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Nature (Hole- or Electron-) of Charge-Transfer Ability of Substituted Cyclopyrenylene Hoop-Shaped Compounds

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Abstract

We theoretically investigate here by means of DFT methods how the selective substitution in cyclic organic nanorings composed of pyrene units may promote semiconducting properties, analyzing the energy needed for a hole- or electron-transfer accommodation as a function of the substitution pattern and the system size (i.e. number of pyrene units). We choose to study both [3]Cyclo-2,7-pyrenylene ([3]CPY) and [4]Cyclo-2,7-pyrenylene ([4]CPY) compounds, the latter already synthesized, with substituents other than hydrogen acting in *ipso* and *ortho* positions, as well as the effect of the *per*-substitution. As substituents, we selected a set of electroactive halogen atoms (F, Cl, Br) and groups (CN) to disclose structure-property relationships allowing thus to anticipate the use of these systems as organic molecular semiconductors.

Introduction

Organic nanorings and nanobelts are emerging carbon nanoforms¹ with promising individual yet challenging supramolecular properties. Whereas their forms arise from fusing conjugated molecules, as in other polycyclic conjugated hydrocarbons, their cyclic topology significantly alters their properties with respect to the corresponding linear oligomers as *has been* intensively reported in recent years.²⁻⁴ The use of these systems as molecular templates to initiate the controlled growth of carbon nanotubes was probably the first envisioned application of these compounds,^{5,6} although many more technological uses are being disclosed thanks to the structural and electronic ability of these systems to accommodate host molecules (e.g. C₇₀) into their cavity,⁷ to serve effectively as seeds for short nanotube segments,⁸ or to act as quantum containers,⁹ to name just a few of them. The number of possibilities for these molecules seems still endless, since all the achievements reached for conjugated oligomers could be potentially exploited in this new field, particularly for semiconducting or excited-state applications for which theoretical studies have contributed so far too.¹⁰⁻¹²

In this regard, we have focused in last years on the differences and similarities between the CycloParaPhenylene (CPP) and CycloPYrenylene (CPY) compounds of increasing size, or $[n]$ CPY with n representing the number of monomers, first validating and next applying a set of adequate theoretical methods for that purpose.^{13,14} Actually, the standarization of the rich Chemistry afforded by these cyclic compounds would systematically need: (i) to explore the differences between the affordable constituent units, e.g. phenylene,¹⁵ naphthylene,¹⁶ phenacene,¹⁷ or pyrenylene rings,^{18,19} to name just a few examples; (ii) to examine the effect of functionalizing the

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8 structure, with the incorporation of electroactive atoms within the rings²⁰
9 or substituents at their periphery;^{21,22} and (iii) to evaluate consequently the
10 impact of these functionalization on selected target properties with respect
11 to the pristine compounds. Note also that the solid-state semiconducting
12 properties (including estimates of hole mobilities of the set of $[n]$ CPPs com-
13 pounds (with $n = 5 - 12$) have been very recently studied²³ with values
14 reaching $2 \text{ cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$. The corresponding $[n]$ CPY derivatives still have
15 not been thoroughly investigated with respect to its functionalization at the
16 periphery or to the system size. Furthermore, and contrarily to $[n]$ CPPs,
17 the pyrene units offer different positions for substitution, which could thus
18 impact on their properties significantly.
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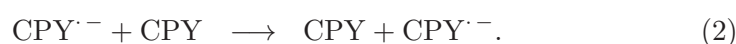
29 We thus continue here along this line of research by systematically in-
30 vestigating, by applying theoretical methods, the effect of size and substi-
31 tution on the not-yet-fully-explored semiconducting properties (i.e. charge-
32 transport reorganization energies) of substituted $[n]$ CPY compounds, taking
33 into account that: (i) [4]Cyclo-2,7-pyrenylene has been already synthesized
34 and characterized, thus disclosing the effect of cyclization on the properties
35 of pyrene oligomers;^{18,19} and (ii) the radical ions of this and related systems
36 can be generated using radiolysis methods,²⁴ comparing favourably with
37 stable CPP radical ions of similar size which shows full delocalization of the
38 charge along the nanoring,^{25,26} contrarily to their linear parent compounds
39 due possibly to edge effects. Note also that pyrene-based materials have
40 been widely employed in Organic Electronics, i.e. tetraphenyl pyrene shows
41 an ambipolar behaviour, and with some substitutions being more favorable
42 than other in previous charge-transport studies.²⁷
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8 It is thus within this context where the role of halogenation has gained
9 much attention as a successful strategy to alter, and thus engineer, the
10 key properties of organic molecular semiconductors such as e.g. linear
11 acenes.^{28–31} For instance, perfluorination of (state-of-the-art) tetracene or
12 pentacene molecules is experimentally known to dramatically influence single-
13 molecule magnitudes³² as well as the corresponding crystal packing,³³ whose
14 effects on molecules with cyclic topology remains still unknown. Up to now,
15 monochlorinated or monobrominated CPP compounds have been achieved^{34,35}
16 with the size-selective synthesis of mono- to tetrabrominated CPPs also re-
17 cently afforded too,³⁶ in addition to polyfluorinated CPP examples.³⁷
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28 These achievements clearly open new possibilities for (symmetrically)
29 multifunctionalized nanorings. Figure 1 thus presents the functionalization
30 strategies tackled here for $[n]$ CPY systems. Note that the crystalline order
31 is known time ago to also be of a key importance for the semiconducting
32 behaviour of organic materials,^{38,39} and that the porous and highly ordered
33 packing of nanorings constitutes an interesting three-dimensional framework
34 allowing possibly high charge-carrier mobilities and/or further crystal engi-
35 neering promoted by this kind of substitution. Therefore, together with the
36 specific partial or full substitution of H by F, Cl, or Br atoms in $[n]$ CPY
37 compounds, we will also investigate the effect of selectively adding a CN
38 group, studying how the fine-tuning of (single-molecule) charge-transport
39 parameters of these nanorings could guide synthetic efforts and/or elucidate
40 structure-property relationships overall.
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Theoretical framework

We model the process of molecular charge-transfer as a self-exchange hole (\cdot^+) or electron (\cdot^-) transfer between two neighbouring CPY (pristine or substituted) molecules, one acting as the donor and the nearest neighbour one as the acceptor, supposing an effective (and ideal) charge-injection process from the corresponding reservoirs:



for which the corresponding charge-transfer (or kinetic) rate (K_{CT}) is expressed as:

$$K_{CT} = \frac{4\pi^2}{h} |V_{if}|^2 \frac{1}{\sqrt{4\pi\Lambda_s k_B T}} \sum_{v=0}^{\infty} \left[\frac{S_{eff}^v}{v!} \exp(-S_{eff}) \exp\left(\frac{-(\Lambda_s + v\hbar\omega_{eff} + \Delta G^\ominus)^2}{4\Lambda_s k_B T}\right) \right], \quad (3)$$

where \hbar and k_B are fundamental constants, and T is the temperature, chosen here to be 298.15 K. Note that this equation includes a quantum-like correction with respect to the semi-classical Marcus expression,^{40,41} through considering a single effective vibrational mode ω_{eff} with associated Huang-Rhys factor $S_{eff} = \Lambda/\hbar\omega_{eff}$. Λ_s is assumed to be here 0.1 eV, according to recent studies⁴² and ΔG^\ominus is set to zero in absence of an applied electric field.

The intramolecular reorganization energy (Λ) for each of these processes, hole- or electron-transfer, is calculated from the adiabatic potential energy surfaces of the reactants as:⁴³⁻⁴⁵

$$\Lambda^+ = \left[E_{\text{CPY}\cdot^+//\text{CPY}} - E_{\text{CPY}\cdot^+} \right] + \left[E_{\text{CPY}//\text{CPY}\cdot^+} - E_{\text{CPY}} \right], \quad (4)$$

$$\Lambda^- = \left[E_{\text{CPY}\cdot^-//\text{CPY}} - E_{\text{CPY}\cdot^-} \right] + \left[E_{\text{CPY}//\text{CPY}\cdot^-} - E_{\text{CPY}} \right], \quad (5)$$

where E_{CPY} or $E_{\text{CPY}\cdot+(-)}$ indicates the total energy of the neutral or ion-

ized molecule at its optimum geometry, respectively, with $E_{\text{CPY//CPY}^{+(-)}}$ and $E_{\text{CPY}^{+(-)//\text{CPY}}$ being the energy of the neutral or ionized molecule at the fully optimized geometry of the other state, respectively. This model assumes a full relaxation of the molecule supporting the positive or negative charge, p- (hole) or n-type (electron) transfer respectively, before any jump to the closest neighbouring molecule occurs across the solvated or crystalline sample of molecules, but neglecting polarization effects at this stage. From this set of individual energies for the involved states, we can also calculate the corresponding Adiabatic Ionization Potentials (AIP) or Electron Affinities (AEA), that is $\text{AIP} = E_{\text{CPY}^{+}} - E_{\text{CPY}}$ and $\text{AEA} = E_{\text{CPY}} - E_{\text{CPY}^{-}}$, as well as the Quasiparticle Energy Gap given by $\text{QEG} = \text{AIP} - \text{AEA}$.

The intermolecular electronic coupling V_{if} is defined as:

$$V_{if} = \langle \Psi_i | \hat{H} | \Psi_f \rangle, \quad (6)$$

where Ψ_j are the many-electron wavefunctions describing an excess charge localized on a different molecule; i.e., the initial and final states. Assuming that both states only differ by the occupancy of the frontier molecular orbitals, that is the Highest (Lowest) Occupied (Unoccupied) Molecular Orbital or HOMO (LUMO), one can rewrite the equation in an one-electron picture as:

$$V_{if} = \langle \phi_i^{\text{HOMO(LUMO)}} | \hat{H} | \phi_f^{\text{HOMO(LUMO)}} \rangle, \quad (7)$$

for hole or electron transport, respectively. Then, due to the non-orthonormality of the monomers HOMO or LUMO orbitals, a final projection (i.e., a Löwdin transformation) is done to obtain the corresponding values:⁴⁶

$$V_{if} = \frac{\tilde{V}_{if} - \frac{1}{2}(e_i + e_f) S_{if}}{1 - S_{if}^2}, \quad (8)$$

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8 with S_{if} the overlap and e_i/e_f the site energies defined as $\langle \phi_i | \hat{H} | \phi_i \rangle$ or
9 $\langle \phi_f | \hat{H} | \phi_f \rangle$. For a fast estimate of values, we will also use the “Energy Split-
10 ting in Dimers” (ESD) approach, where V_{if} is taken directly as half the
11 splitting of the LUMO (HOMO) energies in a neutral dimer for electron
12 (hole) transfer.
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19 Computational details

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21 All closed- (i.e. neutral) or open-shell (i.e. charged) energies of pris-
22 tine and substituted [3]CPY and [4]CPY are calculated here, to obtain the
23 associated Λ values, at the sufficiently accurate B3LYP-D3(BJ)/6-31+G*
24 level^{47,48} of Density Functional Theory (DFT), and with the Gaussian09
25 package.⁴⁹ Note (*vide infra*) that a dispersion-correction, dubbed as D3(BJ)^{50,51}
26 and extensively used, is also added to the underlying density functional for
27 the optimization of all structures, due to the strong (intramolecular) steric
28 interactions expected after substitution of H atoms with more bulky halo-
29 gens and cyano groups. Due to severe convergence problems in some cases,
30 specially for bulky charged species, we also invoked the Newton-Raphson
31 converger, and thus switch off the DIIS algorithm consequently. The choice
32 of the hybrid B3LYP method is complemented by the double-hybrid B2-
33 PLYP-D3(BJ) model,⁵² in which not only the exact-like and exchange den-
34 sity functional terms are hybridized, but also a perturbative correlation cor-
35 rection and the correlation functional, thus allowing to infer the effect of
36 going upwards across the hierarchy of modern DFT methods.^{53,54} The elec-
37 tronic coupling given by eq. (8) is calculated at the B3LYP/6-31G* level,
38 which is known to provide sufficiently accurate results,^{55,56} and with the
39 “J-from-g03” code.^{57,58}
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Results and discussion

Influence of density functionals and/or dispersion correction on reorganization energies

We first qualitatively assess the influence of the correction used [i.e. D3(BJ)] for including the dispersion interactions by comparing the B3LYP-D3(BJ)/6-31+G* and B3LYP/6-31+G* results for Λ values after fully optimizing the neutral and charged structures of [3]CPY at both levels. While its use is negligible for the pristine [3]CPY compound, with differences of only 1 meV for both Λ^+ or Λ^- , its impact for substituted molecules increases with the size of the halogen atom and the substitution pattern. The use of this correction neither significantly affects the results for the *ipso*-substitution (see again Figure 1 for the different substitution pattern selected) but it does up to 10 – 20 % for the cases of *ortho*- and *per*-substitution with Cl or Br atoms, and tends to decrease the values upon release of the steric hindrance. Note that the same behavior was also found when the geometries were optimized with the smaller 6-31G* basis set, i.e. without diffuse functions. This prompts us to recommend the B3LYP-D3(BJ)/6-31G* as the minimum level that should be adopted for this type of calculations.

Despite the fact that the B3LYP method has provided before accurate values of Λ for a wide variety of organic semiconductors at a reasonable computational cost,^{59,60} we also apply here the double-hybrid B2-PLYP-D3(BJ) model to bracket the accuracy of the Λ^+ and Λ^- calculations for the case of unsubstituted [3]CPY. Note that: (i) this family of models (i.e. double-hybrid density functionals) has shown a remarkable performance for geometries of small-/medium-sized organic molecules and other energy magnitudes;⁶¹ (ii) the formal scaling of the computational cost with the system

size is however an order of magnitude higher with respect to hybrid functionals, $O(N^5)$ vs. $O(N^4)$, which thus precludes its application to all the systems tackled along this study, specially the heaviest ones; and (iii) the corresponding extension to deal with (intramolecular) non-covalent interactions is also available, which allows also to truly compare both theoretical methods. The corresponding results at the B2-PLYP-D3(BJ)/6-31G* level are now 252 and 186 meV, respectively, for Λ^+ and Λ^- , compared with values of 196 and 177 meV obtained before with B3LYP-D3(BJ). This increase of values is rationalized by the higher eXact-like EXchange (EXX) introduced into the former (i.e. 53%) vs. the latter B3LYP-D3(BJ) (20%) model, which is known to drive the performance of the method increasing the values concomitantly.⁶⁰ Thus, while the B2-PLYP-D3(BJ) values can be considered as a higher limit, they also serve to bracket the accuracy of B3LYP-D3(BJ) results.

Influence of the substitution pattern on ionization potentials and electron affinities

Table 1 presents the AIP, AEA, QEG, Λ^+ , and Λ^- results for the whole set of [3]CPY compounds at the hereby fixed B3LYP-D3(BJ)/6-31+G* level, underlining how the different substitution patterns largely affect the properties selected. Note that adiabatic values were found to differ in all cases by 0.1–0.2 eV from vertical ones, indicating minor structural relaxation effects, and only the former values are thus presented. The AIP values of all substituted compounds are higher than those values for [3]CPY, considerably for the case of *per*-substitution with halogen atoms roughly increasing the values by 0.9 – 1.3 eV. The introduction of the CN group into the structure leads to a more marked increase of AIP values by around 2 eV. The AEA

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8 values change more markedly than AIP ones, although the QEG remains
9 comprised between 4.3 – 5.0 eV for all substituted compounds, indicating
10 that AIP and AEA values are symmetrically shifted in most cases. These
11 overall trends have also been observed before for other partially or fully sub-
12 stituted polycyclic aromatic hydrocarbons.⁶²
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19 However, we also remark here that any intended process of charge-
20 transport across an organic-based active materials relies on the injection
21 first of charge-carriers. The injection of holes relies on a close match be-
22 tween the ionization potential of the material and the work function (Φ_m)
23 of the (often inorganic) anode used as reservoir, $\phi_{h\cdot+} = \text{AIP} - \Phi_m$; ideally
24 searching a barrierless process in the absence of interfacial and/or polariza-
25 tion effect.⁶³ Taking the example of Indium tin oxide (ITO, $\text{In}_2\text{O}_3\text{-SnO}_2$),
26 whose $\Phi_m \simeq 4.7$ eV, we found a mismatch of around 2 eV between AIP and
27 Φ_m values, although recent strategies for the surface modification of ITO
28 samples with organotin compounds⁶⁴ or phosphonic acids,⁶⁵ to name a pair
29 of examples, can increase its value by more than 1 eV. On the other hand,
30 for the injection of electrons, low-workfunction metals (Φ_m around 2.4 – 2.9
31 eV) like Ca, Na, or Ba, were initially used, although are known to be sensi-
32 tive to moisture and oxygen, and can also be replaced by metals with higher
33 ($\Phi_m > 4.0$ eV) workfunctions like Al, Ag, or Au. The versatility found for
34 this set of substituted [3]CPY compounds shows that substitution might
35 improve the electron injection with respect to [3]CPY, upon the selection
36 of the appropriate cathode, with the hole injection being however slightly
37 disfavoured at this stage.
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Influence of the substitution pattern on reorganization energies

We continue the analysis of the theoretical results by examining next the evolution of the Λ^+ and Λ^- of [3]CPY upon changes in *ipso* positions, in principle the less affected by large structural relaxation upon substitution, see Figure 2, with values roughly decreasing with the size of the halogen atoms as found before for other partially substituted oligoacenes.⁶⁶ The introduction of the CN group decreases both reorganization energies, but affects more markedly the value of Λ^- , as it was also expected from previous studies on anthracene⁶⁷ and tetracene derivatives,⁶⁸ switching from an ambipolar charge conduction mechanism towards an electron-favoured one, as it can be inferred (see also Table 1) in first approximation from the ratio $\frac{\Lambda^+}{\Lambda^-}$.

The *ortho*-substitution seems to significantly alter the results with respect to [3]CPY, for both Λ^+ and Λ^- , decreasing and increasing their values, respectively. Figure 3 shows the large geometrical changes induced by this substitution, which also critically depend on the size of the halogen atom introduced. Particularly remarkable are the cases of Λ^+ (Λ^-) for Cl-*ortho* (Br-*ortho*) for which the value is halved (a 4-fold increase) with halogen substitution. This marked geometrical deformation agrees to that experimentally found upon site-selective bromination of short CPPs,³⁶ since the Br atoms could only be partially incorporated at *ortho* positions into the CPP structures (i.e. at alternating and thus separated rings) to avoid steric pronounced interactions between *ipso* and *ipso'* sites.

The case of *per*-substitution is also found to mostly promote a hole-transport mechanism after the corresponding charge injection, contrarily to what happened for coronene molecules⁶⁹ for which an ambipolar behaviour

could be predicted in *per*-fluorinated or chlorinated compounds. Note that the Λ^+ values are found particularly low for the *per*-cyanated case, showing how the nature and position of the CN groups alter significantly the hole or electron migration.

Furthermore, comparing these results with those found before for the $[n]$ CPP systems,²¹ with $n = 6 - 20$, in which the diameter and the shape of the nanoring was shown to be independent of the *per*-substitution performed with F, Cl, or Br atoms, the rigidity of the pyrene units seems to play a key role here. Actually, for $[n]$ CPPs, the dihedral angles between adjacent rings were shown to increase with the halogen size, and even close to 90° for fully chlorinated or brominated compounds, compared with dihedral angles (standard values) of $23 - 27^\circ$ for pristine $[n]$ CPPs and $45 - 49^\circ$ for fully fluorinated compounds. This clearly explains how the inter-ring flexibility of $[n]$ CPPs would help to release the steric hindrance caused by the equivalent interactions to the *ipso-ipso'* existing for $[n]$ CPYs, which in this case is largely impeded due to the stabilization of the pyrene units by conjugation.

Finally, according to the ratio defined above for Λ values, we have adopted a criteria allowing for qualitatively classifying the systems according to that ratio: $0.9 < \frac{\Lambda^+}{\Lambda^-} < 1.1 \equiv$ Ambipolar, $\frac{\Lambda^+}{\Lambda^-} \gg 1 \equiv e^-$ favoured, and $\frac{\Lambda^+}{\Lambda^-} \ll 1 \equiv h^+$ favoured, with the results also gathered in Table 1. The *ipso*-substitution does not change the initial nature of the mechanism disclosed for pristine [3]CPY, while the case of *ortho*-substitution clearly switches remarkably the behaviour of the systems from an ambipolar to a hole-transport favoured mechanism.

Influence of the size of the nanoring on reorganization energies

We tackle next how the size of the nanoring (i.e. [4]CPY vs. [3]CPY) might impact on the calculated reorganization energies for substituted compounds, which should normally decrease the values according to various previous studies on carbon-based compounds^{70,71} in absence of other dominant effects. We will focus on the reorganization energy difference $\Delta\Lambda^{+(-)} = \Lambda^{+(-)}[4]CPY - \Lambda^{+(-)}[3]CPY$, that is, the variation of values going from [3]CPY to [4]CPY, to emphasize the changes upon the system size. Actually, $\Delta\Lambda^+$ ($\Delta\Lambda^-$) value is -71 (-25) meV, which corroborates this general finding. Note also that we focus in the following only on *ortho* and *ipso* substituted systems, since geometrical changes after *per*-substitutions are expected to be mostly driven by the *ipso-ipso'* interactions.

Figure 4 presents the calculated $\Delta\Lambda$ values for these substituted compounds, for which the following trends are observed when the values for both [4]CPY and [3]CPY are compared: (i) the *ortho* substitution of [4]CPY always helps to significantly reduce the Λ values for both holes and electrons, specially for the latter, providing values (in meV) for Λ^+ (Λ^-) of 67, 64, 58, and 43 (172, 120, 219, and 161), and thus substantially lower than those found for the corresponding *ortho*-substituted [3]CPY (see Table 1) upon release of the steric hindrance; (ii) the *ipso* substitution of [4]CPY does not affect too much (by less than 10 %) the Λ^- values with respect to the corresponding ones found for the [3]CPY case; (iii) on the other hand, the Λ^+ results for *ipso* substitution of [4]CPY with F and Cl atoms are markedly reduced, with bromination showing the opposite behaviour; (iv) according to the ratio $\frac{\Lambda^+}{\Lambda^-}$ employed to classify the nature of the charge-transport, and focusing only on Λ values so far, the *ortho* substitution would promote

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8 a hole-transport mechanism in all cases, with $0.3 < \frac{\Lambda^+}{\Lambda^-} < 0.5$, possibly
9 because negatively charged halogen atoms promote larger steric hindrance;
10 and (v) finally, the *ipso* substitution would also promote a hole-transport
11 ($\frac{\Lambda^+}{\Lambda^-} \simeq 0.4$) for F or Cl, nearly ambipolar ($\frac{\Lambda^+}{\Lambda^-} \simeq 1.2$) for Br, and an
12 electron-transport mechanism ($\frac{\Lambda^+}{\Lambda^-} \simeq 2.0$) for CN substituted compounds.
13 The trends disclosed aims at speculating about the possibility of still de-
14 creasing the values going to larger nanorings (e.g. [5]CPY) if experimentally
15 available.
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25 **Electronic couplings and charge-transfer rates**

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27 The values of V_{if} strongly depend on the solid-state electronic interac-
28 tions between neighboring molecules, which are still unknown for the [3]CPY
29 case. We have thus estimated its evolution as a function of the relative dis-
30 placement of a pair of molecules.⁷² We have chosen two idealized configura-
31 tions, called cofacial and tubular, and thus representing the two limiting
32 situations expected in a dense crystalline packing of cyclic organic nanor-
33 ings,^{73,74} to elaborate the impact on charge-transport when intermolecular
34 contact is maximized compared to unit cells. As starting point, we manually
35 situate two molecules one in front (on top) of the other with their centers of
36 mass separated by 10.0 Å (7.5 Å) corresponding to these cofacial (tubular)
37 configurations, and systematically scan the other two dimensions by reg-
38 ular intervals of 0.5 Å keeping fixed this initial distance. Figure 5 shows
39 the corresponding electronic coupling maps, for both cofacial and tubu-
40 lar configurations, initially estimated with the cost-effective ESD method.
41 Briefly, the V_{if} values for the tubular configuration are an order of magni-
42 tude lower, roughly speaking, than those for the cofacial configuration, as it
43 was expected, showing significant differences depending on the relative ori-
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8 entation of the two weakly interacting monomers. This is attributed to the
9 marked oscillations of the V_{if} values on relative orientations, as previously
10 illustrated for oligoacenes⁷⁵ and cycloparaphenylenes.⁷⁶
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15 The optimal arrangement, in the sense of providing the highest V_{if} val-
16 ues, is found at relative 2D-displacements of 1.5 Å/5.5 Å for both hole and
17 electron transport in the tubular configuration. On the other hand, for
18 the cofacial configuration, the highest V_{if} values are obtained at relative
19 2D-displacements of 0.0 Å/2.0 Å (holes) and 1.5 Å/1.5 Å (electrons), thus
20 resembling a slipped cofacial solid-state arrangement. At this intermolecu-
21 lar orientation, further refinements of the V_{if} values by applying Eq. (8)
22 give very low values of 1 meV for both holes and electrons in the tubu-
23 lar configuration, which translates into charge-transfer rates, see Eq. (3)
24 and neglecting disorder effects, of $9.4 \cdot 10^9 \text{ s}^{-1}$, low but similar for both
25 charge-carriers. On the other hand, further exploring the cofacial configura-
26 tion situating both molecules at an intermolecular distance of 3.5 Å, around
27 $2R_{vdW}^C$, while keeping those lateral displacements found before, leads now
28 to V_{if} values of 18 and 25 meV, again calculated with Eq. (8), for holes and
29 electrons, respectively. The charge-transfer rates are now $2.5 \cdot 10^{12} \text{ s}^{-1}$ and
30 $5.2 \cdot 10^{12} \text{ s}^{-1}$ for holes and electrons, respectively. The large differences found
31 for the K_{CT} values of both tubular and cofacial configuration preliminarily
32 indicate a pronounced bulk charge-transport anisotropy. Given these values,
33 since $\frac{2V_{if}}{\Lambda} < 1$, we expect a hopping-like regime transport⁷⁷ with hole and
34 electron mobilities of 0.66 and 1.38 $\text{cm}^2 \text{ V}^{-1} \text{ cm}^{-1}$, and thus comparable to
35 those estimated before for CPPs.²³
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Conclusions

We have computationally studied the ability of large hoop-shaped molecules (i.e. [3]CPY and [4]CPY) to host and then release a charge-carrier (hole or electron) upon external charge injection. Furthermore, the introduction of electroactive substituents is a molecular design strategy to tune the electronic properties in organic electronics, which is done here by investigating the variations of reorganization energies for pristine and substituted (with F, Cl, Br, and CN) compounds. The larger size of the [4]CPY system allows to delocalize the charge over more conjugated units, and thus to decrease in almost all cases the values of reorganization energies with respect to [3]CPY, as expected. For all the substituents studied, it seems doable to get an ambipolar charge-transfer, in absence of other conditioning factors, for some atoms (i.e. F) and substitution patterns (i.e. *ipso* for [3]CPY and *ortho* for [4]CPY). For an idealized packing of [3]CPY, we also estimated the electronic coupling values, highly anisotropic depending on the relative orientation of the two weakly interacting molecules, and actually indicating competitive charge-transport rates and associated mobilities. These results clearly reveal how molecular design can guide further (theoretical or experimental) studies on semiconducting properties of nanorings with diverse functional units.

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- **Table 1.** Theoretical estimates of Adiabatic Ionization Potentials (AIP, in eV), Electron Affinities (AEA, in eV), Quasiparticle Energy Gaps (QEG, in eV), and hole (Λ^+ , in meV) and electron Λ^- , in meV) reorganization energies for the studied molecules, at the B3LYP-D3(BJ)/6-31+G* level.

Table 1:

	AIP	AEA	QEG	Λ^+	Λ^-	$\frac{\Lambda^+}{\Lambda^-}$	Nature
[3]CPY	6.24	1.27	4.97	195	176	1.11	Ambipolar
<i>F-ipso</i>	7.12	2.19	4.93	218	208	1.05	Ambipolar
<i>Cl-ipso</i>	6.94	2.20	4.74	195	199	0.98	Ambipolar
<i>Br-ipso</i>	6.83	2.15	4.68	188	194	0.97	Ambipolar
<i>CN-ipso</i>	8.20	3.60	4.60	177	98	1.81	e^- -favoured
<i>F-ortho</i>	6.99	1.97	5.02	146	276	0.53	h^+ -favoured
<i>Cl-ortho</i>	6.82	2.03	4.79	91	216	0.42	h^+ -favoured
<i>Br-ortho</i>	6.74	2.42	4.32	104	684	0.15	h^+ -favoured
<i>CN-ortho</i>	8.30	3.65	4.65	65	206	0.32	h^+ -favoured
<i>per-F</i>	7.57	2.85	4.72	186	276	0.67	h^+ -favoured
<i>per-Cl</i>	7.27	2.64	4.63	110	247	0.44	h^+ -favoured
<i>per-Br</i>	6.70	3.46	3.24	970	1479	0.66	h^+ -favoured
<i>per-CN</i>	9.53	5.10	4.43	64	126	0.51	h^+ -favoured

- **Figure 1.** Chemical structure of the investigated [3]CPY compounds, with the different substitutions patterns sketched.
- **Figure 2.** Structural differences between *F-ipso* and *Br-ipso* substituted compounds for all the three (cationic, neutral, and anionic) optimized geometries, at the B3LYP-D3(BJ)/6-31+G* level.
- **Figure 3.** Structural differences between *F-ortho* and *Br-ortho* substituted compounds for all the three (cationic, neutral, and anionic) optimized geometries, at the B3LYP-D3(BJ)/6-31+G* level.
- **Figure 4.** Reorganization energy differences ($\Delta\Lambda$) between *ortho* and *ipso* substituted [4]CPY and [3]CPY compounds, at the B3LYP/6-31+G* level.
- **Figure 5.** Evolution of the V_{if} values (in eV) as a function of the relative displacement between both interacting molecules of [3]CPY, keeping fixed the distance between their centers of mass: (a) hole values for the tubular configuration; (b) electron values for the tubular configuration; (c) hole values for the cofacial configuration; and (d) electron values for the cofacial configuration.

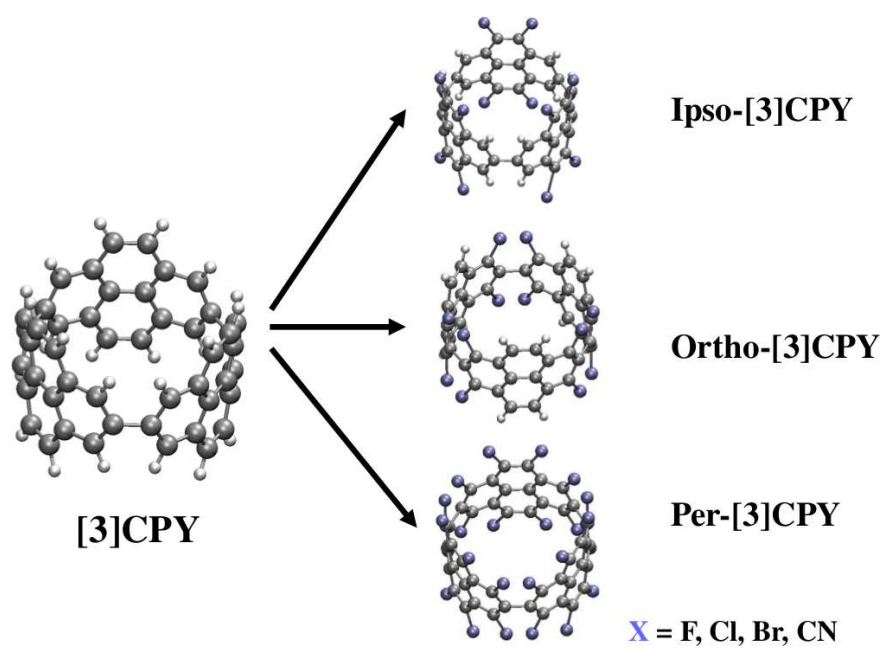


Figure 1.

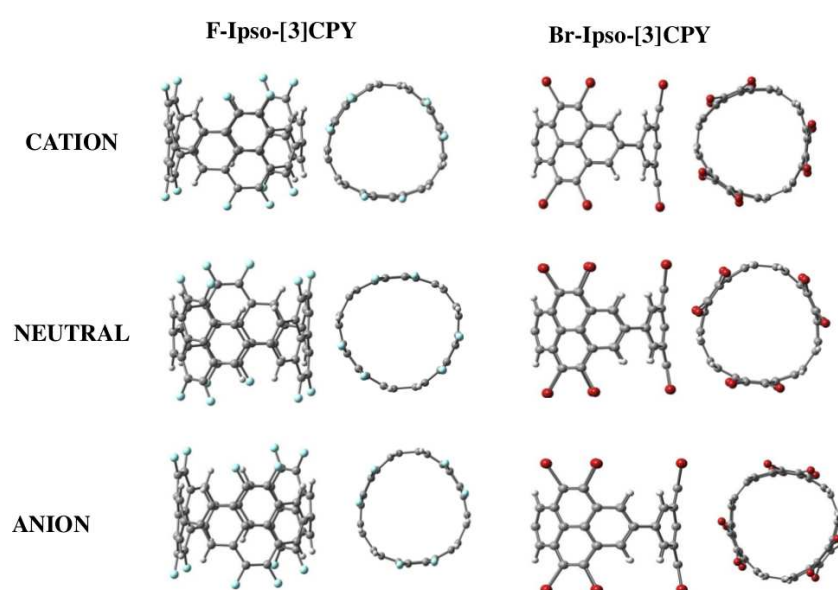


Figure 2.

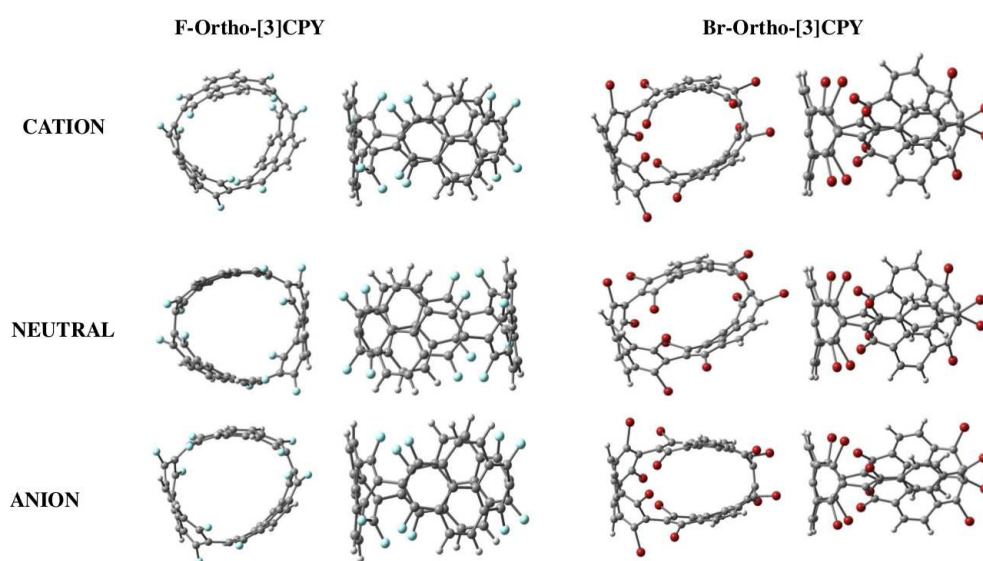


Figure 3.

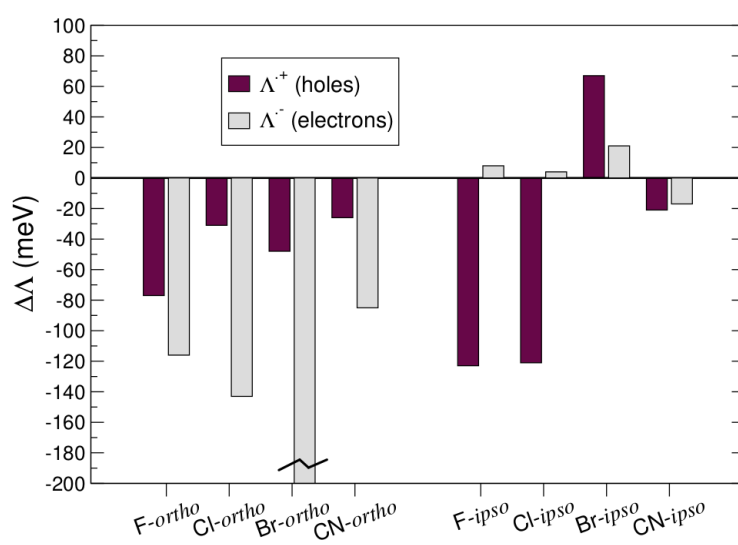


Figure 4.

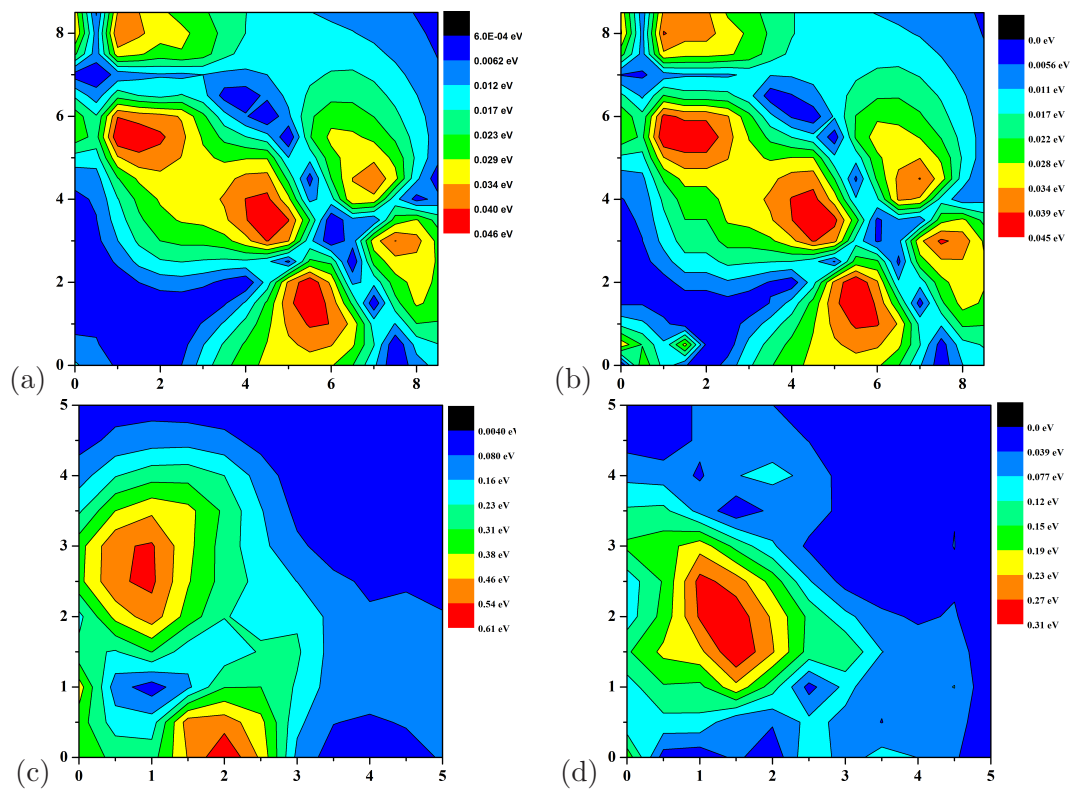


Figure 5.

