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Application of double-hybrid density functionals to charge transfer in N-substituted pentacenequinones

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A set of N-heteroquinones, deriving from oligoacenes, have been recently proposed as n-type organic semiconductors with high electron mobilities in thin-film transistors. Generally speaking, this class of compounds self-assembles in neighboring π -stacks linked by weak hydrogen bonds. We aim at theoretically characterizing here the sequential charge transport (hopping) process expected to take place across these arrays of molecules. To do so, we need to accurately address the preferred packing of these materials simultaneously to single-molecule properties related to charge-transfer events, carefully employing dispersion-corrected density functional theory methods to accurately extract the key molecular parameters governing this phenomenon at the nanoscale. This study confirms the great deal of interest around these compounds, since controlled functionalization of model molecules (i.e., pentacene) allows to efficiently tune the corresponding charge mobilities, and the capacity of modern quantum-chemical methods to predict it after rationalizing the underlying structure-property relationships. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4707466>]

I. INTRODUCTION

Charge transfer among organic compounds, be them oligomers or small molecules, is a topic of the most interest due to the large number of envisioned applications in new emerging technologies.¹ A bottom-up approach is normally followed since simulating the mode of operation of these devices rely first on basic knowledge of properties at a molecular scale; then, bulk properties can be also estimated through multiscale approaches connecting the different time and length scales relevant for the complex mechanism of operation of these devices.² The efficiency of these devices is markedly dominated by the charge carriers mobility, a bulk parameter, which characterizes experimentally the charge transport properties.³ However, the values are ultimately influenced by a set of (slightly unreproducible) factors, such as boundaries, the degree of disorder, impurities and crystal defects acting as traps, induced growths from patterned surfaces, temperature, and device configuration to name just a few; thus, the performance of closely related materials can vary from one study to another.

Besides this variety in mobility values depending on working conditions, the identity of the conjugated molecule(s) acting as active layer(s) plays a central role: it is known how controlled functionalization of commonly used molecules, such as pentacene, is a promising path to develop a library of molecules and to further rationalize the underlying structure-property relationships. For example, the substitution of pentacene by tri-isopropylsilyl groups converts the crystalline structure from herringbone to lamellar, whereas perhalogenation tune⁴ p-type towards n-type semiconductors concomitantly with opening of the herringbone angle⁵ typical of acene-like structures.⁶ Note that the development of

n-type (electron conducting) high-performance semiconductors is a must, although still under scrutiny,⁷ and that exposure to surrounding conditions often rapidly degrades these systems.⁸

Evidently, each molecule will behave differently when charged (uncharged), depending on the capacity of its molecular backbone and/or substituents to accommodate (release) easily the arrival charge, but also due to the existing (strong or not) electronic interactions between neighboring molecules in solid-state samples; the supramolecular organization in thin films is largely driven by weak intermolecular interactions between adjacent molecules. Therefore, a critical issue yet in simulations of crystalline packing of organic molecules is the proper description of noncovalent interactions between molecules. Due to experimental difficulties, there are great opportunities in studying prototype systems featuring the noncovalent interactions of interest (i.e., ultra closely π -stacking motifs) while keeping good single-molecule n-type donor/acceptor properties. In this regards, introduction of pyrazine rings in 6,13-pentacenequinone (see Figure 1) has recently revealed as a reliable strategy giving rise to reasonable electron mobility values in thin-film transistors.⁹

According to these issues, it is time now to introduce the theoretical methods intended to be used within the field at the molecular scale. Note that any method should have predictive character with independence of existing (if any) experimental information, as a consequence of previous validation studies, yet being computationally cost-effective and reliable enough. Due to the good compromise found, density functional theory (DFT) has reached now a leading role among theoreticians, and significant progress has been achieved in the understanding of variations in charge-carrier mobilities with nature of the material; however, which is often overlooked is the great dependence of the results upon the functional form chosen.^{10,11}

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FIG. 1. Chemical structures (from top to bottom, and from left to right) of studied pentacenequinones: pentacene, 6,13-pentacenequinone, 5,7,12,14-tetraaza-6,13-pentacenequinone (TAPQ-I), and 1,4,8,11-tetraaza-6,13-pentacenequinone (TAPQ-II). The hydrogen atoms and corresponding C–H bonds have been omitted for clarity.

Hence, we want to assess here the capacity of a newly developed functional (coined as B2 π -PLYP and specifically devised for π -conjugated systems¹²) with respect to charge-transport properties of N-substituted pentacenequinones.

II. COMPUTATIONAL DETAILS

The class of orbital-dependent functional forms known as ‘double-hybrids’,^{13–15} compared to older ‘hybrids’ as B3LYP (Ref. 16) or PBE0 (Refs. 17 and 18) are, combine perturbative correlation energy (E_c) up to second order (PT2) together with a correlation energy functional, $E_c[\rho]$, additionally to the standard hybrid combination of exact-like exchange (EXX) energy (E_x) and an exchange energy functional $E_x[\rho]$. In our particular implementation suited to π -conjugated systems, the weights given to the different terms are 0.6025, 0.3975, 0.2731, and 0.7950 for E_x^{EXX} , $E_x[\rho]$, E_c^{PT2} , and $E_c[\rho]$, respectively. In this sense, this expression is believed to be less prone to some errors affecting π -conjugated systems the most (i.e., self-interaction error or medium- to long-range correlation effects).^{19,20} These double-hybrid calculations were done here with the ORCA 2.8.0 quantum-chemical package.²¹ We systematically increased (TightScf, TightOpt, Grid6) the default numerical thresholds and employ the ‘resolution-of-the-identity’ (RI) and ‘chain-of-spheres’ (COSX) techniques^{22,23} to alleviate the computational cost of the more demanding steps (full optimization of interacting pairs of molecules). The auxiliary basis functions to accompany the cc-pVDZ (default for all geometry optimizations) or cc-pVTZ basis sets were taken from the corresponding hardwired library.

III. SUPRAMOLECULAR ORGANIZATION OF THE SAMPLES

Order at all length scales is believed to be the most important parameter governing the efficiency and performance of organic semiconductors.²⁴ Because of the weakness of

the intermolecular forces between two interacting organic molecules, non-covalent interactions are called to play a major role in the control of the supramolecular organization of the samples. Since these weak interactions strongly depends on the presence or absence of substituents, either peripheral or within the backbone, despite being both rigid and planar molecules, substituted pentacenequinones crystallize in a completely different fashion than pentacene²⁵ does; whereas the latter is known to do it in a herringbone-like structure typical of acene molecules, where molecules are not cofacially stacked, single crystals of the former molecules have revealed dominant π - π interactions leading to quasi-1D crystals and thus to highly anisotropic conduction paths. Such ultra-closely π -stacked arrangement, note that the intermolecular distances extracted from X-ray data⁹ were 3.37 and 3.39 Å for TAPQ-I and TAPQ-II, respectively, is tightened in the case of the former due to favorable intermolecular hydrogen bonds between the neighboring parallel stacks.

A deeper understanding of the relationships between the efficiency of charge transport and the chemical morphology of the samples is essential for the improvement of device performance. We will try to address next how this can be accurately achieved by employing double-hybrid models. First of all, the modeling of the weak interactions governing molecule-to-molecule orientation is accomplished through the addition of atom-pair wise interactions between weakly overlapping fragments. Thus, for a pair of atoms A and B separated by a distance R_{AB} , the stabilizing dispersion energy (E_{disp}) is given by the following function:²⁶

$$E_{\text{disp}} = \sum_{A \neq B} \sum_{n=6,8,\dots} s_n \frac{C_n^{AB}}{R_{AB}^n} f_{n,d}(R_{AB}), \quad (1)$$

where C_n^{AB} is the n -th order dispersion coefficient for the atomic pair AB , and the s_n are the functional-dependent scaling parameters used to efficiently couple the electronic and the added dispersion energy. A damping function $f_{n,d}(R_{AB})$ is always considered²⁷ to ensure the adequate switching from short to long distances between atomic pairs. If we keep only

FIG. 2. Optimized structure of a dimer of TAPQ-I (top) and TAPQ-II (bottom) within a stack from perpendicular (left) and side (right) views.

the first term of the expansion, one might use $s_6 = 0.55$ for the B2 π -PLYP-D2 model, the -D2 means dispersion added, as determined previously.¹³

The application of the aforesaid correction to a pair of interacting molecules leads to the (fully optimized) microstructures shown in Figure 2, close intermolecular contacts within a stack are obtained, where it can be observed how the solid-state packing would result from repetition of these configurations. The interaction energy of the dimers is calculated by the supermolecular approach using the expression $\Delta E = E_{\text{dimer}}(d) - 2E_{\text{monomer}}$, being $E_{\text{dimer}}(d)$ the total energy of the dimer at the optimized intermolecular distance d between the center of mass of the monomers. Not surprisingly, very similar values are obtained, -24.9 and -24.5 kcal/mol, for TAPQ-I and TAPQ-II, respectively. Meanwhile, basis set superposition error (BSSE) was estimated by using a larger basis set (cc-pVTZ) to recalculate the value of ΔE for a frozen

TABLE I. Estimates of molecular packing parameters in the studied molecules: optimized intermolecular distance (d , in Å), and relative displacements along the short and long molecular axes (Å).

Displacement	TAPQ-I		TAPQ-II	
	Theory ^a	Experiment ^b	Theory ^a	Experiment ^b
d	3.14	3.37	3.16	3.39
Long axis	0.11	0.21	0.13	0.00
Short axis	1.81	1.95	1.54	1.73

^aCalculated here with the B2 π -PLYP-D2/cc-pVDZ model.

^bTaken from Ref. 9.

dimer: -21.1 and -21.2 kcal/mol, for TAPQ-I and TAPQ-II, respectively. Finally, the extrapolation to the complete basis sets limit (cc-pVnZ) by a n^{-5} -like function,²⁸ taking the cc-pVDZ and cc-pVTZ values, provided a final estimate of -20.5 and -20.7 kcal/mol. Notwithstanding the marked influence of BSSE on the initial values, as expected, the interest was mainly to confirm the energy range for the π -stacking of both molecules. Even if crystallization kinetics or nucleation dynamics may further complicate things, note that the plausibility of more than one minima can not be completely excluded, generally, the experimentally known structures are to be found among those predicted at the theoretical level, provided this is accurate enough. It can be expected that in most cases only the stable polymorph, and possibly some of the metastable polymorphs with slightly higher lattice energy, can be crystallized, as it seems to happen here. Note also that the lattice energy of organic solids can be estimated from calculations on symmetry-related dimers, as recently shown in the case of the benzene crystal.²⁹

The relative displacements obtained are compared to crystallographic data in Table I. Note that we reasonably reproduce not only the intermolecular distance (d) between the layers, but also the shift of the upper molecule along the short and long molecular axes (y and x axis, respectively). However, a systematic error of -0.2 Å still remains, in agreement with previous studies on substituted tetracenes,³⁰ which prompted us to further explore other possibilities attempting to improve it. To do so, we concentrate next on TAPQ-I and resort to a more sophisticated form of Eq. (1), the recently introduced and so-called DFT-D3 model²⁶ although, however, using another functional form (PBE0) due to the lack of parameters for our B2 π -PLYP implementation. Thus, we will compare in the following the PBE0-D2, PBE0-D3, and B2 π -PLYP-D2 models among them and with respect to the experimental value for intermolecular displacements. While the -D3 function clearly improves the value of d with respect to -D2, 3.45 Å vs. 3.15 Å, it still fails to describe the large asymmetry of shifts between interacting monomers, no matter the structure taking as starting point for the optimization process; similar values (Å) are found now along the short (long) molecular axes: 1.2 (1.3) and 2.0 (1.7), for PBE0-D2 and PBE0-D3, respectively, which might have a significant impact on the corresponding electronic couplings (*vide infra*). If we average the error for displacements along all (xyz) spatial coordinates, we obtain a mean absolute deviation (MAD, in Å) of 0.67 , 0.52 , and 0.16 , for PBE0-D2, PBE0-D3, and

TABLE II. Estimates (in eV) of adiabatic (A) and vertical (V) ionization potentials (IP) and electron affinities (EA), as well as hole (Λ_{h+}) or electron (Λ_{e-}) intramolecular reorganization energies (in meV) for pentacene, TAPQ-I, and TAPQ-II.

Molecule	VIP	AIP	VEA	AEA	Λ_{h+}	Λ_{e-}
Pentacene	6.22 (6.57) ^a	6.17 (6.55) ^a	1.07 (1.21) ^a	1.14 (1.39) ^a	95 (102) ^b	131 (n.a.)
TAPQ-I	9.22	8.90	1.64	1.70	476	126
TAPQ-II	9.26	8.88	1.44	1.49	555	200

^aHighly accurate *ab initio* values taken from Refs. 39 and 40.^bGas-phase experimental (UPS) results taken from Ref. 41.

B2 π -PLYP-D2, respectively. All-in-all, even when the -D2 function is believed to slightly overestimate the dispersion interactions, and thus to underestimate the intermolecular distance, the use of the underlying double-hybrid model seems to give a more complete and accurate picture of the interactions between the monomers. As the electronic coupling is extremely sensitive to these face-to-face interactions,³¹ we will use from now on the configurations saved by the B2 π -PLYP-D2 functional. Note also that further studies on crystals should include many body dispersion effects and the correct description of H-bonds. Thus, in order to do so, further extensions of the dispersion-corrected methodology, such as more refined forms for the damping function or the (possible) influence of three-body interactions, are also envisioned and work is in progress to assess their final influence on charge-transport properties.

IV. MARCUS ELECTRON TRANSFER RATE

In the limit of the weak-coupling regime, assisted by thermal activation of intra- and inter-molecular vibrations near room-temperature,³² the charge-transfer process can be modelled through a sequence of hole/electron ($h^{\cdot+}/e^{\cdot-}$) hops between neighboring molecules (M and N) occupying well-defined sites on a crystalline lattice,

which consequently undergo a large geometry relaxation allowing charge localization and self-trapping. Under these conditions, the electron transfer rate reads as,³³

$$k_{CT} = \frac{2\pi}{\hbar} |V_{if}|^2 \frac{1}{\sqrt{4\pi \Lambda k_B T}} \exp \left[-\frac{\Lambda}{4k_B T} \right], \quad (3)$$

where T denotes the temperature, and $\hbar$ and k_B are fundamental constants. One of the main advantages of the hopping model described above is the fact that transport parameters depend only on a pair of adjacent sites, and that information can be thus fully extracted from first-principles calculations. The intermolecular electronic coupling is defined³⁴ as,

$$V_{if} = \langle \Psi_i | \hat{H} | \Psi_f \rangle, \quad (4)$$

Ψ_j are the (Hartree-Fock) open-shell many-electron wavefunctions describing an excess charge localized on molecule M or N; i.e., the initial and final states. On the other hand, the energy needed to switch from the initial $|\Psi_{M^{+(-)}} \Psi_N\rangle$ to the final $|\Psi_M \Psi_{N^{+(-)}}\rangle$ state, the molecular reorganization energy (Λ), is computed normally from the adiabatic potential

energy surfaces of the reactants³⁵ according to

$$\Lambda = [E_{M^{+(-)}/N} - E_{M^{+(-)}}] + [E_{N/M^{+(-)}} - E_N], \quad (5)$$

with E_N or $E_{M^{+(-)}}$ indicating the total energy of the unionized or ionized molecule at its optimum geometry, respectively, and $E_{N/M^{+(-)}}$ or $E_{M^{+(-)}/N}$ the energy of the unionized or ionized molecule at the optimized geometry of the other state. Note that Λ was calculated thanks to the analytical gradient implementation of double-hybrid functionals.³⁶ The coupling was calculated by the NWChem 6.0 (Ref. 37) electron transfer module³⁸ at the optimized microstructures shown in Figure 2, and using (verified) localized states for electron transfer reactant and product states after applying the fragment molecular orbital guess.

Before applying our B2 π -PLYP model to compounds TAPQ-I and TAPQ-II, we have first calibrated it for single-molecule magnitude of the pentacene molecule thanks to the existence of: (i) benchmark values of ionization potentials (IPs) and electron affinities (EAs) of oligoacenes;^{39,40} and (ii) gas-phase experimental (UPS) value of Λ (Ref. 41) for (more favored in this case) hole transport. Table II shows the accuracy of the method, considering that errors higher than 0.5 eV for IP and EA were obtained before with the (less sophisticated) B3LYP or PBE0 models.⁴² Note that IPs and EAs of the active molecules are key parameters, not only because of its relation with the corresponding Λ values for hole or electron transfer, respectively, since they also largely determine the ability to reduce or oxydize upon unisolated atmospheres, as well as the efficiency for injection of charges from the electrodes: a barrierless process, in absence of interface dipole effects, would imply a close match between these magnitudes and the work function of the cathode and anode. Furthermore, the ease of charge injection from source electrodes, concomitantly with the intrinsic ability of the material to transport the generated carriers, often determines the p- and/or n-type behavior of the material. Upon inspection of Table II, we can easily see how $\Lambda_{h+} \gg \Lambda_{e-}$ for TAPQ-I and TAPQ-II, which would manifest in much lower charge-transfer rates for holes than for electrons. In fact, this situation correlates to the n-type performance of N-substituted pentacenequinones found in thin-film transistors.⁹ Since intramolecular reorganization energies largely depend on geometrical changes upon oxidation/reduction, it seems that introduction of pyrazine rings at the end leads to slightly larger deformations. To further disentangle the role played by pyrazine rings, we have also calculated Λ values for 6,13-pentacenequinone, indeed a major impurity in pentacene, to find the opposite behavior since $\Lambda_{h+} < \Lambda_{e-}$, as found for pentacene too. It thus seems

TABLE III. Estimates of hole and electron electronic couplings (V_{if} , in meV) and corresponding charge-transfer rates (k_{CT} , $\times 10^{14} \text{s}^{-1}$) for the optimized dimer structures of TAPQ-I and TAPQ-II.

Molecule	V_{if}^{h+}	$k_{CT}(h^{+})$	V_{if}^{e-}	$k_{CT}(e^{-})$
TAPQ-I	44	0.002	309	3.74
TAPQ-II	233	0.019	255	1.08

that the introduction of pyrazine rings confirms at a molecular scale the successful strategy followed before to have n-conducting molecules,⁹ or even ambipolar behavior,⁴³ exhibiting π -stacking motifs.

We also intend to (qualitatively) incorporate the changes in electronic polarization of the surrounding molecules (medium) upon arrival of the charge, the so-called external contribution (Λ_s), which is however difficult to calculate theoretically⁴⁴ and normally fixed as a tunable parameter.⁴⁵ Actually, recent calculations on anthracene single crystals⁴⁶ predicted a value of 52 meV to be compared to a value of 182 meV for the internal (intramolecular) part (Λ_i). Furthermore, the molecular size dependence was studied for oligoacenes in Ref. 47, showing a consistent decrease with size. However, deformations of the lattice in the immediate vicinity of the polarized atoms in TAPQ-I and TAPQ-II might possibly increase the values with respect to the corresponding unsubstituted oligoacenes. Thus, as a compromise, we will take here a value of 0.1 eV for Λ_s , considered to be an upper limit. Note that we are more interested in understanding the differences between similar materials (and corresponding ideal devices) than in the deficiencies of the hopping mechanism;⁴⁸ if the basic assumption of charge localization does not longer remain, there exists other models with larger range of validity⁴⁹ which, however, exceeds the purpose of the present discussion.

We have calculated next the electronic coupling arising from the two nearly cofacial molecules found in the optimized structures of TAPQ-I and TAPQ-II, see Figure 2. Table III gathers the corresponding values obtained with Eq. (4). Note that the splitting approach commonly used yields overestimated values due to the non-centrosymmetric dimeric forms found.⁵⁰ Additionally, the electronic coupling between parallel stacks can be considered small,⁵¹ promoting indeed a high mobility anisotropy, as found also before for collinear arrays of unsubstituted pentacene.⁵² When inserting the values of Λ_{e-} and corresponding V_{if} into Eq. (3), we obtain high electron hopping rates of $3.7 \times 10^{14} \text{s}^{-1}$ for TAPQ-I and $1.1 \times 10^{14} \text{s}^{-1}$ for TAPQ-II, see Table III. We are also aware of the slight overestimation of V_{if} values suffered from the slightly tighter packing predicted by the calculations. Actually, for a dimer of TAPQ-I extracted from the crystalline structure, $d = 3.37 \text{\AA}$, we calculate now $V_{if} = 170 \text{ meV}$, significantly lower than previous estimate based on optimized dimer configuration; the hopping rate being now $1.1 \times 10^{14} \text{s}^{-1}$ but still high. Actually, for closely related slipped π -stacked structures, the exponential-like decay of V_{if} with the intermolecular distance is expected to dominate the charge-transfer rates.⁵³ As a matter of exam-

ple, if we increase the intermolecular distance to $d = 3.5 \text{\AA}$, while keeping unchanged the relative position of the two molecules, the electronic coupling dramatically decrease to less than 5 meV. Finally, as the magnitude of V_{if} depends on the amount of overlap between reactant and product states, we have also analyzed the possible influence of diffuse functions (aug-cc-pVDZ) with negligible influence.

V. LINK TO CHARGE MOBILITY VALUES

With knowledge of charge-transfer rates between neighboring molecules within the crystal, obtained through Eq. (3) upon optimization of a pair of interacting molecules, the charge mobility can be evaluated through random walk simulations,⁵⁴ when different transport networks are expected, or by the use in the case of highly ordered systems of the Einstein-Smoluchowski equation for diffusion of charged particles, as it is the case here, and if the relative (optimized) position of the interacting molecules is known,

$$\mu = \frac{D}{k_B T} \propto \frac{d^2 k_{CT}}{k_B T} \quad (6)$$

owing to the fact that site energies and electronic coupling keep the same values along the stack,⁵⁵ as well as does the diffusion constant D and the related intermolecular distance d . Whereas the calculated hole mobilities for TAPQ-I and TAPQ-II are very low, less than $0.1 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$ in fact, electron mobilities as high as 14.4 and $4.2 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$ are predicted, respectively. Furthermore, we are aware about the slight overestimation expected for theoretical electronic couplings, which together with its modulation by the lattice fluctuations^{56,57} might have some impact on the final values. This is why we will discuss hereafter the calculated mobility values primarily on a relative basis. However, note that the ratio $\frac{d^2 k_{CT(I)}}{d^2 k_{CT(II)}}$, being I (II): X-ray (B2 π -PLYP-D2) results, is still close to unity.

We have compared next the room-temperature relative values obtained for the two derivatives (TAPQ-I and TAPQ-II) by estimating their ratio according to the following expression:⁵⁸

$$\frac{\mu_{\text{TAPQ-II}}}{\mu_{\text{TAPQ-I}}} \propto \frac{V_{\text{TAPQ-II}}^2}{V_{\text{TAPQ-I}}^2} \sqrt{\frac{\Lambda_{\text{TAPQ-I}}}{\Lambda_{\text{TAPQ-II}}}} e^{(\Lambda_{\text{TAPQ-I}} - \Lambda_{\text{TAPQ-II}})/4 k_B T}, \quad (7)$$

with V and Λ defined, respectively, by Eqs. (4) and (5). Note also that we assume the same intermolecular distance within the dimers for all transfer events despite possible lattice vibrations. Feeding our results into the above expression, we obtain a ratio of 0.26 between the expected mobilities of TAPQ-II and TAPQ-I, which reproduces the experimentally observed trend since lower mobilities are found⁹ for the former, $2 - 6 \cdot 10^{-5}$ and $0.05 - 0.12 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$, respectively. However, the poor performance of thin-film transistors built using TAPQ-II as active layer (by few orders of magnitude) was mainly attributed to the amorphous nature of the films; thus, our results seem to indicate that there is still door for further improvements. Note also that calculated electron affinity of TAPQ-II (1.5 eV) is around 0.2 eV lower than for TAPQ-I, and then less prone to ambient degradation. However, the

energy barrier for injection of electrons relies on a close match between electron affinities and the work function (Φ_m) of the inorganic electrode material used as reservoir, and thus minimizing the barrier when using Au as electrode ($\Phi_m \sim 5$ eV) would actually need tuning the surface metal work function by deposition of ultrathin oxide films. In short, we would expect a (rather close) similar behavior of these two molecules in real devices under the same working conditions if current technical difficulties were successfully overcome.

VI. CONCLUSIONS

The selection of molecules acting as molecular semiconductors in organic-based devices, and their self-assembly largely guided by weak intermolecular forces, should be thoroughly motivated for maximizing efficiency and lifetime. In this respect, quantum-chemical calculations at the nanoscale can bring the main geometrical and energetical parameters affecting charge-transfer rates, and associated mobilities, provided that (i) they accurately calculate single-molecule energies related to the charging/decharging process upon hopping; and (ii) they accurately predict the most favoured molecule-to-molecule interactions, paving the way towards electronic couplings between neighboring molecules in a further step, which seems to be a challenging task for most of the quantum-chemical methods currently in use. Taking N-substituted pentacenequinones as examples, we have shown that modern DFT-based methods (orbital-dependent functionals with dispersion interactions approximately incorporated) are able to realistically predict the main parameters from first-principles calculations. Concerning the study of supramolecular entities, somehow the bottleneck of molecular calculations, the dispersion correction does not correct all shortcomings of the different density functionals, which leads to different intermolecular orientation and distances depending on the functional form used (PBE0 and B2 π -PLYP) and thus to varying electronic couplings and hopping rates. Whereas the intermolecular distance is better predicted by PBE0-D3, this method failed to simulate the asymmetrical displacements of the upper molecule with respect to the short and long intermolecular axis. The latter feature is, however, better predicted by B2 π -PLYP-D2 although underestimating the intermolecular distance. After careful study of the possible influence of the different orientations found by the two methods, the electronic coupling is known to be largely sensitive to the packing of molecules, we conclude that B2 π -PLYP-D2 is the best compromise here with respect to the intermolecular orientations. Interestingly, our results confirm at a molecular scale that (i) introduction of pyrazine rings seems to be a successful strategy to switch from p-type to n-type conduction mechanism, while keeping moderately low reorganization energies for the latter; and (ii) the herringbone packing, typical of acene-like molecules, is altered to π -stacking, which promotes higher electronic couplings. We hope to extend in the near future this kind of computational studies, which are expected to play an increasing role in future applications, to the rational design of new engineered acene-based compounds.

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