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Bis(arylene-ethynylene)-s-tetrazines: A Promising Family of *n*-Type Organic Semiconductors?

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ABSTRACT

We theoretically describe in this work the *n*-type semiconducting behavior of a set of bis(arylene-ethynylene)-s-tetrazines ((ArCC)₂Tz), by comparing their electronic properties with those of their parent diaryl-s-tetrazines (Ar₂Tz) after the introduction of ethynylene bridges. The significantly reduced internal reorganization energy for electron transfer is ascribed to an extended delocalization of the LUMO for (ArCC)₂Tz as opposite to that for Ar₂Tz, which was described mostly localized on the *s*-tetrazine ring. The largest electronic coupling and the corresponding electron transfer rates found

for bis(phenyl-ethynylene)-*s*-tetrazine, as well as for some halogenated derivatives, are comparable to those reported for the best performing *n*-type organic semiconductor materials such as diimides and perylenes. The theoretical mobilities for the studied compounds turn out to be in the range $0.3 - 1.3 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, close to values experimentally determined for common *n*-type organic semiconductors used in real devices. In addition, ohmic contacts can be expected when these compounds are coupled to metallic cathodes such as Na, Ca and Sm. For these reasons, the future application of semiconducting bis(phenyl-ethynylene)-*s*-tetrazine and its fluorinated and brominated derivatives in optoelectronic devices is envisioned.

INTRODUCTION

Tetrazine derivatives represent the most electron-deficient aromatic family¹⁻³ and exhibit interesting semiconducting and opto-electronic properties such as redox reversibility on reduction at low potentials^{2-4,5} and a characteristic $n \rightarrow \pi^*$ low energy transition,⁵⁻⁸ which can be exploited in the fabrication of OLEDs,⁹ OFETs,¹⁰ and solar cells.^{11,12} *N*-type semiconducting properties have been profusely studied either for 3,6-diphenyl-*s*-tetrazine (Ph₂Tz, see Chart 1) and other diaryl-*s*-tetrazines (Ar₂Tz).^{3,4,7,8,13-17} An essential drawback of Ar₂Tz to suitably act as a *n*-type organic semiconductor concerns the localized character of the Lowest Unoccupied Molecular Orbital (LUMO) which does not allow an easy accommodation of an extra electron (see Figure 1).^{8,16,17} In the framework of Marcus theory for charge transfer, typically employed to describe the hopping-like charge transport in molecular crystals at room temperature¹⁸ (vide infra), this situation gives rise to a high electron reorganization energy (λ_i). Hence the improvement of the electron transport properties of Ar₂Tz derivatives might thus rely on a decrease of the reorganization energy needed to accommodate that incoming charge.¹⁷

The electron transfer rate critically depends on this reorganization energy, as well as on the electronic coupling between donor and acceptor interacting molecules. Actually for some Ar₂Tz halogenated derivatives, the calculated electronic coupling values appear to be of the same order of magnitude than those reported before for the best naphthalene diimide¹⁹ and perylene *n*-type semiconductors,^{20,21} which have been successfully used in electronic devices.²²⁻²⁶ Nevertheless, the high values of internal reorganization energy (λ_i) predicted for those Ar₂Tz derivatives might preclude their use as reliable semiconducting materials.¹⁷ The increase in the delocalization of the LUMO orbital could be achieved by the introduction of ethynylene groups (–C≡C–) as a bridge between the three aromatic rings; in fact the ethynylene group, due to its axial symmetry, could allow to extend the conjugation to adjacent arylene groups.²⁷⁻³² Note also that the actual synthesis of *s*-tetrazine ethynylene derivatives is possible through cross-coupling reactions on some *s*-tetrazine compounds (compounds a and b in Chart 1), as shown by Novák and Kotschy,³³ though we are not aware of any attempt for (ArCC)₂Tz compounds.

For those reasons, we aim thereby to explore the electronic properties of this new family of potential *n*-type semiconducting compounds based on bis(arylene-ethynylene)-*s*-tetrazine structures, (ArCC)₂Tz (see also Chart 1).

Chart 1. Chemical structures of diphenyl-*s*-tetrazine derivatives, bis(phenyl-ethynylene)-*s*-tetrazine derivatives and related synthetic precursors as phenyl-ethynylene-*s*-tetrazines derivatives (*a* and *b*).

Figure 1. Shape (isocontour plots) of the frontier orbitals of Ph_2Tz (left, References 8, 17) and $(\text{PhCC})_2\text{Tz}$ (right, this work), calculated at the B3LYP/6-31+G* level, in which the size and colours of the orbital lobes are related to their amplitude and sign, respectively.

THEORETICAL METHODOLOGY

Typically charge motion in π -conjugated organic crystal materials, due to small bandwidths (electronic couplings $\ll 1$ eV) at room temperature and strong electron-phonon coupling, is generally assisted by a hopping mechanism, which can be described within the framework of Marcus-Levich-Jortner (MLJ) model as a self-exchange electron-transfer (ET) reaction between neighboring molecules of the lattice.^{34,35} Accordingly, the rate constant (k_{ET}) for this process can be expressed as:

$$k_{ET} = \frac{4\pi^2}{h} t_{12}^2 \sqrt{\frac{1}{4\pi\lambda_s k_B T}} \sum_{n=0}^{\infty} \left[\exp(-S_{eff}^n) \times \frac{S_{eff}^n}{n!} \times \exp\left(\frac{-(\lambda_s + n\hbar\omega_{eff} + \Delta G^0)^2}{4\lambda_s k_B T}\right) \right] \quad (1)$$

where k_B and h are Boltzmann's and Planck's constants, respectively; T is the temperature, fixed at 300 K; ΔG^0 is the free energy difference between the electronic states involved in the charge transfer process (equal to zero for an ideal self-exchange process); t_{12} stands for the electronic coupling (also called charge transfer integral) and λ_s for the "solvent" contribution to the reorganization energy, respectively. Generally speaking, in organic molecular crystals the outer contribution λ_s is of the order of one tenth of eV,^{36,37} contrarily to charge transfer in solution wherein the external part might dominate,³⁷⁻⁴² and is fixed here at 0.1 eV. Conversely, the internal reorganization energy λ_i is calculated at the Density Functional Theory (DFT) levels and enters into equation (1) through the Huang-Rhys factor $S_{\text{eff}} = \lambda_i/\hbar\omega_{\text{eff}}$, with ω_{eff} being the frequency of an effective vibrational mode assisting the hopping process, fixed here at $\hbar\omega_{\text{eff}} \sim 0.2$ eV. Note that λ_i consists of two terms corresponding to the geometry relaxation energies upon going from the neutral-state geometry to the charged-state one and *vice versa* (Nelsen's four-point method).^{43,44}

$$\lambda_i = \lambda_1 + \lambda_2 \quad (2)$$

$$\lambda_1 = E^0(G^*) - E^0(G^0) \quad (3)$$

$$\lambda_2 = E^*(G^0) - E^*(G^*) \quad (4)$$

where $E^0(G^0)$ and $E^*(G^*)$ are the ground-state energies of the optimized neutral and ionic states, respectively, $E^0(G^*)$ is the energy of the neutral molecule at the optimal ionic geometry, and $E^*(G^0)$ is the energy of the ionic state at the optimal geometry of the neutral molecule.³⁹⁻⁴²

The transfer integral is defined by the matrix element:

$$t_{12} = \langle \psi_1 | \hat{H} | \psi_2 \rangle \quad (5)$$

where $\hat{H}$ is the one-electron Hamiltonian of the system, and ψ_1 and ψ_2 are the wavefunctions of the initial and final charge-localized states.^{18,42,45} The charge transfer

integral reflects the strength of the electronic interactions between pairs of molecules in the crystal and thus critically depends on their relative supramolecular arrangement. The charge transfer integral is calculated within the fragment approach at the DFT level as implemented in the Amsterdam Density Functional (ADF) package.⁴⁶ In this approach, the orbitals of the dimer are expressed as a linear combination of the molecular orbitals of the individual units (*i.e.*, fragments) that are obtained solving the Kohn-Sham equations. Since the fragment orbitals form a non-orthogonal basis set, the corresponding transfer integral depends on the choice of the energy origin so that the transfer integral is no longer an invariant. The problem is solved by applying a Löwdin transformation to the initial electronic Hamiltonian and the transfer integral t_{12} is finally obtained:

$$t_{12} = \frac{\tilde{t}_{12} - \frac{1}{2}(\varepsilon_1 + \varepsilon_2)S_{12}}{1 - S_{12}^2} \quad (6)$$

where $\tilde{t}_{12}$, ε_i , S_{12} are the transfer integral ($\langle \psi_1 | \hat{H} | \psi_2 \rangle$), the site energies ($\langle \psi_i | \hat{H} | \psi_i \rangle$) and the overlap matrix element ($\langle \psi_1 | \psi_2 \rangle$) defined in the non-orthogonal basis set.

For an n -dimensional, spatially isotropic system, where homogeneous charge diffusion can be assumed, the diffusion coefficient for charge-carriers (D) can be evaluated as:

$$D = \frac{1}{2n} \lim_{t \rightarrow \infty} \frac{\langle [r(t) - r(0)]^2 \rangle}{t} \approx \frac{1}{2n} \sum_i r_i^2 k_i p_i \quad (7)$$

where i runs over all nearest adjacent molecules, n is the dimensionality of the process while r_i and k_i are the corresponding center-to-center hopping distance and the electron transfer rate constant obtained from equation (1), respectively, with $p_i = k_i / \sum_j k_j$ as the hopping probability to the i -th neighbour.^{45,47,24} Since the crystal structure of the studied molecules is unknown, this work focuses on the study of the charge transport

along an ideal one dimensional stack with spacing d ($n = 1$, $p_i = 1/2$, $D = \frac{1}{2}d^2k_{ET}$).

Hence, in the zero field limit, the charge carrier mobility (μ_{hop}) can be obtained from Einstein's relation:

$$\mu_{hop} = \frac{eD}{k_B T} = \frac{e d^2 k_{ET}}{2 k_B T}. \quad (8)$$

where e is the elementary charge and d is the center-to-center distance for the π -stacked dimer, calculated as $d = (x^2 + y^2 + z^2)^{1/2}$, where x , y and z are the displacements along the three directions defined in Figure 2.^{45,47,24}

The electron injection efficiency from an electrode to the *s*-tetrazine derivatives is estimated by considering two key physical properties: (i) the energy difference between the LUMO level (E_{LUMO}) of the organic semiconductor and the work function (Φ) of the electrode. The metal-semiconductor interface is usually treated as a Mott-Schottky barrier, where the barrier height is given by the difference between Φ and the semiconductor HOMO or LUMO level.^{38,48} Although in this ideal model interfacial effects between electrode and semiconductor are not taken into account,³⁷ the comparison of Φ with HOMO/LUMO levels of the semiconductor helps to find out the likeliness of charge injection and the magnitude of the contact resistance; (ii) the electron affinity (EA) defined as the energy released when one electron is added to the system in the gaseous state. EA of a semiconductor should amount at least to 3.0 eV for an easy electron injection.^{38,49} However, its stability in ambient conditions could be compromised by high EA values as well as other factors as the crystal packing and film morphology.^{38,50-52} The adiabatic (AEA) and vertical (VEA) electron affinity were calculated as follows

$$AEA = E_0(G_0) - E^*(G^*) \quad (9)$$

$$VEA = AEA + \lambda_2 \quad (10)$$

where $E_0(G_0)$, $E^*(G^*)$ and λ_2 are the same quantities appearing in equations (3) and (4).

COMPUTATIONAL METHODS

With the purpose of achieving the best tradeoff between accuracy and computational cost, we have performed Density Functional Theory (DFT) calculations with the well-established and widely used B3LYP^{53,54} and M06-2X⁵⁵ functionals, as implemented in Gaussian09 (revision **B.01**).⁵⁶ Geometries were optimized at the B3LYP/6-31+G* level, and the nature of the minima was confirmed by means of the eigenvalues (all positive) of the corresponding Hessian matrices. The M06-2X/6-31G* model chemistry was used for the calculation of the binding energy for (ArCC)₂Tz dimers, defined as the energy difference between the dimer and the isolated molecules. On the one hand, we have calculated the binding energy for two molecules that we have kept with face-to-face planes at a distance of 3.4 Å along z-direction (see Figure 2), corresponding to a typical π -stacking distance. While the position of one of the molecules was kept fixed, the second molecule was displaced along x- and y-axes in a grid of 0.2 Å in both directions. In addition, we have calculated the binding energy as a function of the z-axis displacement, fixing x- and y-axes to the values giving the lowest binding energy in the previous (x,y) energy scan. Although traditional DFT functionals perform poorly for non-covalent interactions, the M06 family of functionals has been shown to give reasonably accurate stacking geometries for a variety of dispersion-dominated systems, such as perylenediimides and quaterthiophenes,^{57,58} as well as DNA base pairs,⁵⁹ and aromatic systems used as organic semiconductors, such as quaterthiophene, in which the electronic coupling and binding energies calculated at M06-2X level yield similar results to those obtained with other (dispersion-corrected) functionals like PBE0-dDsC/def2-SVP.⁵⁸ The transfer integral t_{I2} was calculated with the B3LYP functional and the double zeta polarized (DZP) basis set, while the

remaining key electronic properties (E_{LUMO} , EA, λ_i) were calculated at the B3LYP/6-31+G* level of theory. Although Koopmans theorem is not rigorously applicable to Kohn-Sham orbital energies, Perdew proved a connection between ionization potentials/electron affinities and HOMO/LUMO energies through Janak's theorem (see, e.g. ref. 60-62 and references therein). In this sense, B3LYP has been proven to be accurate enough for predicting EAs^{63,64} and provides theoretical λ_i values in good quantitative agreement with the experimental ones from gas-phase ultraviolet photoelectron spectroscopy.⁶⁵ Zhang and Musgrave have also reported that B3LYP yields lower errors in the LUMO energy of small organic molecules as compared to other DFT methods with a higher percentage of Hartree-Fock exchange.⁶⁶ The 6-31+G* basis set is recommended in calculations involving anionic species and was therefore used here.⁶²

The spatial variation of the electron coupling has been scanned as a function of the x- and y-axes displacement at fixed $z = 3.4 \text{ \AA}$. In addition, t_{12} has been calculated for different configurations of the molecules considered in this study corresponding to a minimum in the binding energy.

Figure 2. (Br₂PhCC)₂Tz dimer in the position $x = 2.0 \text{ \AA}$, $y = 3.4 \text{ \AA}$ and $z = 3.4 \text{ \AA}$, where (x,y,z) is the relative displacement between the tetrazine units along the short (x) and long (y) molecular axes, and the π -stacking direction (z).

RESULTS AND DISCUSSION

The internal reorganization energies (λ_i) previously reported for a set of Ar₂Tz derivatives lie in the range $0.48 - 0.62 \text{ eV}$ ¹⁷ *i.e.* about twice the values obtained for typical *n*-type organic semiconductors such as perfluoropentacene (0.24 eV),³⁹ diimides ($0.22 - 0.35 \text{ eV}$),²⁴ fluoroarene-oligothiophenes ($0.22 - 0.34 \text{ eV}$)⁶⁷ and core-twisted chlorinated perylene bisimide ($0.30 - 0.34$).⁶⁸ However, the presence of the ethynylene bridges in (ArCC)₂Ph derivatives substantially lowers λ_i to values comparable to those reported for the above mentioned reference compounds (see Table 1). The decrease of λ_i is closely related to the change in the shape of the LUMO, which becomes completely delocalized for (ArCC)₂Tz (see Figure 1 for (PhCC)₂Tz). In addition, we have observed a cross correlation between the shapes of the LUMO and LUMO + 1 orbitals for Ph₂Tz and (PhCC)₂Tz. Similar correlation is also observed for the HOMO and HOMO-1 orbitals (see Figure 1).

Table 1. Internal reorganization energy (λ_i) for (Ar₂CC)₂Tz derivatives (this work) and for Ar₂Tz (ref. 17). Calculations were carried out at the B3LYP/6-31+G* level.

Compounds	λ_1/eV	λ_2/eV	λ_i/eV	Compounds	λ_1/eV	λ_2/eV	λ_i/eV
Ph ₂ Tz	0.30	0.29	0.60	(PhCC) ₂ Tz	0.10	0.12	0.22
(F ₂ Ph) ₂ Tz	0.22	0.31	0.53	(F ₂ PhCC) ₂ Tz	0.11	0.16	0.27
(Cl ₂ Ph) ₂ Tz	0.31	0.30	0.61	(Cl ₂ PhCC) ₂ Tz	0.13	0.13	0.26
(Br ₂ Ph) ₂ Tz	0.31	0.31	0.62	(Br ₂ PhCC) ₂ Tz	0.14	0.12	0.26
(CN ₂ Ph) ₂ Tz	0.26	0.23	0.48	(CN ₂ PhCC) ₂ Tz	0.11	0.12	0.23

The electron transfer rate also strongly depends on electronic coupling values, which reveals the strength of the electronic interactions between neighboring molecules, and thus critically depends on the relative spatial arrangement in the bulk. However, to

the best of our knowledge, these compounds have not been synthesized yet. Therefore, X-ray structures are not available for any of the $(\text{ArCC})_2\text{Tz}$ compounds; consequently, in order to use a plausible crystal structure in the calculations, the arrangement of every pair of molecules is modeled assuming a stacked disposition typical for similar Ar_2Tz systems.^{17,69,70} Based on these structures, the transfer integrals are corresponding computed.

Also the binding energy is calculated for stacking dimers as a function of the relative (x,y) displacement between both molecules keeping z fixed at 3.4 Å. A large number of energetically accessible stacking geometries are considered (see Figure 3). For all the compounds, a broad minimum appears for x- and y-displacements lower than 2 Å and the binding energy reaches a maximum value for the fully overlapped dimer. A second minimum, placed at $x \approx 3 - 4$ Å and $y < 1$ Å, is also observed for all of them with the exception of the brominated derivative. A complex landscape with up to four energy valleys is observed for $(\text{PhCC})_2\text{Tz}$. The position of the global minimum in the binding-energy landscape is found by displacing the molecules along the long axis direction ($x \sim 0$, $y = 1.4 - 1.6$ Å) for $(\text{Br}_2\text{PhCC})_2\text{Tz}$ and $(\text{NC}_2\text{PhCC})_2\text{Tz}$, while the global minimum for the rest of compounds is placed along the x-displacement ($x = 1.2 - 3.4$ Å). In general, we found that the binding energies minima are located inside the region $1 < (x^2 + y^2)^{1/2} < 2$ (see Figure 3) with the exception of $(\text{PhCC})_2\text{Tz}$. Once the global minima are localized on the energy landscapes, the binding energy was also monitored as a function of the z-displacement being $z = 3.2$ Å the displacement that mostly lowers it (see Figure 4). The largest (minimum) binding energy was obtained for $(\text{Br}_2\text{PhCC})_2\text{Tz}$, ~ -1.4 eV, about twice as large as that for the rest of compounds (see Table 2).

Table 2. Largest binding energy ($E_{b,min}$) and the corresponding relative x,y,z-positions of the molecules within stacked dimers of the $(ArCC)_2Tz$ family studied here. Charge transfer integral, t_{I2} transfer rates k_{ET} , mobility and relative mobility with respect to $(PhCC)_2Tz$ calculated from equation (8) at the corresponding dimer geometries.

Compound	$E_{b,min} / \text{eV}$	$x / \text{\AA}$	$y / \text{\AA}$	$z / \text{\AA}$	t_{I2} / meV	k_{ET} / s^{-1}	$\mu / \text{V}^{-1} \text{cm}^2 \text{s}^{-1}$	μ_{rel}
$(PhCC)_2Tz$	-0.648	0.0	3.4	3.2	74	3.67×10^{13}	0.727	1.000
$(F_2PhCC)_2Tz$	-0.712	0.6	1.2	3.1	48	1.20×10^{13}	0.266	0.365
$(Cl_2PhCC)_2Tz$	-0.798	0.0	1.6	3.3	24	3.16×10^{12}	0.082	0.113
$(Br_2PhCC)_2Tz$	-1.389	1.4	0.0	3.3	99	5.38×10^{13}	1.337	1.839
$(CN_2PhCC)_2Tz$	-0.777	1.6	0.6	3.2	1	6.38×10^9	0.0001	0.0002

Figure 3. Binding energy for a) $(\text{PhCC})_2\text{Tz}$; b) $(\text{F}_2\text{PhCC})_2\text{Tz}$; c) $(\text{Cl}_2\text{PhCC})_2\text{Tz}$; d) $(\text{Br}_2\text{PhCC})_2\text{Tz}$ and e) $(\text{CN}_2\text{PhCC})_2\text{Tz}$ dimers vs. stacking geometry ($z = 3.4 \text{ \AA}$).

Figure 4. Binding energy dependence as a function of the z -displacement for the $(\text{PhCC})_2\text{Tz}$, $(\text{F}_2\text{PhCC})_2\text{Tz}$, $(\text{Cl}_2\text{PhCC})_2\text{Tz}$, $(\text{Br}_2\text{PhCC})_2\text{Tz}$ and $(\text{CN}_2\text{PhCC})_2\text{Tz}$ dimers.

Unexpectedly, the highest values of binding energies are observed for slightly displaced geometries (see Table 2) rather than for those at a perfectly cofacial disposition (at $x = y = z = 0 \text{ \AA}$, see Figure 5), allowing us to conclude that nuclear repulsion dominates the binding energy landscapes in this region (Figure 3). Coming back to Table 2, which collects the t_{12} values calculated for the arrangements with the lowest binding energies, we can observe that the largest electronic coupling is obtained for $(\text{Br}_2\text{PhCC})_2\text{Tz}$ (99 meV) followed by $(\text{PhCC})_2\text{Tz}$ (74 meV) and $(\text{F}_2\text{PhCC})_2\text{Tz}$ (48 meV). All these values are larger than those calculated for Ph_2Tz , $(\text{F}_2\text{Ph})_2\text{Tz}$ and $(\text{Br}_2\text{Ph})_2\text{Tz}$ crystals (18, 45 and 51 meV, respectively) previously studied.¹⁷ In general, t_{12} values calculated for $(\text{PhCC})_2\text{Tz}$, $(\text{F}_2\text{PhCC})_2\text{Tz}$ and specially $(\text{Br}_2\text{PhCC})_2\text{Tz}$ are close to those reported for oligoacenes including pentacene (131 meV calculated at the

B3LYP/TZP level),⁴⁶ for the perylene derivatives studied by Wang et al. (26 – 64 meV, calculated at the PW91PW91/6-31G* level),²⁵ for the sets of diimides derivatives studied by Chen et al. (21.6 – 87.5 meV, calculated at the PW91PW91/6-31G* level)²⁴ and by Di Donato et al. (74 – 96 meV, calculated at the B3LYP/3-21G level).²⁶

Figure 5. Electron couplings for a) $(\text{PhCC})_2\text{Tz}$; b) $(\text{F}_2\text{PhCC})_2\text{Tz}$; c) $(\text{Cl}_2\text{PhCC})_2\text{Tz}$; d) $(\text{Br}_2\text{PhCC})_2\text{Tz}$ and e) $(\text{CN}_2\text{PhCC})_2\text{Tz}$ dimers vs. stacking geometry ($z = 3.4 \text{ \AA}$) as surface plot.

When comparing the molecules studied here with the tetrazine derivatives previously published,¹⁷ we observe the highest k_{ET} and μ values were obtained for (PhCC)₂Tz and its brominated and fluorinated derivatives, which have mobilities (0.30 – 1.34 cm² V⁻¹ s⁻¹) at least one order of magnitude higher than those reported for the corresponding parent compounds Ph₂Tz, (F₂Ph)₂Tz and (Br₂Ph)₂Tz (~ 0.006 – ~ 0.026 cm² V⁻¹ s⁻¹) at the same level of theory.¹⁷ Similar values of electron mobilities have been calculated for sets of perylene dibisimide derivatives (0.007 – 1.45 cm² V⁻¹ s⁻¹),⁷¹ tetracarboxylic diimide derivatives (0.08 and 0.34 cm² V⁻¹ s⁻¹)⁷² and core-twisted chlorinated perylene bisimide (0.004 – 0.28 cm² V⁻¹ s⁻¹)⁶⁸ employing the MLJ formulation. Mobilities estimated for (PhCC)₂Tz, (F₂PhCC)₂Tz and (Br₂PhCC)₂Tz lie close to the range of the values experimentally determined for common *n*-type organic semiconductors. For instance, experimental μ values measured under vacuum for electron-deficient N,N'-substituted arylenediimides and perfluoroalkyl oligothiophenes turn out to be in the ranges of 0.02 – 0.35 and 0.03 – 1.7 cm² V⁻¹ s⁻¹, respectively.⁷³ The OFET performances of bis(thienyl)-*s*-tetrazine bridged to naphthalene diimide moieties have been recently studied (μ values within 0.005 – 0.14 cm² V⁻¹ s⁻¹ were reported) showing the potential of *s*-tetrazine derivatives as *n*-type semiconductors.⁷⁴ Nevertheless, we must emphasize that the comparison between experimental and theoretical mobilities is far from trivial due to some assumptions in the theoretical model, in particular the geometry chosen for the calculation, together with other experimental factors (for example, traps) intrinsically difficult to be taken into account. However, without trying to reproduce the absolute experimental values, the results show an undeniable comparative characteristic.

The performance of an organic semiconductor device does not only depend on the bulk charge mobility of the semiconducting material but also on the efficiency of the electron injection at the electrodes. The interface between metal (cathode) and *n*-type organic semiconductor is usually treated as a Mott-Schottky barrier, where the barrier height is given by the difference between the metal work function (Φ) and the (gas) semiconductor LUMO level (E_{LUMO}).³⁸ A good ohmic contact between semiconductor materials and electrodes is generally expected only for potential barriers lower than 0.2 – 0.3 eV,^{75,76} while for larger barriers interfacial effects such as metal reactivity, polarization processes and inter-diffusion within the metal-organic interface and temperature cannot be neglected.^{38,77-79} For this reason, the sole analysis of Φ and E_{LUMO} values cannot provide a quantitative evaluation of the injection barrier but it nevertheless serves as a guide to predict the alignment of levels at the interface and the electron injection barrier, as well as to interpret trends within a set of related compounds.^{48,79-81} Figure 6 shows the calculated E_{LUMO} for the set of (ArCC)₂Tz and their corresponding parent compounds, Ar₂Tz. This figure also collects reduction potentials recently reported for some aryl-*s*-tetrazine derivatives (shown in Figure 7) and their E_{LUMO} estimated by using of an empirical equation proposed by De Leeuw et al.⁸² The introduction of ethynylene bridges produces an increase within 0.3 – 0.6 eV in E_{LUMO} with respect to the corresponding parent compounds. Even so, E_{LUMO} values calculated for (ArCC)₂Tz, excepting only (PhCC)₂Tz, are comparable to those estimated for other aryl-*s*-tetrazine derivatives. In this sense, the presence of halogen atoms and especially cyanide groups in the (ArCC)₂Tz compounds significantly lowers E_{LUMO} with respect to (PhCC)₂Tz which should bring on a more efficient charge injection^{38,49,52,83} and could also help the environmental stability of the material.^{52,84} Interestingly, E_{LUMO} is decreased by 0.4 – 0.5 eV with respect to (PhCC)₂Tz due to the

presence of four halogen atoms and *ca.* 1.1 eV by the inclusion of the cyanide groups, reaching a minimum value of - 3.68 eV. Energy barriers, $\Phi - |E_{\text{LUMO}}|$, lower than 0.3 eV were calculated for all the studied compounds with respect to some common electrodes used for electron injection, *i.e.* Na ($\Phi = - 2.6$ eV), Ca ($\Phi = - 2.8$ eV eV) and Sm ($\Phi = - 2.7$ eV).⁸⁵⁻⁸⁹ Furthermore, ohmic contact is also expected for (CN₂PhCC)₂Tz with respect to the Mg electrode ($\Phi = - 3.2$ eV).^{88,90}

Figure 6: Experimental reduction potentials (red lines) and corresponding LUMO energies (blue dashed lines) estimated with the empirical equation ($E_{\text{LUMO}} = -[E_{\text{red}} + 4.4]$ eV; reference 82) are shown. Calculated LUMO energies for the parents compounds (reference 17) at B3LYP/6-31+G* level and LUMO and HOMO energies evaluated at the B3LYP/6-31+G* level for the series of (ArCC₂)Tz derivatives studied here. The values for aryl-*s*-tetrazine derivatives 1-5 (see Figure 7) have been extracted from references 74 and 91-93.

Electron injection efficiency is also related to vertical electron affinity, VEA, which increases between 0.2 and 0.4 eV with respect to Ar_2Tz derivatives, due to the presence of the ethynylene groups (see Table 3).¹⁷ The adiabatic electron affinity, AEA, also increases of 0.5 – 0.6 eV for the tetrahalogenated derivatives and 1.1 eV for the cyanide derivative with respect to $(\text{PhCC})_2\text{Tz}$, with AEA consistently larger of about 0.1 – 0.2 eV for $(\text{ArCC})_2\text{Tz}$ compounds as compared to Ar_2Tz . This observation is in agreement with some literature results and with chemical intuition, suggesting that the addition of electron-withdrawing substituents to the aromatic cores increases the electron affinity values, as well as the air stability of the electron-transporting materials.²² For instance, Kuo et al. have observed that the introduction of a few CN groups in pentacene raises the EA to values even larger than those of perfluoropentacene.⁸³

Figure 7. Chemical formulae of the *s*-tetrazine derivatives mentioned in Figure 6.

Table 3. Adiabatic (AEA) and vertical (VEA) electron affinity calculated at B3LYP/6-31+G* level for $(\text{ArCC})_2\text{Tz}$ and comparison with the values reported for their parent compounds, Ar_2Tz (Reference 17).

Compounds	AEA / eV	VEA / eV	Compounds	AEA / eV	VEA / eV
Ph_2Tz	1.51	1.22	$(\text{PhCC})_2\text{Tz}$	1.78	1.66
$(\text{F}_2\text{Ph})_2\text{Tz}$	2.16	1.84	$(\text{F}_2\text{PhCC})_2\text{Tz}$	2.28	2.13
$(\text{Cl}_2\text{Ph})_2\text{Tz}$	2.15	1.85	$(\text{Cl}_2\text{PhCC})_2\text{Tz}$	2.34	2.20
$(\text{Br}_2\text{Ph})_2\text{Tz}$	2.17	1.86	$(\text{Br}_2\text{PhCC})_2\text{Tz}$	2.35	2.22

(CN ₂ Ph) ₂ Tz	2.86	2.63	(CN ₂ PhCC) ₂ Tz	2.92	2.80
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CONCLUSIONS

The electronic properties of the *n*-type semiconducting bis(arylene-ethynylene)-*s*-tetrazine, (ArCC)₂Tz derivatives were theoretically studied employing state-of-the-art DFT calculations. These compounds might promisingly be applied in real devices. In fact, we note first that the reorganization energies calculated for (ArCC)₂Tz derivatives are substantially lower than those reported for their parent compounds, Ar₂Tz, studied previously.¹⁷ The change in the shape of the LUMO, which is completely delocalized for (ArCC)₂Tz and localized on the Tz ring for Ar₂Tz is the origin of this difference. Indeed the λ_i values calculated for (ArCC)₂Tz compounds are comparable to those reported for typical *n*-type organic semiconductors such as perfluoropentacene, diimides and fluoroarene-oligothiophenes.^{24,39,67} The second reason for stimulating practical applications is that the electronic couplings *t*₁₂, calculated for the dimers at the lowest binding energy geometry, are rather large, with (Br₂PhCC)₂Tz, (PhCC)₂Tz and (F₂PhCC)₂Tz showing the largest electronic couplings, again higher than those calculated for their parent compounds,¹⁷ and comparable to the values reported for different diimides and perylenes with assessed *n*-type semiconductor character.²⁴⁻²⁶ Also the electron mobilities estimated for these compounds are in line with the values reported for perylene bisimide derivatives and tetracarboxylic diimide derivatives^{71,72} and lie on the range of the values experimentally determined for common *n*-type organic semiconductors such as N,N'-substituted arylenediimides and perfluoroalkyl oligothiophenes.⁷³ Regarding electron injection, ohmic contact can be expected for all the studied (ArCC)₂Tz derivatives with respect to some of the common electrodes used

for electron injection such as Na, Ca and Sm. Therefore, (PhCC)₂Tz, (F₂PhCC)Tz and particularly (Br₂PhCC)₂Tz might be considered as promising compounds which could exhibit a *n*-type semiconductor character.

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