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The Effect of Cyclic Topology on Charge-Transfer Properties of Organic Molecular Semiconductors: The Case of Cycloparaphenylene Molecules

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Abstract

We have studied the role played by cyclic topology on charge-transfer properties of recently synthesized π -conjugated molecules, namely the set of $[n]$ cycloparaphenylene compounds, with n the number of phenylene rings forming the curved nanoring. We estimate the charge-transfer rates for holes and electrons migration within the array of molecules in their crystalline state. The theoretical calculations suggest that increasing the size of the system would help to obtain higher hole and electron charge-transfer rates, and that these materials might show an ambipolar behavior in real samples, independently of the different mode of packing followed by the $[6]$ cycloparaphenylene and $[12]$ cycloparaphenylene cases studied.

1 Introduction

The emerging areas of organic electronics and photovoltaics need the endless search of materials with enhanced optoelectronic and charge-conducting properties, owing to the underlying structure-property relationships that can be fine-tuned first, and then further exploited following a bottom-up approach to the built-in devices. The efficiency of any of these devices is largely dominated by the charge carriers mobility, a bulk parameter characterizing experimentally the charge transport properties.¹ The chemical nature of the molecules constituting the active layer is undoubtedly key to the final performance of the devices, although the experimental conditions (boundaries and impurities, crystal defects acting as traps, engineered surfaces to modify the crystal growth, and environmental effects, to name just a few of them) often preclude to establish firmly the role played by the molecules themselves. Thus, theoretical estimates of the charge-transfer rates and other related properties can help us to achieve further discoveries within the field.

Following the charge injection from the electrodes, or the bulk formation of charge carriers after exciton dissociation, a molecule close to the interface will experience an inter-molecular charge/uncharge process assisted by electron-phonon and disorder effects² by energetically favouring the accommodation (release) of the arrival (salient) charge. Obviously, for the bulk propagation of these charge carriers, the electronic interactions between closely packed molecules is also key in solid-state samples, which is driven by the way in which the weakly bound molecules orient and finally interact.³ An issue still under development is the discovery of new *n*-type organic semiconductors (favouring electron vs. hole migration), or even ambipolar ones,⁴ the latter favouring equally hole or electron migration across the samples.

We therefore explore here the possibilities of a new family of molecules, obtained upon progressively bending phenylene units to form a cyclic nanohoop, see Figure 1, as suitable candidates for organic-based devices. These molecules, called $[n]$ cycloparaphenylenes ($[n]$ CPPs), where n refers to the number of phenylene units connected in *para* position, have recently attracted a world-wide interest (for some recent and comprehensive reviews see Refs.⁵⁻⁸) as well as their radical cation and anion forms.⁹⁻¹⁴ This is mostly due to the fact that: (i) they can be viewed as precursors of cage-like structures, able to encapsulate fullerenes which can be exploited for host-guest nanoelectronic applications,¹⁵⁻¹⁸ or carbon nanotubes of controlled size and chirality;¹⁹ and (ii) their versatile and gram-scale synthesis is already not a promise but a reality²⁰ with their crystal packing fully resolved and showing interesting features. Note that the parent linear compounds, the (oligo)phenylene molecules, have been widely studied before²¹ allowing thus the comparison between these two forms, linear and cyclic, if needed. Furthermore, whereas other widely studied compounds, such as for instance (oligo)acenes, display a decrease in the band gap as a function of their system size, which might degrade any transport property upon exposure to air, these compounds keep a quasi-constant value of that band gap independently of their size.²² It is in this context that we aim here to establish whether these molecules might be used as active materials for electronics applications in the near future.

2 Theoretical details

We assume in the following a weak-coupling regime between a pair of interacting $[n]$ CPP molecules,²³⁻²⁵ whose orientation is extracted from the

crystalline data, and thus model the hole/electron (h^+/e^-) transfer by a sequence of concerted hops between two neighbouring molecules, using for that (in chemical notation) the following self-exchange hole/electron transfer reaction:

which will propagate the charge-carriers along all the crystallographic directions depending on the mutual orientation between molecules. Note that this process is thermally activated at room temperature, and assisted by intra- and intermolecular vibrations.²⁶ The charge-transfer rate (k_{CT}) is semi-classically given by the Marcus-Levitch-Jortner expression:²⁷

$$k_{CT} = \frac{4\pi^2}{h} |V_{if}|^2 \frac{1}{\sqrt{4\pi\Lambda_s k_B T}} \sum_{v=0}^{\infty} \left[\frac{S_{eff}^v}{v!} \exp(-S_{eff}) \exp\left(\frac{-(\Lambda_s + v\hbar\omega_{eff} + \Delta G^\ominus)^2}{4\Lambda_s k_B T}\right) \right], \quad (2)$$

where $\hbar$ and k_B are fundamental constants, and T is the temperature, chosen here to be 298.15 K. Note that V_{if} is the electronic coupling between the initial (reactants) and final (products) states, depending on the mutual orientation and overlapping of any pair of molecules considered within the lattice configuration of samples. The effective Huang-Rhys factor, $S_{eff} = \Lambda/\hbar\omega_{eff}$, depends on the internal reorganization energy for every one-hop charge-transfer event, which it will thus be calculated using energies of isolated molecules, with $\hbar\omega_{eff}$ the vibrational mode assisting the hopping process (fixed here as 0.2 eV). Note that we neglect at this stage: (i) any contribution to $\Delta G^\ominus$, since we rely on equivalent molecules and don't apply any electric field during the calculations; and (ii) the effect of disorder on V_{if} values, caused by vibrational fluctuations of molecules at room temperature.^{28,29} However, we do necessarily consider the contribution to Λ caused by the reorganization of the dielectric medium upon arrival of the charge carrier, normally dubbed as Λ_s , which is taken here as a fixed value of 0.1

eV, in agreement with recent studies on oligoacenes and related systems.^{30–32}

We use the following (standard) definition for internal reorganization energies:^{33–35}

$$\Lambda_{h(e)+(-)} = [E_{M^{+(-)}/N} - E_{M^{+(-)}}] + [E_{N/M^{+(-)}} - E_N], \quad (3)$$

where E_N or $E_{M^{+(-)}}$ refers to total energy of the neutral or charged molecules, at their respective optimised geometries. These geometries were verified, by inspecting the Hessian (all positive) eigenvalues, to be the corresponding global minimum for each system and state under consideration. Owing to the fact that charge-transfer can be semiquantitatively modelled through concerted steps, $E_{N/M^{+(-)}}$ or $E_{M^{+(-)}/N}$ denotes the energy of the neutral or charged molecules at the optimised geometry of the other involved state. These reorganization energies for holes (Λ_{h+}) and electrons (Λ_{e-}) are calculated at the Density Functional Theory (DFT) level with the B3LYP functional^{36,37} and the 6-31+G* basis set. This model chemistry provides accurate values of Λ at a moderate cost.^{38–40} On the other hand, the use of a dispersion correction, the B3LYP-D3(BJ)/6-31+G* modified level,⁴¹ only marginally affected the values of Λ by less than 10 % for the [4]CPP and [5]CPP cases, with a negligible impact on longer oligomers where geometrical constraints due to their cyclic forms are largely released. These calculations also give associated energy values such as Adiabatic Ionization Potentials (AIP) or Electron Affinities (AEA), which are defined as the difference of total energies between charged and neutral systems, $AIP = E_{M^{+}} - E_M$ and correspondingly $AEA = E_M - E_{M^{-}}$, whereas the Quasiparticle Energy Gap is given by $QEG = AIP - AEA$. Finally, we remind that closed- or open-shell calculations are done for neutral or charged (doublet) states, respectively. These calculations were done with the Gaussian 09 package,⁴² unless oth-

erwise noticed, and always incrementing the default thresholds to reduce numerical errors as much as possible.

The expression used for the calculation of V_{if} needs some additional considerations. The coupling between the initial and final states is defined⁴³ as one half of the energy difference between the adiabatic potential energies at the geometry (Q_c) where the diabatic (localised) potential energy surfaces cross each other,

$$V_{if} = \frac{1}{2} [E_+(Q) - E_-(Q)]_{Q=Q_c} . \quad (4)$$

These two-state model involves solving the usual secular equation,

$$\begin{vmatrix} H_{ii} - E & H_{if} - ES_{if} \\ H_{fi} - ES_{fi} & H_{ff} - E \end{vmatrix} = 0 \quad (5)$$

from which

$$V_{if} = \frac{1}{1 - S_{if}^2} \left[H_{if} - \frac{S_{if} (H_{ii} + H_{ff})}{2} \right], \quad (6)$$

with $S_{if} = \langle \Psi_i | \Psi_f \rangle$, $H_{if} = \langle \Psi_i | \hat{H} | \Psi_f \rangle$, $H_{ii} = \langle \Psi_i | \hat{H} | \Psi_i \rangle$, and similarly H_{ff} . We use in the following the Unrestricted Hartree-Fock wavefunction (Ψ_j , $j = i, f$) to describe an excess charge (hole or electron) localised on molecule M or N; ie., the initial and final states for an hole or electron transfer reaction. Note that true localised states for reactant and product states were always obtained, with that excess charge completely localised either on molecule M or on molecule N during the set of calculations performed. These calculations were done with the cc-pVDZ basis set, and can be thus dubbed as UHF/cc-pVDZ. This choice has been sufficiently validated before^{44,45} although it is also known to provide an upper limit of V_{if} values with respect to experimental estimates.⁴⁶ The NWChem 6.3 package, thanks to the electron transfer module implemented on it,^{47,48} was employed for this part of the calculations.

3 Results and discussion

3.1 Reorganization energies and associated magnitudes

3.1.1 Benchmarking values for the [6]CPP molecule

We take this molecule as a benchmark system due to some concurring and appealing features: (i) the size of its inner cavity, measured by a diameter of 8.4 Å (defined as the distance between the *ipso*-carbon atoms at opposite faces of the nanoring), can be considered as a threshold for having marked intra-molecular non-covalent interactions between the phenylene units situated on different sides of the ring;⁴⁹ and (ii) its linear analogue, *para*-hexaphenylene (6PP) has been thoroughly studied before as a promising organic molecular semiconductor,⁵⁰ and will be thus used (*vide infra*) for comparison.

The B3LYP/6-31+G* optimized structures of the neutral, cationic, and anionic forms of [6]CPP revealed a marked change in the distance between the *ipso*-carbon atoms belonging to neighbouring phenylene rings, the $C_{ipso}-C_{ipso}$ bond length, decreasing from a value of 1.491 Å in the neutral form to 1.469 Å for the charged forms. This feature, together with the concomitant increase of the $C_{ipso}-C_{ortho}$ and $C_{ortho}-C_{ortho}$ bond lengths of the phenylene rings, clearly suggest a more quinoid (or less benzenoid) character of the charged forms with respect to the neutral molecule. The dihedral angle $C_{ortho}-C_{ipso}-C_{ipso}-C_{ortho}$ between the phenylene rings also decreases, from an average value of 28.0° for [6]CPP to 14.8° (16.1°) for [6]CPP⁺ ([6]CPP⁻). We also note an equal distribution of spin and charges over all phenylene rings, with all these findings highlighting thus the delocalization of the polaron over all phenylene units. We note that the radical cation of [6]CPP

has been recently generated by chemical oxidation,¹⁴ showing a completely delocalized spin and charge over all rings in complete agreement with our theoretical results.

The values of the different energy magnitudes, and or the various theoretical methods analyzed, related to the charge/uncharge process followed by these molecules are gathered in Table 1. First, by comparing B3LYP and B3LYP-D3(BJ) results, the latter method including a dispersion-like correction for non-covalent intra-molecular effects,⁴¹ we don't observe a significant influence of the latter effects on any magnitude, contrarily to what happened with [4 – 5]CPP, probably due to their reduced diameter, which prompts us to report in the following only dispersion-uncorrected results in agreement with recent theoretical studies.⁵¹ We also compare the results with those obtained with the ω B97X method,^{52,53} a range-separated functional related to the older CAM-B3LYP method⁵⁴ which has been applied before to this kind of systems, and with the B2-PLYP method,⁵⁵ a double-hybrid functional incorporating non-local correlation effects very efficiently. These values are subsequently listed in Table 1, showing that: (i) the Λ_{h+} and Λ_{e-} yielded by B3LYP are only slightly lower than those provided by B2-PLYP; and (ii) the ω B97X method seems to strongly localize the polaron formed upon charge injection, concomitantly increasing the QEG and the Λ_{h+} or Λ_{e-} values. Altogether, these findings prompt us to discard the use of the ω B97X method, reporting only B3LYP-based results in the following.

We focus next on the influence of the molecular arrangement topology by comparing the values of AIP, AEA, Λ_{h+} and Λ_{e-} obtained for cyclic ([6]CPP) and linear (6PP) forms of the hexaphenylene oligomer. These cal-

culations were done with the ORCA 3.0.2 package,⁵⁶ and with the B3LYP-D3(BJ)/def2-TZVP level to discard any basis set size and dispersion effects. Interestingly, while the AIP (AEA) changes from 6.09 to 6.67 eV (from 1.19 to 0.80 eV) increasing the QEG by almost 1 eV when going from the cyclic to the linear case, Λ_{h+} shows almost no change (from 365 to 370 meV). However, Λ_{e-} increases from 347 to 480 meV, which is detrimental for electron transfer as deduced from the form of Eq. (2). Note also that the ratio $\frac{\Lambda_{h+}}{\Lambda_{e-}}$ is very close to unity in the case of [6]CPP, which might manifest in some ambipolar behavior showing thus more balanced charge-transfer rates for both hole and electron carriers. The similarity of hole reorganization energies for [6]CPP and 6PP systems points to similar charge delocalization in both cases,¹² whereas an increase of around 40 % for the Λ_{e-} value of 6PP allows us to speculate about a more localized character of its electron distribution due to chain-end effects. However, an intrinsic difference (sometimes neglected) between [6]CPP and 6PP are the geometries observed in the crystal structure. Whereas for [6]CPP no significant geometrical changes are expected upon crystallization due to their closed form, 6PP is known to undergo a marked solid-state planarization. Thus, we have repeated the calculations but constraining the 6PP molecule to planarity, thus freezing all dihedral angles during the optimization process, observing that Λ_{h+} (Λ_{e-}) reduces now from 370 to 158 meV (from 480 to 191 meV) which helps to explain better the large mobilities found in real samples of 6PP, although they do not behave as a completely ambipolar material.⁵⁰

3.1.2 Increasingly longer $[n]$ CPPs

Having established the potential of the $[6]$ CPP system to undergo an efficient charge-transfer process, Table 2 extends the previous results to the full set of $[4 - 12]$ CPP systems investigated here. The calculated AIP values for the whole set of compounds are comprised between 6.0 – 6.3 eV, with a slight stabilization beyond $[6]$ CPP around 6.2 – 6.3 eV. The adiabatic values are just between 0.1 – 0.2 eV lower than vertical ones. The same minor changes upon increasing the number of cycles are also obtained for AEA values, ranging between 1.2 – 1.4 eV. These values of AIP or AEA also serve to qualitatively estimate the ease of charge injection from the electrodes acting as reservoir, neglecting any interfacial effect. Injection of holes (electrons) relies on a close match between the ionization potential (electron affinity) of the organic material and the work function of the inorganic material (Φ_m) behaving as anode (cathode). If we compare the values of AIP with, for instance, the $\Phi_m = 4.7$ eV of the widely used Indium Tin Oxide (ITO, $\text{In}_2\text{O}_3\text{-SnO}_2$) we can see an energy barrier of around 1.5 eV, and thus precluding ohmic (i.e. barrierless) contact. However, recent research has shown the large possibilities of crystal and/or interface engineering of new materials for a closer match, and thus a higher efficiency.⁵⁷ For instance, chlorinated ITO facilitates a workfunction of $\Phi_m = 6.1$ eV,⁵⁸ with other existing high work function electrodes such as MoO_3 ($\Phi_m = 6.6$ eV⁵⁹) available too. Furthermore, it has been recently shown that decorating the surface of gold electrodes with self-assembled monolayers of alkanethiols or phenylthiols can significantly increase the Φ_m value to 5.5 – 5.8 eV with respect to the values of uncoated gold (e.g. 4.8 eV for the polycrystalline or 4.9 eV for the 111 face),⁶⁰ and the same response was found for Ag electrodes too.⁶¹ Considering now the low values of AEA theoretically obtained, values for

Φ_m as low as possible would be preferred⁶² as those given by alkali elements (e.g. Cs), despite their high reactivity in non-inert atmospheres which may be nonetheless reduced by co-depositing or coating these elements.

The energy of frontier Molecular Orbitals (MO) of these compounds, i.e. the Highest Occupied (HOMO) and Lowest Unoccupied (LUMO) ones, have been extensively discussed in the literature.^{63,64} We only qualitatively compare herein their values with electrochemical measurements against the formal potential of ferrocene, neglecting solvent and supporting electrolyte effects, by using the expression (in eV) $E_{\text{HOMO}} = - (E_{[\text{onset, ox vs Fc/Fc}^+]} + 5.39)$.⁶⁵ This gives an energy between 5.8 – 6.2 eV for the set of [6 – 12]CPP compounds, slightly increasing with system size, which is in reasonable agreement with the values theoretically found here (5.2 – 5.6 eV) accepting a systematic bias of around 0.4 eV. We also note that our theoretical values evolve slightly different as a function of n for odd- and even- compounds, as it was also previously found in the literature.⁶³ The values of the QEG slightly increase from 4.6 eV, showing a peak for [7]CPP at 5.1 eV, and then slightly decrease until approximately 4.8 eV.

Figure 2 presents the evolution of Λ values, for both hole and electron transfer events, upon increasing the size of the system. Interestingly, the values seem to saturate with system size, and the ratio between Λ_{h^+} and Λ_{e^-} progressively decreases from 1.2 for [4]CPP to 0.8 for [12]CPP, being these values lower than the corresponding ratio for pentacene⁶⁶ (around 1.4) which is often regarded as a benchmark hole-transporting organic molecular semiconductor. To rationalize the evolution of the values with the number of units, we note first that the monomeric form of the [8]CPP^{•+} radical

cation was recently isolated and characterized,¹¹ after oxidation of [8]CPP ($E_{[\text{onset, ox vs Fc/Fc}^+]} = 0.59 \text{ V}$), clearly revealing a geometrical shape (preserving the concentric shape of the neutral form) fully consistent with full delocalization of that positive charge.⁹ Furthermore, a recent study extended the synthesis and characterization to the set of $[n]\text{CPP}^+$ ($n = 5, 6, 8, 10, 12$) cations.¹⁴ The authors unambiguously found, as noted by ESR and NMR experiments, that the positive charge and spin fully delocalize over all phenylene units for all compounds, which is consistent with the progressive and smooth decrease of Λ_{h^+} values with the increasing number of conjugated units.

3.2 Electronic couplings in supramolecular samples

3.2.1 Interacting [6]CPP molecules

The packing of all these molecules closely follows a herringbone pattern except for the [6]CPP case, for which a completely different molecular arrangement is found.⁶⁷ The latter involves the linear alignment of [6]CPP molecules forming a discontinuous (nanotube-like) channel,⁶⁸ whose main microstructures are presented in Figure 3, as taken from the Cambridge Crystallographic Data Centre (code archive CCDC 852989; $a = b = 19.3957 \text{ \AA}$, $c = 6.1998 \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$) and used rigidly herein. We can observe three pairs named here as slipped-lateral (i.e. two adjacent molecules belonging to the same layer and interacting along the a, b directions), tubular-like (i.e., two adjacent and superimposed molecules belonging to different layers and interacting along the c axis), and diagonal (i.e., two molecules belonging to different layers but not superimposed). This particular supramolecular organization of [6]CPP has recently received a large interest for its possible use in a bottom-up template-driven synthesis of carbon nanotubes of con-

trolled porous size. Since the binding energy of the tubular-like dimer is roughly twice the value of the slipped-lateral dimer,⁴⁹ one could even speculate about a controlled growing mechanism of the crystalline samples after deposition of the first monolayer, by fine-tuning the underlying substrate-adsorbate physisorption, which might be found useful for the development of solid-state organic electronics devices.

Furthermore, looking at the calculated values (see Table 3) of V_{if} , following Eq. (6), this way of packing reveals some important features: (i) the electronic coupling for electrons appears clearly favoured, and considerably large, for the slipped-lateral dimer, with a relative value of $\frac{V_{if}(e^-)}{V_{if}(h^+)} \simeq 4$; (ii) the electronic coupling for both holes and electrons is negligible for the tubular-like arrangement of molecules, which precludes the contribution of this mode of packing to the transport mechanism; and (iii) the electronic coupling for both holes and electrons appears similar, and reasonably large around 50–60 meV, for the diagonal dimer, with a relative value of $\frac{V_{if}(e^-)}{V_{if}(h^+)} \simeq 1$, which might manifest into an ambipolar transport of both charge carriers. Overall, the values obtained for the charge-transfer rates (around $10^{12} - 10^{13} \text{ s}^{-1}$) are high enough to speculate about an efficient transport of both holes and electrons across the sample in all directions, although electrons might follow preferentially a path along the (layered) slipped lateral dimers.

3.2.2 Interacting [12]CPP molecules

The packing of [12]CPP molecules was also disclosed by Segawa *et al.*⁶⁹ ($a = 18.5827 \text{ \AA}$, $b = 8.1878 \text{ \AA}$, $c = 23.6701 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 106.157^\circ$) observing the four unique dimers displayed in Figure 4. Besides the her-

ringbone pattern typically found in other conjugated molecules, we found also a channel-like structure which could also be employed as template for their oxidative self-assembly towards the synthesis of nanotubes. Table 3 gathers the calculated values of V_{if} according to Eq. (6). Interestingly, the electronic coupling values (specially for holes) are considerably large (between 200 – 300 meV) for all dimers; these values are thus 2 – 3 times higher than those obtained before for other state-of-the-art molecules such as tetracene, pentacene or rubrene.^{70,71} Additionally, $V_{if}(h^+) > V_{if}(e^-)$ for all the dimers studied, with the tubular-like orientation being particularly detrimental for the electron transport. Note also the high values obtained for those dimers belonging to different channels (i.e., dimers numbered as 3 and 4 in Figure 4) which might indicate an efficient bulk transport in all directions. Overall, the values obtained for the charge-transfer rates (around 10^{14} s^{-1}) compared favourably to the best suited materials currently in use, such as pentacenequinones⁶⁶ and/or phthalocyanines.⁷² The densely packed form of these [12]CPP molecules helps to explain the high values found for V_{if} . Whereas for [6]CPP the closest distance between two C atoms belonging to different interacting monomers is 3.49 Å, 3.95 Å, and 3.95 Å, for the slipped-lateral, tubular-like, and diagonal configurations, respectively, this distance reduces to 3.4 – 3.6 Å for each of the [12]CPP dimers, except of the dimer 2 shown in Figure 4. These shortest distances clearly lie at the interface between the van der Waals surfaces of both monomers (e.g., the van der Waals radii of C is 1.7 Å). Note that experimentally it is known that there exists at least a set of close intermolecular C–C distances of around 3.5 Å for all the $[n]$ CPP crystallographic structures resolved up to now.²² These short distances, together with favourable face-to-face π - π interactions in all the dimers, shows again the relevance of the supramolecular order for

the final values of charge-transfer rates and concomitant bulk mobilities.

4 Conclusions

The calculations performed in this work indicate that $[n]$ cycloparaphenylenes are promising candidates to build efficient organic electronic devices, given the high charge-transfer rates found, k_{CT} . The robustness of the calculations has been adequately validated by their agreement with previous experimental and theoretical data present in the literature. We have shown that k_{CT} , for both hole and electron transfer, increases with n , and is particularly favoured in some crystallographic directions, as a combined effect of lower reorganization energies (Λ) and higher electronic couplings (V_{if}). The cyclic nature of the systems is key to the observed lowering of Λ , because it allows for a better delocalization of the charge as compared to their planar analogues, which also improves with the size of the nanoring. On the other hand, the molecular arrangements found in the crystalline state (with close intermolecular contacts) helps to explain the large values found for V_{if} . We hope that the above results had provided insights to exploit experimentally these challenging but promising nanorings for materials science and organic electronics applications.

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- **Table 1.** Estimates at the B3LYP/6-31+G* level of Adiabatic Ionization Potentials (AIP, in eV), Electron Affinities (AEA, in eV), Quasi-particle Energy Gaps (QEG, in eV), as well as intra-molecular hole (Λ_{h+} , in meV) and electron Λ_{e-} , in meV) reorganization energies, for the [6]CPP case.
- **Table 2.** Estimates at the B3LYP/6-31+G* level of Adiabatic Ionization Potentials (AIP, in eV), Electron Affinities (AEA, in eV), Quasi-particle Energy Gaps (QEG, in eV), as well as intra-molecular hole (Λ_{h+} , in meV) and electron Λ_{e-} , in meV) reorganization energies, for the set of [n]CPP studied molecules.
- **Table 3.** Estimates at the UHF/cc-pVDZ level of hole and electron electronic couplings (V_{if} , in meV) and corresponding charge-transfer rates (k_{CT} , in $\times 10^{12} \text{ s}^{-1}$) for the referred dimers of the [6]CPP and [12]CPP cases.

Table 1:

Method	AIP	AEA	QEG	Λ_{h^+}	Λ_{e^-}
B3LYP/6-31+G*	6.19	1.29	4.91	380	373
B3LYP-D3(BJ)/6-31+G*	6.20	1.26	4.94	378	365
CAM-B3LYP/6-31G* ^a	5.37	1.77	3.49	-	-
ω B97X/6-31+G*	6.93	0.70	6.23	687	705
B2-PLYP/6-31+G*	5.89	0.54	5.36	411	430

^a Taken from Ref. ¹³

Table 2:

$[n]$ CPP	AIP	AEA	QEG	Λ_{h^+}	Λ_{e^-}
$n = 4$	6.00	1.37	4.63	463	379
$n = 5$	6.07	1.37	4.70	372	320
$n = 6$	6.19	1.29	4.91	380	373
$n = 7$	6.33	1.19	5.14	294	294
$n = 8$	6.24	1.29	4.94	281	302
$n = 9$	6.33	1.34	4.98	241	268
$n = 10$	6.24	1.32	4.91	231	266
$n = 11$	6.20	1.37	4.83	200	240
$n = 12$	6.21	1.36	4.85	191	233

Table 3:

$[n]$ CPP	Dimer	$V_{\text{if}}(\text{h}^+)$	$k_{\text{CT}}(\text{h}^+)$	$V_{\text{if}}(\text{e}^-)$	$k_{\text{CT}}(\text{e}^-)$
$n = 6$	Dimer 1 (Slipped lateral)	41	5.05	156	75.7
	Dimer 2 (Tubular-like)	3	0.03	1	0.003
	Dimer 3 (Diagonal)	62	11.6	54	9.08
$n = 12$	Dimer 1 (Herringbone)	369	1050	141	125
	Dimer 2 (Tubular-like)	207	331	7	0.31
	Dimer 3	329	837	156	153
	Dimer 4	329	837	156	153

- **Figure 1.** Chemical structure of the investigated $[n]$ CPP compounds.
- **Figure 2.** Evolution of the reorganization energies of $[n]$ CPP compounds, as a function of the system size.
- **Figure 3.** Ball-and-stick view of the $[6]$ CPP dimer interactions found from its supramolecular organization: (a) dimer 1 (slipped-lateral); (b) dimer 2 (tubular-like); and (c) dimer 3 (diagonal)
- **Figure 4.** Ball-and-stick view of the $[12]$ CPP dimer interactions found from its supramolecular organization: (a) dimer 1 (herringbone); (b) dimer 2 (tubular-like); (c) dimer 3; and (d) dimer 4.

Figure 1.

Figure 2.

(a)

(b)

(c)

Figure 3.

(a)

(b)

(c)

(d)

Figure 4.

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