \frac{\partial E_{\mathrm{HOMO}}}{\partial S_i} = \sum_{j,k} C_j C_k \frac{\partial \beta_{j,k}}{\partial S_i}, \tag{14}$$

$$\beta_{ij} = \langle \phi_i \, |\mathbf{F}| \, \phi_j \rangle. \tag{15}$$

Here, the ϕ_i terms represent the atomic orbital basis set in the tight-binding model; β_{ii}, the site energies, and β_{ij}, the transfer integrals (resonance integrals) between atoms i and j. In practice, the variations of the resonance integral β_{ij} between atoms i and j were obtained from the dependence of the DFT Fock matrix components on the inter-atomic bond lengths.

III. RESULTS AND DISCUSSION

The computed reorganization energies of the parent indolo[3,2-b]carbazole molecule and its derivatives obtained

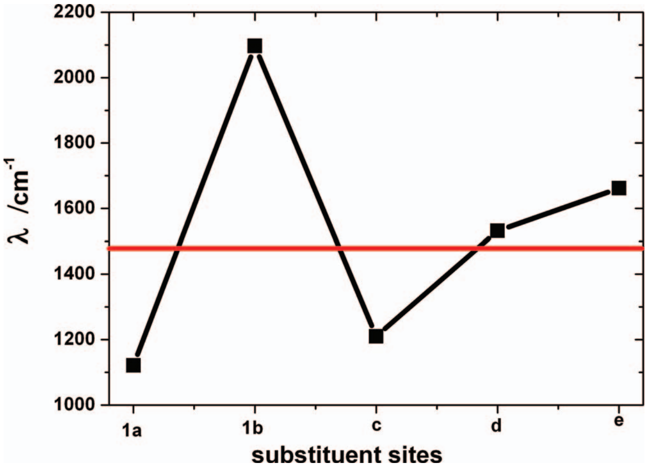


FIG. 3. Dependence of the calculated reorganization energy on substitution. The red line corresponds to the reorganization energy of unsubstituted indolo[3,2-b] carbazole.

by substitution of two chlorine atoms at two symmetry equivalent positions are depicted in Figure 3. As can be seen, the substituent position has a prominent effect on the reorganization energy. The reorganization energy of the parent molecule **1** is about 1480 cm^{-1}. The largest changes are observed in **1a** and **1b**; in **1a**, the reorganization energy decreases to 1120 cm^{-1} while it increases in **1b** to 2100 cm^{-1}. These results underline that the *exact positions of the substituents significantly influence the magnitude of the reorganization energy*.

Figure 4 illustrates decomposition of the reorganization energies ($\lambda^{(1)}$) into the contributions from the normal modes for the two chlorination patterns of the parent molecule that lead to the largest and smallest reorganization energies. A simple change in substitution position not only leads to a significant change in reorganization energy, but also to significant redistributions of the total reorganization energy among the normal modes. We find that the normal modes that most contribute to the reorganization energy involve several bond stretching vibrations, related in particular to bond lengths N–C$_1$, C$_1$–C$_2$ and C$_2$–C$_3$ (see bond labels in Fig. 5).

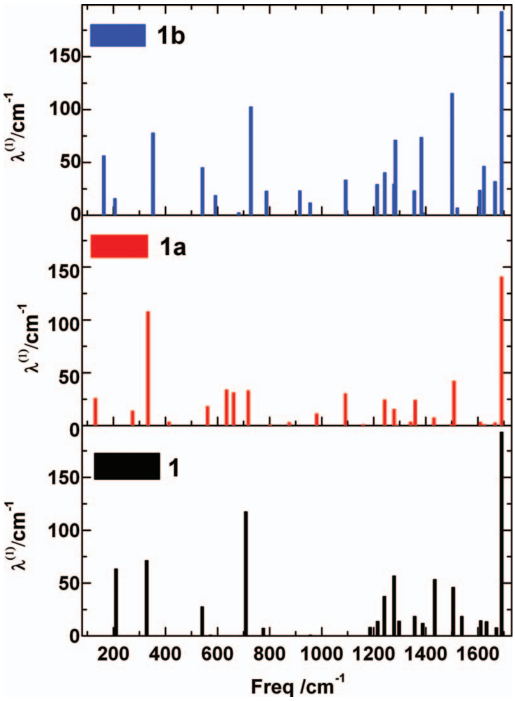


FIG. 4. The relaxation energies ($\lambda^{(1)}$) projected into the normal modes for **1a**, **1b**, and **1**.

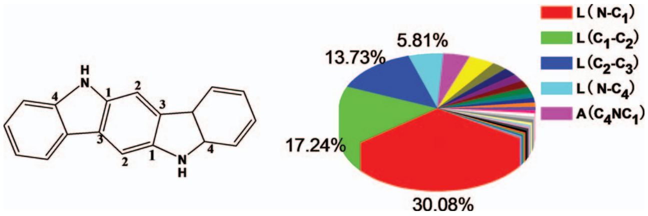


FIG. 5. Contributions to reorganization energy from structural parameters: bond lengths (L), bond angles (A), and dihedral angles, as a percentage of the total reorganization energy for **1**.

In order to gain a better understanding, the reorganization energies were further projected into internal coordinates. The results derived for **1** are shown in Fig. 5. It is found that the largest contribution (about 30%) to the reorganization energy comes from the relaxation along the N–C$_1$ bonds. An additional 30% contribution is due to the combined relaxations along the C$_1$–C$_2$ (~17%) and C$_2$–C$_3$ bonds (~14%). It should be borne in mind that the internal coordinate projection scheme we use, works well only when the non-diagonal terms in Eq. (6) are small. We collect in Table I the diagonal and non-diagonal contributions for a number of bond-length relaxations. The overall non-diagonal contributions are found to be lower than 20% for all important bond lengths, which confirms the validity of the present approach.

The effect of chlorination is illustrated for **1a** and **1b** in Fig. 6. Upon chlorination, there occurs a significant contribution to the reorganization energy from the relaxation processes along the C–Cl bonds in both molecules. However, in **1a**, the contributions from other bond are lessened (especially for N–C$_1$) and, as a result, the overall reorganization energy is even smaller than in the parent molecule **1**. In contrast, all these contributions increase for **1b**, resulting in a much larger reorganization energy for **1b** than both **1** and **1a**. In particular, we notice a very significant role of the contribution from the relaxation along N–C$_1$ and the dependence of this contribution on the chlorination pattern.

From our qualitative analysis, we observe that most of the reorganization energy originates in the present case from the polarization due to the nitrogen atoms, as seen from the

TABLE I. Diagonal and non-diagonal contributions to the reorganization energies for parent molecule **1**.

Bond length	Diagonal λ_j /cm^{-1}	Non-diagonal λ_{jm} /cm^{-1}	Diagonal/total $\lambda_j/\lambda_j + \lambda_{jm}$
L(N–C$_1$)	425.8	18.8	95.8%
L(C$_1$–C$_2$)	214.7	40.1	84.3%
L(C$_2$–C$_3$)	171.7	31.3	84.6%
L(N–C$_4$)	70.8	13.2	84.3%

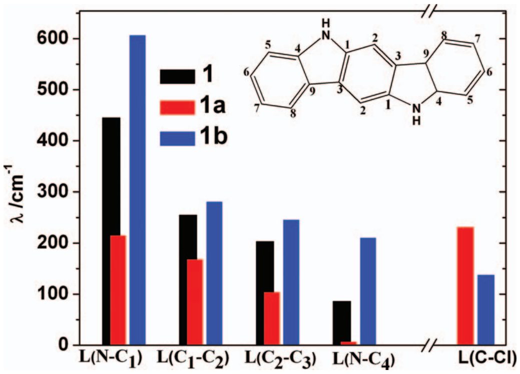


FIG. 6. Reorganization energy projected into internal bond-length coordinates for **1a**, **1b**, and **1**.

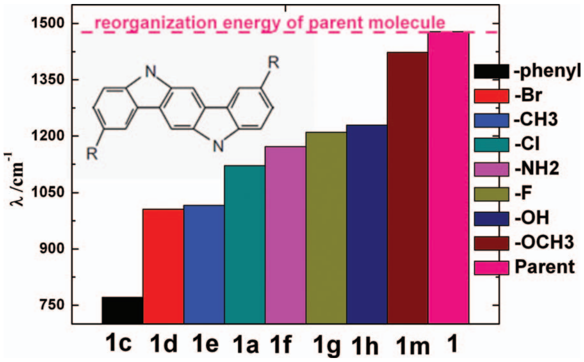


FIG. 7. Reorganization energies of the derivatives of **1** as a function of substituents in para positions with respect to the nitrogen sites: **1a** (R = Cl), **1c** (R = phenyl), **1d** (R = Br), **1e** (R = CH_3), **1f** (R = NH_2), **1g** (R = F), **1h** (R = OH), **1m** (R = OCH_3).

major contribution from bond length N–C_1. The substituents can lead to charge redistribution within the molecule; once the charge redistribution cancels the polarization effect related to the nitrogen atoms, the reorganization energy can be reduced.

As mentioned in Sec. II, the reorganization energy of a particular internal coordinate can be expressed in terms of the normal-mode vibronic coupling constants. At the Koopmans' theorem level, Eq. (14), the hole vibronic coupling along a specific bond can be related to the product of the HOMO coefficients on the two atoms forming the bond (which is approximately equal to the bond order in the HOMO orbital if one neglects atomic orbital overlap) and the first-order derivative of the resonance integrals with respect to the internal coordinate (bond length). The corresponding results for the N–C_1 bonds in **1**, **1a**, and **1b** are displayed in Table II. Only minor changes in transfer integral derivatives are found upon chlorination. Therefore, the change in relaxation energy along the N–C_1 bond can be essentially attributed to the modifications in the wavefunction amplitudes on the N and C_1 atoms induced by the chlorine substitution. Indeed, as shown in Table II, the charge density on the C_1 atoms in **1a** is significantly smaller than in **1**. An opposite trend (but to a lesser extent) is observed for **1b**. Similar analyses can be applied to other internal coordinates.

In addition to chlorination, we also investigated the effect of several other substituents such as phenyl or alkoxy at para positions with respect to the nitrogen sites. The numerical results are displayed in Fig. 7. It is seen that all the substituents we chose can reduce the reorganization energy to some extent; among all these substituents, the phenyl groups lead to the smallest reorganization energy and the methoxy groups, to the largest. This finding is intriguing, since, as pointed out earlier, with the exception of the cyano and isobenzo groups,[15–20] most substituents usually increase the reorganization energy of the parent molecules.

The relaxation energy related to the N–C_1 bonds, see Fig. 8, is found to be reduced significantly for the various substituents, by about half in the case of the F, Cl, Br, and alkyl substituents. The N–C_1 relaxation energy is reduced even further for phenyl substitution and becomes negligible in the case of alkoxy, hydroxyl, and amino substitutions. As discussed above, the first-order derivatives of the transfer integrals with respect to the N–C_1 bond hardly depend on the substitution; thus, the change in relaxation energy can be attributed to the modification of the wavefunction coefficients on the N and C_1 atoms upon substitution. As can be seen from Table S1 in supporting information,[32] F, Cl, Br, and CH_3 present similar charge densities on the C_1 atoms, while the phenyl, alkoxy, hydroxyl, and amino substitutions lead to smaller atomic densities on the C_1 atoms.

Chemical substitution by an X group usually introduces an additional component to the reorganization energy, for instance due to the C–X bond itself that needs to be taken into account. Considering the magnitude of the additional C–X bond contributions, we can classify the substituents into three

TABLE II. Top: HOMO coefficient on various atoms for compounds **1, 1a**, and **1b.** Bottom: Derivatives of the transfer integrals with respect to the N-C_1 bond lengths.

Basis	N		C_1		C_2		C_3	
Compounds	$2P_Z$	$3P_Z$	$2P_Z$	$3P_Z$	$2P_Z$	$3P_Z$	$2P_Z$	$3P_Z$
1	0.2759	0.2506	−0.1546	−0.1206	−0.2028	−0.1607	0.0846	0.0609
1a	0.2700	0.2452	−0.1350	−0.1062	−0.2040	−0.1616	0.0670	0.0483
1b	0.2758	0.2493	−0.1619	−0.1255	−0.2060	−0.1618	0.0861	0.0613
Compounds	$\frac{\partial\beta_{N,C_1}^{2P_Z,2P_Z}}{\partial S_{L(N-C_1)}}$ (eV/Å)	$\frac{\partial\beta_{N,C_1}^{2P_Z,3P_Z}}{\partial S_{L(N-C_1)}}$ (eV/Å)	$\frac{\partial\beta_{N,C_1}^{3P_Z,2P_Z}}{\partial S_{L(N-C_1)}}$ (eV/Å)	$\frac{\partial\beta_{N,C_1}^{3P_Z,3P_Z}}{\partial S_{L(N-C_1)}}$ (eV/Å)				
1	8.003	6.3049	5.5892	2.7276				
1a	8.054	6.2477	5.7047	2.9878				
1b	8.095	6.3158	5.5947	2.7783				

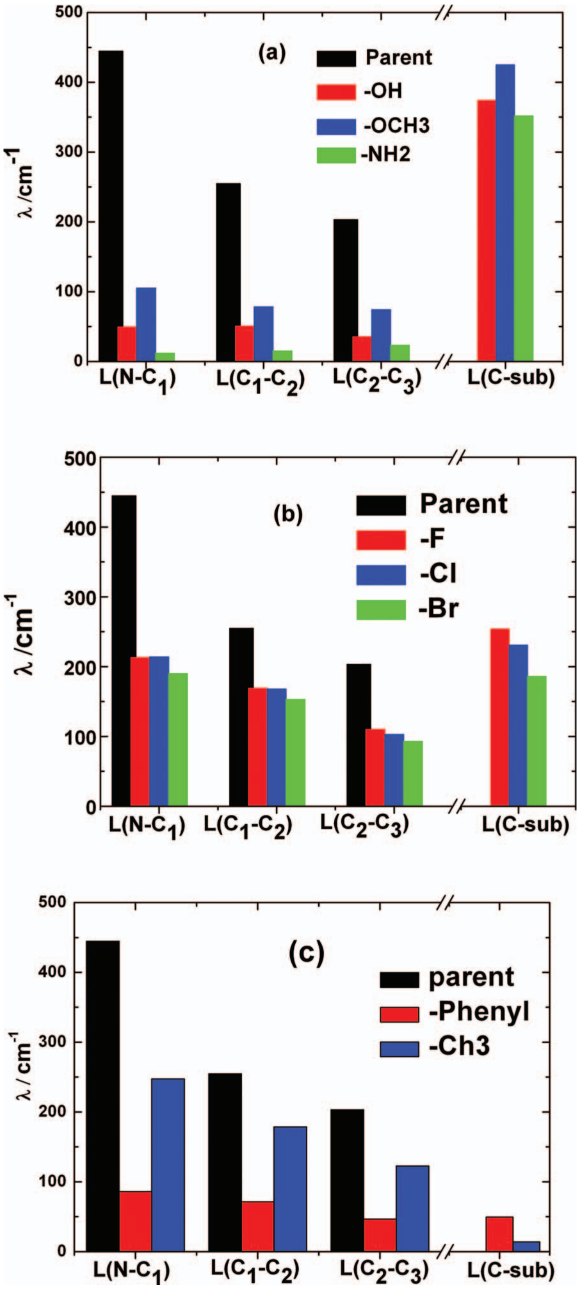


FIG. 8. Decomposition of the reorganization energy into internal coordinates for different substituents.

groups (see Fig. 8): (i) X = alkoxy, hydroxyl, and amino groups, where the extra reorganization energy is very large (∼400 cm^{-1}); (ii) X = halogen (F, Cl and Br) where it is moderate (∼200 cm^{-1}); and (iii) X = CH_3 and phenyl, with a small additional reorganization energy (less than 100 cm^{-1}).

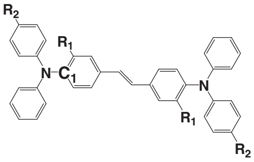
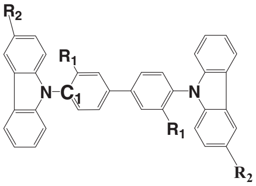
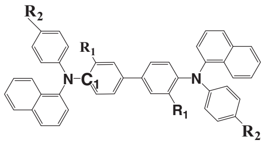
The HOMO coefficients and the derivatives of the transfer integrals with respect to the internal coordinate for different substituents are displayed in Table S2 and Table S3 in supporting information,[32] respectively. For the first group (alkoxy, hydroxyl, and amino), the HOMO coefficient on the X atom is large and, at the same time, the transfer integral derivatives are the largest among all substitutions. In the case of the phenyl and CH_3 substituents, even though the related transfer integral derivatives are large, the HOMO coefficients on the X atoms are very small. As a result, for these groups, the contribution from C-X to the total relaxation energy is the smallest.

It is of interest to evaluate whether the trends found above could be applied to other charge-transport materials as well. We considered several triarylamine-based molecules (labeled **2**, **3**, and **4** in Table III) that have been widely employed as hole-transport materials in optoelectronic applications.[30,31] The computed reorganization energies of the parent molecules **2**, **3**, and **4** and of their derivatives obtained by substitution with two chlorine atoms at symmetrically equivalent positions are collected in Table III. Substitution type **(a)** can lead to much lower reorganization energy than substitution type (**b**). This can be understood from the modification of the molecular orbital coefficients upon chlorination, as mentioned above. Since the N-C_1 bonds have large contributions to the relaxation energy, we display the variations in the HOMO molecular orbital coefficients on the C_1 atom for molecules **2**, **3**, and **4** in Table S4 in supporting information.[32] Substitution type (**a**) results in smaller coefficients than those for the parent molecules and substitution type (**b**), which confirms the molecular design rule for lowering the reorganization energy by virtue of Eqs. (13)–(15).

IV. CONCLUSION

To summarize, we have demonstrated an approach by which it is possible to decompose the total reorganization

TABLE III. Effect of chlorination on the reorganization energy of triarylamine derivatives, calculated at the B3LYP/6–31G* level.

λ /cm^{-1}		λ /cm^{-1}		λ /cm^{-1}	
					
2	**2689**	**3**	**1095**	**4**	**2226**
2a	**1851**	**3a**	**650**	**4a**	**1312**
2b	**2645**	**3b**	**1062**	**4b**	**2223**
2: R1 = R2 = H		**3**: R1 = R2 = H		**4**: R1 = R2 = H	
2a: R1 = Cl, R2 = H		**3a** R1 = Cl, R2 = H		**4a**: R1 = Cl, R2 = H	
2b: R2 = Cl, R1 = H		**3b** R2 = Cl, R1 = H		**4b**: R2 = Cl, R1 = H	

energy into internal coordinates. This allows one to rationalize the effects of chemical substitution in terms of the frontier orbitals and the first-order derivatives of the transfer integrals with respect to local geometry parameters. We have found that chlorine substitutions at appropriate positions in the case of indolo-carbazole can reduce the reorganization energy significantly, in contrast to the increase that is generally observed; several other substitution groups can also play a similar role, to a greater or lesser extent. The value of the reorganization energy also displays a similar dependence on the exact positions of chlorination in the case of triarylamine derivatives. Thus, the nature of the substituents and their exact positions are important factors to be considered in order to design organic materials with higher charge mobilities.

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[1] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. dos Santos, J. L. Bredas, M. Logdlund, and W. R. Salaneck, Nature (London) **397**, 121 (1999); H. E. Katz, A. J. Lovinger, J. Johnson, C. Kloc, T. Siegrist, W. Li, Y. Y. Lin, and A. Dodabalapur, Nature (London) **404**, 478 (2000).

[2] C. R. Newman, C. D. Frisbie, D. A. da Silva Filho, J. L. Bredas, P. C. Ewbank, and K. R. Mann, Chem. Mater. **16**, 4436 (2004).

[3] K. Hannewald, V. M. Stojanovic, J. M. T. Schellekens, P. A. Bobbert, G. Kresse, and J. Hafner, Phys. Rev. B **69**, 075211 (2004); A. Troisi and G. Orlandi, J. Phys. Chem. A. **110**, 4065 (2006); R. W. Munn and R. Silbey, J. Chem. Phys. **83**, 1843 (1985); Y. C. Cheng and R. J. Silbey, J Chem Phys. **128**(11), 114713 (2008).

[4] L. Wang, G. Nan, X. Yang, Q. Peng, Q. Li, and Z. Shuai, Chem. Soc. Rev. **39**, 423 (2010); Z. G. Shuai, L. J. Wang, and Q. K. Li, Adv. Mater. **23**, 1145 (2011); L. J. Wang, Q. Peng, Q. K. Li, and Z. G. Shuai, J. Chem. Phys. **127**, 044506 (2007).

[5] G. Nan, X. Yang, L. Wang, Z. Shuai, and Y. Zhao, Phys. Rev. B **79**, 115203 (2009); L. J. Wang, Q. K. Li, Z. G. Shuai, L. P. Chen, and Q. Shi, Phys. Chem. Chem. Phys. **12**, 3309 (2010).

[6] T. Sakanoue and H. Sirringhaus, Nat. Mater. **9**, 736 (2010).

[7] J. L. Bredas, J. P. Calbert, D. A. da Silva, J. Cornil, Proc. Natl. Acad. Sci. U.S.A. **99**, 5804 (2002); E. G. Kim, V. Coropceanu, N. E. Gruhn, R. S. Sanchez-Carrera, R. Snoeberger, A. J. Matzger, J. L. Bredas, J. Am. Chem. Soc. **129**, 13072 (2007).

[8] S. W. Yin, Y. P. Yi, Q. X. Li, G. Yu, Y. Q. Liu, and Z. G. Shuai, J. Phys. Chem. A **110**, 7138 (2006); X. D. Yang, Q. K. Li, and Z. G. Shuai, Nanotechnology **18**, 424029 (2007); X. D. Yang, L. J. Wang, C. L. Wang, W. Long, and Z. G. Shuai, Chem. Mater. **20**, 3205 (2008).

[9] S. Chen and J. Ma, J. Comput. Chem. **30**, 1959 (2009).

[10] B. S. Ong, Y. L. Wu, and P. Liu, Proc. IEEE **93**, 1412 (2005); Y. L. Guo, H. P. Zhao, G. Yu, C. A. Di, W. Liu, S. D. Jiang, S. K. Yan, C. Y. Wang, H. L. Zhang, X. N. Sun, X. T. Tao, and Y. Q. Liu, Adv. Mater. **20**, 4835 (2008).

[11] S. Subramanian, S. K. Park, S. R. Parkin, V. Podzorov, T. N. Jackson, J. E. Anthony, J. Am. Chem Soc. **130**, 2706 (2008).

[12] C. R. Swartz, S. R. Parkin, J. E. Bullock, J. E. Anthony, A. C. Mayer, G. G. Malliaras, Org. Lett. **7**, 3163 (2005).

[13] M. L. Tang, J. H. Oh, A. D. Reichardt, and Z. N. Bao, J. Am. Chem. Soc. **131**, 3733 (2009); M. L. Tang and Z. Bao, Chem. Mater. **23**, 446 (2011).

[14] Y. Sakamoto, T. Suzuki, M. Kobayashi, Y. Gao, Y. Fukai, Y. Inoue, F. Sato, and S. Tokito, J. Am. Chem. Soc. **126**, 8138 (2004).

[15] S. E. Koh, C. Risko, D. A. da Silva, O. Kwon, A. Facchetti, J. L. Bredas, T. J. Marks, and M. A. Ratner, Adv. Funct. Mater. **18**, 332 (2008).

[16] Y. H. Kan, K. Wu, Y. L. Zhu, L. M. Hou, Z. M. Su, Acta Phys. Chim. Sin. **26**, 1423 (2010).

[17] H. Y. Chen and I. Chao, Chem. Phys. Lett. **401**, 539 (2005).

[18] M. C. R. Delgado, K. R. Pigg, D. A. da Silva Filho, N. E. Gruhn, Y. Sakamoto, T. Suzuki, R. M. Osuna, J. Casado, V. Hernandez, J. T. Lopez Navarrete, N. G. Martinelli, J. Cornil, R. S. Sanchez-Carrera, V. Coropceanu, and J. L. Bredas, J. Am. Chem. Soc. **131**, 1502 (2009).

[19] S. Salman, M. C. R. Delgado, V. Coropceanu, and J. L. Bredas, Chem. Mater. **21**, 3593 (2009).

[20] G. R. Hutchison, M. A. Ratner, and T. J. Marks, J. Am. Chem. Soc. **127**, 2339 (2005).

[21] M. Y. Kuo, H. Chao, Chem. Eur. J. **13**, 4750 (2007).

[22] (a) P. L. T. Boudreault, A. A. Virkar, Z. Bao, and M. Leclerc, Org. Electron. **11**, 1649 (2010); (b) P. L. T. Boudreault, S. Wakim, M. L. Tang, Y. Tao, Z. N. Bao, J. Mater. Chem. **19**, 2921 (2009); (c) P. L. T. Boudreault, S. Wakim, N. Blouin, M. Simard, C. Tessier, Y. Tao, and M. Leclerc, J. Am. Chem. Soc. **129**, 9125 (2007); (d) Y. Li, Y. Wu, S. Gardner, and B. S. Ong, Adv. Mater. **17**, 849 (2005).

[23] M. Pope and C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd ed. (Oxford University Press, New York, 1999).

[24] E. A. Silinsh and V. Capek, *Organic Molecular Crystals: Interaction, Localization, and Transport Phenomena* (AIP, New York, 1994).

[25] J. R. Reimers, J. Chem. Phys. **115**, 9103 (2001).

[26] GAUSSIAN09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, Gaussian, Inc., Wallingford CT, 2009.

[27] V. Coropceanu, M. Malagoli, D. A. da Silva Filho, N. E. Gruhn, T. G. Bill, and J. L. Bredas, Phys. Rev. Lett. **89**, 275503 (2002).

[28] V. Coropceanu, J. Cornil, D. A. da Silva, Y. Olivier, R. J. Silbey, and J. L. Bredas, Chem. Rev. **107**, 2165 (2007).

[29] O. Kwon, V. Coropceanu, N. E. Gruhn, J. C. Durivage, J. G. Laquindanium, H. E. Kata, J. Cornil, and J. L. Bredas, J. Chem. Phys. **120**, 8186 (2004).

[30] C. Adachi, T. Tsutsui, and S. Saito, Appl. Phys. Lett. **55**, 1489 (1989).

[31] M. Stolka, J. F. Yanus, and D. M. Pai, J. Phys. Chem. **88**, 4707 (1984); K. Okumoto and Y. Shirota, Mater. Sci. Eng. **B85**, 135 (2001); K. Okumoto, K. Wayaku, T. Noda, H. Kageyama, and Y. Shirota, Synth. Met. **111**, 473 (2000); K. Okumoto and Y. Shirota, Chem. Lett. 1034 (2000); Y. B. Song, C. A. Di, X. D. Yang, S. Li, Wei Xu, Y. Liu, L. Yang, Z. Shuai, D. Zhang, and D. Zhu, J. Am. Chem. Soc. **128**, 15940 (2006).

[32] See supplementary material at http://dx.doi.org/10.1063/1.3632105 for theoretical study of substitution effects on molecular reorganization energy in organic semiconductors.