

Excitonic versus electronic couplings in molecular assemblies: The importance of non-nearest neighbor interactions

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We demonstrate that for a range of phenylene- and thiophene-based conjugated polymers of practical relevance for optoelectronic applications, exciton couplings in one-dimensional stacks deviate significantly from the nearest neighbor approximation. Instead, long-range interactions with non-nearest neighbors have to be included, which become increasingly important with growing oligomer size. While the exciton coupling vanishes for infinitely long ideal polymer chains and provides a sensitive measure of the actual conjugation length, the electronic coupling mediating charge transport shows rapid convergence with molecular size. Similar results have been obtained for very different molecular backbones, thus highlighting the general character of these findings.

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INTRODUCTION

Molecular order is a key parameter for the performance of optoelectronic devices based on π -conjugated organic materials. In particular, the optical,¹ charge,² and energy transport properties³ are strongly affected by the specific arrangement and separation of adjacent molecules. Reliable prediction of the solid-state optical and energy transport properties or the extraction of effective conjugation lengths from optical spectra of polymer samples thus requires the knowledge of the exciton coupling terms of all molecules in a three-dimensional assembly. In order to reduce the computational effort, approximations are commonly introduced, based, e.g., on the point-dipole approximation (PDA) and, further, on the nearest-neighbor approximation (NNA), where only the interaction with the adjacent neighbor molecules is considered. While the PDA is known to fail for short distances between molecules and is thus often replaced by atomistic quantum-chemical calculations of the excitonic interactions,^{4,5} the NNA is still widely used due to the extensive reduction of the computational effort. In this framework, for cofacial parallel pairs^{5,6} and aggregates⁷ of longer oligomers, a peak behavior with a slight increase followed by a dramatic drop of the exciton coupling energies with increasing length of the considered oligomer has been theoretically predicted.⁵ Namely, in the plane-wave approximation, the excitonic interaction in pairs of conjugated chains decreases as $1/L$ with L the chain length.⁷ This points to very small

interaction energies of adjacent polymer chains, and therefore only small electronic matrix elements for energy hopping.

Due to the crucial importance of this issue, we have calculated the exciton couplings in idealized one-dimensional (1D) assemblies of oligomers with different repetition units in a full quantum-chemical approach. In re-examining the validity of the NNA, we demonstrate that long-range interactions with remote non-nearest neighbor molecules become of importance for long oligomers and polymers, and cannot be neglected in the calculation of exciton couplings in molecular assemblies. Various repetition units are explored, thus providing trends for oligothiophene (nT), -phenylene (nP), -phenylenevinylene (nPV), and -phenyleneethynylene (nPE), which can be rationalized by the polarizabilities of the different molecular backbones. Due to the fact that weak exciton dispersion is often associated with small intermolecular interactions, we finally investigate the chain-length dependence of electronic coupling (or charge transfer integral) mediating charge transport. In contrast to exciton coupling, the transfer integral features a fast saturation to nonzero values in the long chain limit, so that correlation between excitonic and electronic couplings should be considered with care.

EXCITONIC COUPLING IN MOLECULAR DIMERS

The nature of electronic transitions in conjugated oligomers of different chain length n can be assessed from quantum-chemical methods. A good compromise between accuracy and computational prize, even for very long oligomers,⁸ is usually obtained by the semiempirical intermediate neglect of differential overlap (INDO) method as parametrized by Zerner for spectroscopic applications.⁹ For

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the calculation of exciton couplings V in the solid state, a further complication is induced by the large number of molecules that has to be taken into account to represent the crystal in a reasonable way. Since large molecular assemblies are not easy to handle at a realistic level, even with standard quantum-chemical methods, approximate solutions are commonly chosen. One possibility is to apply the PDA as proposed early by Kasha,¹⁰ which reads for the exciton coupling V

$$V_{\text{PDA}} = \frac{3e^2}{16\pi^3 c^2 m_e \epsilon_0} \cdot \frac{\kappa f}{d^3 E_0}, \quad (1)$$

where e is the electrical charge, c is the velocity of light, m_e is the electronic mass, and ϵ_0 is the permittivity of vacuum. The variables f and E_0 are the oscillator strength and the transition energy of the monomer and d is the intermolecular separation; the orientation factor equals unity, $\kappa=1$, for a cofacial dimer pair. Based on the PDA, the overall coupling in the crystal can then be calculated in an Ewald sum,^{11,12} an approach widely applied to periodic systems.¹³ In a quantum-chemical approach, the NNA is generally used. This approximation considers only the interaction between the two adjacent molecules in a 1D molecular stack [four in a two-dimensional (2D) layer] and thus reduces the task to a single “dimer” problem.¹⁴

For molecular dimer pairs, the PDA breaks down, both for decreasing separation between the molecules and for increasing chainlength n of the molecular backbone,⁵ and thus more elaborated quantum-chemical approaches are demanded. Within the framework of exciton theory, the excitonic coupling V_{AB} between molecules A and B can be calculated via¹⁵

$$V_{AB} = \frac{1}{4\pi\epsilon_0} \sum_i \sum_j q_A(i) q_B(j) F(r_{ij}), \quad (2)$$

where $q_A(i)$ denotes the transition density on site i associated with the lowest electronic excitation of molecule A and $F(r_{ij})$ is the electron-electron interaction potential (that scales as $1/r_{ij}$ at long distances).¹⁶ Here, we have used the Mataga-Nishimoto potential as implemented in the INDO/S Hamiltonian,¹⁷ on the basis of ground-state geometries of the isolated molecules optimized at the semiempirical AM1 (Austin model 1) level.¹⁸ In both cases, the INDO method was coupled to a single configuration interaction (SCI) scheme, involving all occupied and unoccupied p -type orbitals. It is well known that SCI yields overestimated transition dipole moments and therefore also exciton couplings, yet the method can be applied to much larger systems than for instance the more accurate coupled cluster with singles and doubles (CCSD) formalism.¹⁹ To check the general applicability of the conclusions above, we have calculated INDO atomic transition densities for n Ts of increasing size at the SCI and CCSD levels, which have subsequently been injected in Eq. (2) to compute the (excitonic) dimer and 1D stack excitonic interactions, respectively. We find that a good fit between the SCI and CCSD transition moments for the lowest optically allowed excitation could be obtained by rescaling (down) the INDO/SCI transition densities (by a factor

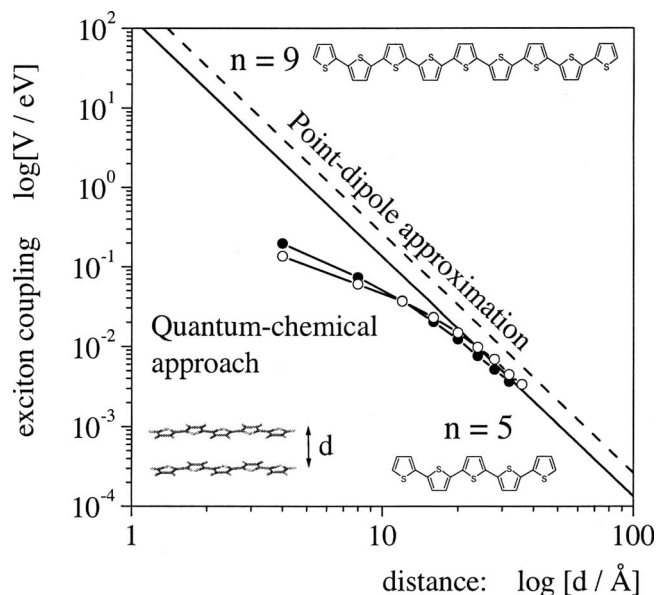


FIG. 1. Distance dependence of the exciton coupling V for a cofacial pair of 5T (closed symbols, solid line) and 9T (open symbols, dashed line) in the point-dipole approximation (PDA, lines) and in the quantum-chemical approach (circles).

of 1.32). In the following, we thus applied the same correction factor for the calculation of the exciton couplings providing SCI couplings very close to the CCSD values in short chains. PDA dependencies on d were obtained by inserting the single molecule quantum-chemical results on f and E_0 into Eq. (1).

Recapitulating Ref. 5, the PDA is strongly overestimating the exciton coupling with decreasing distance in a perfect cofacial dimer pair, as exemplified here for pairs of oligothiophenes, see the calculations in Fig. 1. A particular behavior was observed for the chain length dependence: in contrast to the PDA, where an increase in the chainlength n is accompanied by an increase of the exciton coupling [essentially due to the linear increase of f , see Eq. (1)], the quantum-chemical calculations predict a “peak behavior,” i.e., an increase until a certain size, which depends on the type of the molecular backbone and the intermolecular separation, followed by a sharp decrease.^{5–7} The general behavior for cofacial oligothiophenes is demonstrated in Fig. 2. At a distance of 12 Å, the quantum-chemical results diverge from the PDA result for $n > 2$ and the peak for maximum coupling is at $n_{\text{peak}}=6$. For decreasing interchain separation d , the peak is shifted toward smaller chain length, so that for a distance of 4 Å, which is rather the upper limit for a cofacial arrangement found in experiments, the peak is found for 3T. The calculations indicate a steady decrease of the dimer interaction with increasing chainlength for $n > 3$, and thus only a (vanishing) small coupling at the polymer limit.

EXCITONIC COUPLING IN MOLECULAR CLUSTERS

Following the idea of the NNA, it is thus expected that with increasing chain length the apparent exciton coupling, which is observable in the splitting of the main absorption band of molecular clusters, such as nanoparticles or thin films, should show a significant decrease with decreasing

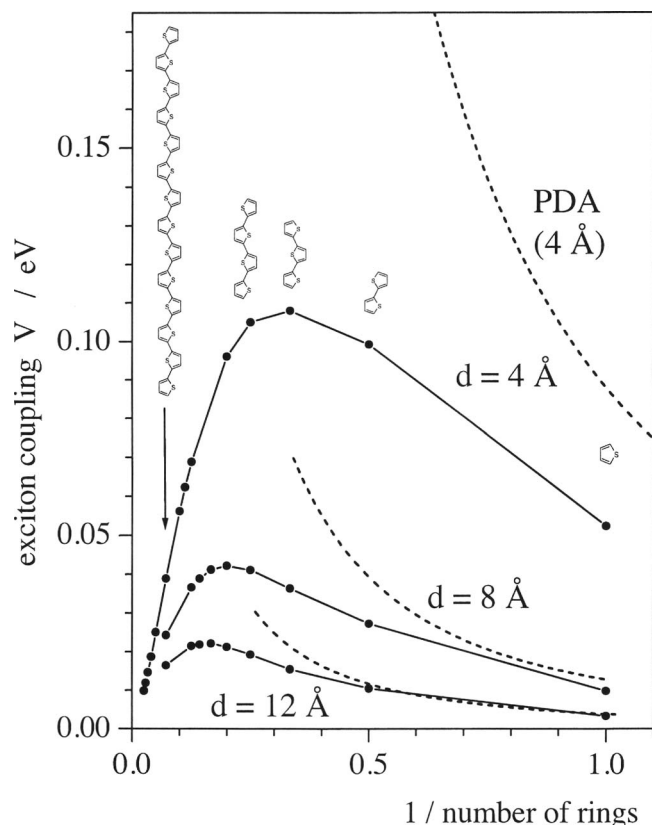


FIG. 2. Dependence of the exciton coupling V for cofacial pairs of oligothiophenes (nT) as a function of the inverse number of rings $1/n$ in the quantum-chemical approach at intermolecular separations of 4, 8, and 12 Å. Results within the PDA are shown as dashed lines.

chainlength n . This is, however, apparently not the case for the range of oligothiophene sizes that have been investigated so far. In an experimental investigation on vapor-deposited monolayers of oligothiophenes with n ranging from 4 to 8, a more or less constant splitting of about 1 eV was observed.²⁰ Similar splitting is found in 4T and 5T nanoaggregates,²¹ while a small decrease with n has been reported for finite 1D stacks of nT (with $n=5-7$) with terminal ester functionalization.^{22,23} We attribute the difference between the experimental results with the prediction of the NNA to interactions with remote non-nearest neighbors, which are suggested to vary largely for different n , thus recommending to go beyond the NNA in the description of molecular aggregates. The reason for this different behavior can be easily seen in comparing the distance dependence of the exciton coupling for dimer pairs of 5T and 9T, see Fig. 1: While the coupling in 9T is only 65% compared to that in 5T at a distance of 4 Å, it must necessarily be higher at large distances (typically $>10-20$ Å), since the interaction should then follow the PDA, as indeed seen in Fig. 1. This crossing of the distance dependencies suggests stronger contributions of remote neighbor interactions to the overall exciton coupling in molecular crystals with increasing chainlength.

In order to check to which extent non-nearest neighbor interactions contribute to the coupling, simple 1D clusters of i perfectly cofacial oriented oligothiophenes of different chainlength n were calculated by solving the excitonic Hamiltonian.²⁶ This gives V_{1D} , defined as half the excitonic

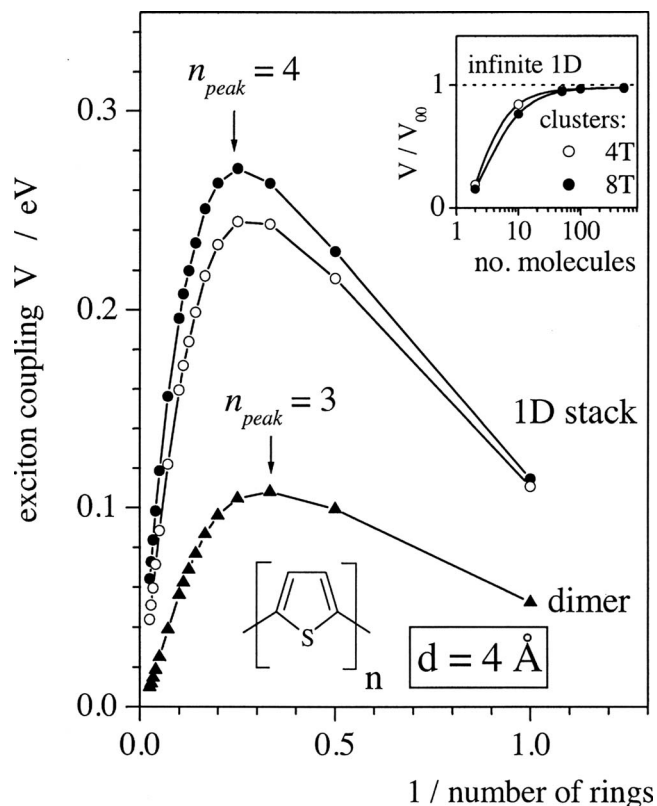


FIG. 3. Dependence of the exciton coupling V for a cofacial pair and a 1D stack of nT s as a function of the inverse number of rings $1/n$ at a distance of 4 Å. Open circles: SCI with screening according to Eq. (3). Inset: relative exciton coupling V/V_∞ for finite 1D stacks of cofacial 4T and 8T molecules, respectively; dashed line: infinite 1D stack.

bandwidth. The inset of Fig. 3 shows the dependence of V_{1D} on i , demonstrating that the infinite 1D stack is essentially reached for $i > 50$. The resulting exciton coupling in infinite 1D stacks for different nT oligomers is depicted in Fig. 3. Also, here, a peak behavior is observed as in the dimer pair calculations, although shifted toward longer oligomers, i.e., at 4 Å $n_{\text{peak}}=4$ for the stack, compared to $n_{\text{peak}}=3$ for the dimer, thus indicating that indeed long-range intermolecular interactions with remote neighbors become more important for larger n .²⁷

Self-screening of the molecules in the crystal may have a significant impact on the results, which is not included in the quantum-chemical calculations above, and affect both the exciton coupling and the overall energetic position (gas-to-crystal shift). At the simplest level, the problem can be tackled using a polarizable continuum model, where the environment of the interacting molecules is simply represented by its relative permittivity ϵ . In the long distance limit, the excitonic interaction between two linear point dipoles embedded in a dielectric environment with relative permittivity ϵ should then scale as $s_\infty=1/\epsilon$ as predicted by Förster. Clearly, this correction does not apply at short distances, which calls for a distance-dependent screening effect. The latter has been explored by Curutchet *et al.*²⁸ who showed that dielectric screening effects could be accounted for by weighting the excitonic couplings by a distance-dependent s factor of the form

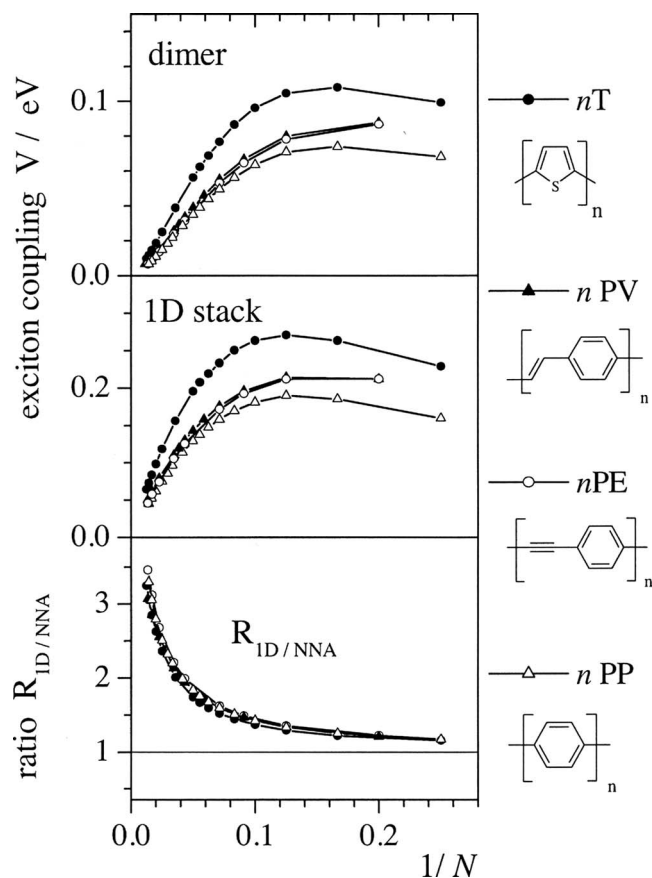


FIG. 4. Exciton coupling V for different classes of conjugated organic materials as a function of $1/N$ (see text) for dimer pairs (top) and 1D stacks (center). Bottom: ratio $R_{1D} = V_{1D}/V_{NNA}$ of the exciton couplings in a 1D stack according to Eq. (4) against the NNA result ($V_{NNA} = 2V_{AB}$) as a function of the number of rings. The NNA limit is indicated.

$$s = Ae^{-\beta d} + s_{\infty}. \quad (3)$$

In a first attempt to account for dielectric screening effects, we have computed the interaction energies using Eq. (3) with $A=1.35$, $\beta=0.27$, and $s_{\infty}=0.54$. This empirical scaling factor ensures that $s=1$ for a distance $d=4$ Å between two neighbors in the stacks and converges to $1/\epsilon$ with $\epsilon_{\infty}=1.85$ at large d . The results reported in Fig. 3 show the expected decrease in the stack exciton coupling after correction for screening compared to the bare interactions, though V_{1D} peaks at approximately the same length (4T). In fact, the shift in ϵ going from the dimer to the full 1D array is primarily due to the next nearest neighbor interactions (at intermediate distances) that are only weakly affected by the screening function.

The importance of non-nearest neighbor interactions for longer chains become even more evident by plotting the ratio $R_{1D} = V_{1D}/V_{NNA}$ between the infinite 1D stack and the NNA value ($V_{NNA} = 2V_{AB}$), see Fig. 4. For thiophene, $n=1$, the value is close to unity. For oligomer lengths of practical relevance, typically between two and eight units, the use of the NNA implies significant errors, e.g., for 5T the ratio yields $R_{1D,5T}=1.4$. Note that for the simple cofacial 1D stacks employed here, the exciton couplings upon going from four- to seven-ring oligomers decrease less strongly than for dimers, in agreement with experimental results.^{20–23} For very long

chains, the strong increase of R due to remote neighbor interactions can partly compensate the decrease of the dimer coupling, so that for nonideal, i.e., finite polymers, a small but nonzero coupling in the range of a few tens of meV is expected. This coupling might be even lower in slightly shifted 1D stacks, for example, in regioregular polyhexylthiophene P3HT, where there is no explicit correlation between adjacent chains along the molecular backbones. Experimentally, full excitonic bandwidths varying from 20 to 120 meV have been reported for P3HT films spun from different solvents.²⁹ The free exciton bandwidths can be correlated to the degree of intramolecular order and the resulting averaged conjugation length. By extrapolating the results obtained for infinite 1D stacks in Fig. 3, we associate the 120 meV bandwidth a conjugation length of ~ 40 (30) thiophene units for the unscreened (screened) intermolecular potential; it is worth stressing that a significantly smaller conjugation length (~ 15 – 20 units) would be obtained within the NNA (for which the total bandwidth is four times V_{AB}) showing again the importance of accounting for long-range interactions.

Similar small exciton couplings for finite polymers are expected for other backbones under investigation, see Fig. 4. Here, for better comparison, all exciton couplings are depicted as a function of $1/N$, where N is the number of double bonds along the shortest path connecting the terminal carbon atoms of the molecular backbone. The excitonic coupling evolves with the polarizability of the repeating unit (i.e., with the squared transition dipole moment in the point dipole approximation): the smallest couplings are calculated for the less polarizable oligophenylenes (nP), -phenylenevinylene (nPV), and -phenyleneethynylenes (nPE), while significantly higher values are obtained for the highly polarizable oligothiophenes (nT). For all oligomers, the maximum exciton coupling is at $N_{\max}=5$ – 6 for the dimers and $N_{\max}=6$ – 8 for the 1D stacks, depending mainly on the presence of (hetero)aromatic rings in the repetition unit. Finally, R_{1D} (Fig. 4) shows an identical behavior on N for all oligomers under investigation, indicating that the extent of non-nearest neighbor interactions is rather independent of the chemical structure of the interacting chains.

ELECTRONIC COUPLINGS FOR CHARGE TRANSPORT

Small changes in the absorption properties in comparing solution and solid state systems are often associated with weak intermolecular interactions and, as a result, poor charge transport properties. To investigate this issue, we have calculated the transfer integrals V_T , using here a direct method based on perturbation theory.³⁰ V_T for both the highest occupied molecular orbital (HOMO) (hole transport) and lowest unoccupied molecular orbital (LUMO) (electron transport) is shown as a function of oligomer size in Fig. 5. A slight decrease (increase) of V_T for the LUMO (HOMO) level is first observed with increasing n , however, converging to a nonzero value for about $n > 5$.³¹ This contrasting behavior of V_T with respect to V_{AB} (or V_{1D}) can be easily understood from the nature of the involved interactions. For optically

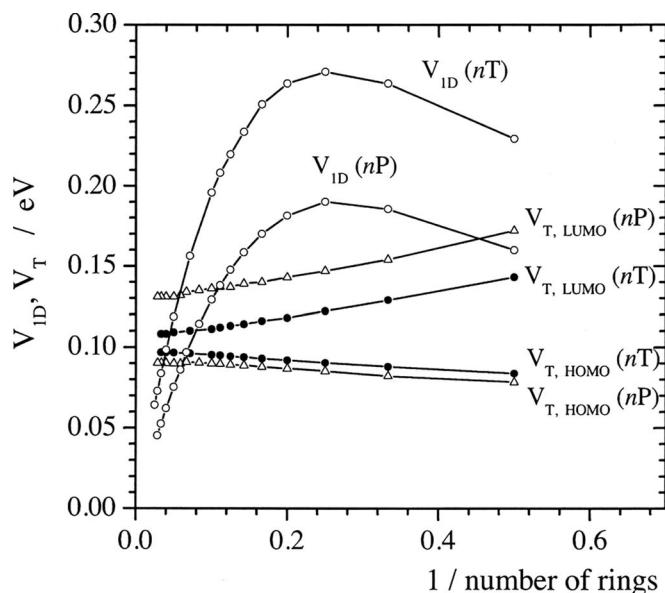


FIG. 5. Evolution of the transfer integrals V_T for the HOMO and LUMO orbitals and of the excitonic couplings V_{ID} with chainlength for oligophenylenes (nP) and oligothiophenes (nT).

allowed electronic excitations and not too small intermolecular distances (so that both exchange and charge-transfer contributions can be neglected), V_{AB} is dominated by long-range Coulomb interactions that give rise to a I/L dependence in the plane-wave approximation in conjunction with the line dipole model.⁷ V_T , on the other hand, depends on the spatial overlap between the molecular orbital wave functions, namely, for hole transport,

$$V_T = \langle \phi_{\text{HOMO}}^1 | h | \phi_{\text{HOMO}}^2 \rangle = \sum_{\mu} \sum_{\nu} C_{\text{HOMO},\mu} C_{\text{HOMO},\nu} \langle \chi_{\mu} | h | \chi_{\nu} \rangle, \quad (4)$$

where ϕ_{HOMO} denotes the HOMO molecular orbital for the individual chains and χ_{μ} the atomic orbital centered on atom μ . As the LCAO (linear combination of atomic orbitals) coefficients in Eq. (4) scale as $1/\sqrt{N}$ (normalization coefficient), with N the number of sites along the polymer chains, the transfer integral that involves $\sim N$ dominant terms (with $\mu = \nu$) is size independent.³² Although this is a very rough estimation that does not take into account the real phase of the interacting wave functions and the off-diagonal ($\mu \neq \nu$) overlap, it provides a simple explanation on the very different behavior of V_T and V_{AB} .

An important conclusion from Fig. 5 is that while improving the degree of order along the polymer chains is expected to be highly detrimental to *intermolecular* exciton transport properties (namely, highly extended π systems show vanishingly small excitonic couplings), this is not true for charge transport where the matrix elements for charge hopping are weakly sensitive to the actual conjugation length.

CONCLUSIONS

We have investigated the chain length dependence of excitonic V_{ID} and electronic couplings V_T in 1D molecular

arrays, being key parameters in exciton and charge transport, respectively. We have demonstrated that for most molecules of practical relevance for (opto-) electronic application, exciton couplings in molecular assemblies cannot be sufficiently described within the nearest neighbor approximation NNA; instead, non-nearest neighbor interactions have to be included, which become increasingly important for longer chain lengths. Among the oligomers under study, the impact of long-range interactions is independent of the chemical nature of the molecular backbone.

While a high degree of order along the polymer chain is detrimental for exciton transport due to vanishing V_{ID} , in ideally conjugated infinite polymers, this is not the case for charge transport, since V_T is only weakly sensitive to the conjugation length. The different sensitivity also demonstrates the care which has to be taken in correlating excitonic and electronic properties.

It will be subject to future studies to explore molecular assemblies in more detail under “real” conditions, i.e., to calculate quasi-1D, 2D, and three-dimensional assemblies inserting known crystal parameters, and to take into account Davydov splitting for translationally nonequivalent molecules in the unit cell.

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- ²⁶ Typically, dimers are not arranged in a perfect cofacial fashion (although almost perfect cofacial arrangements are found for some oligomers with electron withdrawing substituents, see, e.g., Ref. 1). However, in this paper, we present a proof of principle. This is only possible if all oligomers under study are in exactly the same arrangement *independent* of the chain length. Introduction, e.g., of a shift will induce very different effects on the interactions between oligomers of different chain length, so that a meaningful comparison is not possible.
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