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Influence of methoxy groups on the properties of 1,1-bis(4-aminophenyl) cyclohexane based arylamines: experimental and theoretical approach[†]

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Three new isomeric cyclohexylidene linked triphenylamines containing methoxy groups in different positions were synthesized via Ullmann coupling from 1,1-bis(4-aminophenyl)cyclohexane and respective arvl iodides. Thermal behaviour, optical and photoelectrical properties of the obtained materials were investigated. Calculations based on the density functional methods (DFT) were also carried out in order to better understand structure-property relationships. Methoxy-substituted derivatives of 1,1-bis(4-aminophenyl)cyclohexane show lower ionization potentials and higher hole drift mobilities than the corresponding derivative having no methoxy groups. The ionization potentials of the solid samples of the methoxy-substituted compounds established by the electron photoemission technique are in the range of 5.34–5.55 eV. Hole-drift mobility values of the amorphous layers of the methoxy-substituted materials established by the time-of-flight technique range from 4.0×10^{-4} to 1.2×10^{-3} cm² V⁻¹ s⁻¹ at the electric field of 10^6 V cm⁻¹. The highest hole mobilities were observed for the para-substituted derivative. Theoretical results suggest that the hole mobility in the bulk materials is driven by the electronic coupling parameter whilst the reorganization energy parameter predicts the wrong mobility trend. The role of the methoxy groups is found to be related to the well-known mesomeric (π -donor) effect and the possibility to establish C-H··· π (Ph) and C-H···X (X = O, N) hydrogen bonds. The effect of these properties on the enhanced Stokes shifts of the para-methoxysubstituted compound, on the decrease of the ionization potentials for the methoxy substituted compounds as compared to the non-substituted one, and on the enhanced possibility to establish considerable electronic couplings between adjacent molecules is discussed in detail.

1. Introduction

Arylamines represent a class of organic charge-transporting materials widely studied and used as the components of different optoelectronic devices including electrophotographic photoreceptors, organic light emitting diodes, solar cells, *etc.*¹⁻⁴ They exhibit quite sufficient charge transport properties, their

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ionization potentials can be varied in a rather wide range, and their devices show stable performance under ambient conditions.

In some fields of application, such as dye sensitized solar cells, hole-transporting materials with low ionization potentials are required. Triphenylamine (TPA) based compounds have attracted much interest in this respect and the role of different substituents in the ionization potentials and other parameters has been considered.⁵⁻⁹ It is known that introduction of methoxy groups into the structures of organic p-type semiconductors leads to the decrease of their ionization potentials,⁵ with stronger influence found in the case of para-methoxy substituted TPA compounds as compared to the meta-substituted ones.⁶ As for the influence of these substitutions on the hole mobilities, lower mobility has been measured for instance in the case of *p*-methoxy and p-butoxy substituted N,N'-bis(m-tolyl)-N,N'-diphenyl-1,1'biphenyl-4,4'-diamine (TPD) as compared to the non-substituted TPD⁷ which has been partly explained by the change in dipole moment upon substitution. Due to this kind of substitutions, the efficiencies of different devices may be strongly affected. The hole-injection barrier differences for instance, which are strongly related to the highest occupied molecular orbital (HOMO)

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[†] Electronic supplementary information (ESI) available: Values of Δd parameter and $\Delta E(H - H_{-1})$; excitation energy values of the first ten excited states for compounds **1–4** along with the corresponding oscillator strengths; optimized geometries of compounds **2–4**; UV-VIS absorption spectra from the TDDFT calculations; sketches of some relevant orbitals for compound **4**; details on the estimation of $k_{\rm HT}$ values. See DOI: 10.1039/c2jm14387a

energy, could dominate the efficiencies of devices using this kind of materials as has been shown in the case of some OLED applications.⁸

It is interesting to note that while these studies point to the effect of the *para*-methoxy substitutions on some charge-transport properties, there is a lack of systematic studies concerning the role of the methoxy group position in the optical, electronic, and hole-transporting properties of the TPA based compounds. A deeper insight on the mechanisms by which the methoxy group influences these properties may be very helpful in the design of new hole-transporting materials.

In order to understand experimental results and to predict strategies for designing new charge transporting materials, theoretical approaches on the molecular level have been extensively employed. Different strategies have been used for the charge-mobility calculations.^{10–12} In the case of amorphous materials one can consider that the elementary step of the charge transport is the charge transfer between two adjacent molecules in which case the determination of hole-transfer rate-constants ($k_{\rm HT}$, eqn (1)) based on Marcus^{13–16} theory can give very helpful information.

$$k_{\rm HT} = \frac{4\pi}{h} \frac{1}{\sqrt{4\pi\lambda k_{\rm B}T}} t^2 \exp\left[-\frac{\left(\Delta G^\circ + \lambda\right)^2}{4k_B \lambda T}\right]$$
(1)

In this equation t is the electronic coupling between two adjacent molecules, ΔG° is the CT reaction free energy (which is zero in the case of hole transfer between identical molecules) and λ is the reorganization energy. This last parameter is the sum of two terms: (i) λ_s , representing the contribution from the medium polarization energy and (ii) λ_i , representing the energetic effort due to the intramolecular geometric relaxations upon CT between two adjacent molecules.

In order to obtain high $k_{\rm HT}$ values the electronic coupling parameter (t) should be maximized whereas the reorganization energy ($\lambda = \lambda_{\rm s} + \lambda_{\rm i}$) should be minimized. While the knowledge of all these parameters is necessary for the calculation of $k_{\rm HT}$, still other parameters need to be known in order to calculate charge mobilities. However, each of these parameters considered individually can be helpful in designing new materials. The intramolecular reorganization energy parameter, for instance, has been frequently used to deduce trends in a series of similar compounds, which is based on the assumption that, in this case, the variation of the electronic couplings should be smaller than the variation of the reorganization energies. While this might hold true in some cases, in the present study we show that the application of this criterion is subtle.

The aim of this work is the investigation of the influence of the methoxy group position on ionization potentials, charge-transporting and other properties of 1,1-bis(4-aminophenyl)cyclohexane based arylamines. With this aim we have synthesized and characterized three new isomeric 1,1-bis(4-aminophenyl)cyclohexane linked triphenylamines containing methoxy groups in different positions. Density functional calculations (DFT)¹⁷ were also carried out in order to obtain more insight on the mechanisms by which the presence and the positioning of the methoxy groups influence the electronic, optical and hole-transporting properties.

2. Experimental

2.1 Instrumentation

NMR spectra were recorded using a Varian Unity Inova (300 MHz) apparatus. IR spectra were obtained on a Perkin-Elmer Spectrum GX II FT-IR System spectrometer. Mass spectra (MS) were obtained using a Waters ZQ 2000 system. Elemental analyses were performed with an Exeter Analytical CE-440 Elemental Analyzer. UV spectra were recorded on a Perkin Elmer Lambda 35 spectrophotometer. Photoluminescence (PL) spectra were recorded using a Hitachi MPF-4 spectrophotometer. Differential scanning calorimetry (DSC) measurements were carried out using a DSC Q100 calorimeter with a heating/ cooling rate of 10 °C min⁻¹ under nitrogen. Thermogravimetric analysis (TGA) was performed on a Mettler TGA/SDTA851e/ LF/1100 apparatus with a heating rate of 20 °C min⁻¹ under nitrogen. The ionization potentials (I_p) of the solid samples were measured by electron photoemission in the air method as described before.¹⁸ The measurement method was, in principle, similar to that described by Miyamoto et al.¹⁹ Hole drift mobilities were measured by a xerographic time-of-flight (XTOF) method.^{20,21} The samples for the charge carrier mobility measurements were prepared by casting tetrahydrofuran (THF) solutions of compounds or their mixtures with bisphenol-Zpolycarbonate (PC-Z) on polyester films with aluminium layer.²² The thickness of the charge-transporting layers varied in the range of 2-8 µm.

2.2 Materials

1,1-Bis(4-aminophenyl)cyclohexane was purchased from Tokyo Chemical Industry. Iodobenzene, 2-, 3- and 4-iodoanisoles, odichlorobenzene, 18-crown-6, copper powder and potassium carbonate were obtained either from Sigma-Aldrich or Fluka. All the materials were used as received. Compounds 1-4 were synthesized by the following general procedure. 1,1-Bis(4-aminophenyl)cyclohexane (0.8 g, 3 mmol), aryl iodide (18 mmol), either iodobenzene (3.7 g) or iodoanisole (4.2 g), and 18-crown-6 (0.16 g, 0.6 mmol) were dissolved in 10 ml of o-dichlorobenzene in a two-necked round-bottom flask equipped with a magnetic stirrer and under nitrogen blanket. When the mixture was heated above 150 °C dry potassium carbonate powder (1 g, 7.5 mmol) and copper bronze (0.38 g, 6 mmol) were added. The mixture was kept under reflux (ca. 180 °C) controlling by TLC. The reaction was stopped after ca. 20 hours, the mixture was cooled down, filtered and o-dichlorobenzene was removed by distillation. The products were further purified by silica gel column chromatography and crystallized from the methanol and tetrahydrofuran (THF) mixture. Compound 1 was crystallized from the eluent mixture.

1,1-Bis[4-(*N*,*N***-diphenyl)aminophenyl] cyclohexane (1).** Pale grey crystals. Yield 1.09 g (64%). Mp: 171–173 °C. ¹H NMR (CDCl₃, 300 MHz) ppm: 1.46–1.65 (m, 6H, CH₂ cyclohexylidene), 2.16–2.28 (m, 4H, CH₂ cyclohexylidene), 6.94–7.04 (m, 8H, phenyl), 7.04–7.10 (m, 4H, phenyl), 7.07 (d, 4H, *p*-phenylene, J = 8.8 Hz), 7.13 (d, 4H, *p*-phenylene, J = 8.8 Hz), 7.18–7.28 (m, 8H, phenyl). ¹³C NMR (CDCl₃, 300 MHz) ppm: 22.9, 26.4, 37.3, 45.5, 122.4, 123.5, 124.1, 127.9, 129.1, 142.9, 144.9,

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147.9. FT-IR (KBr) cm⁻¹: 3034 (ν C–H aromatic), 2963, 2926, 2855 (ν C–H aliphatic), 1592, 1507, 1493, 1465 (ν C=C aromatic), 1327 (ν C–N aromatic), 862, 803, 695 (γ C–H aromatic). MS (APCI⁺, 20 V) *m*/*z* 571.5 ([M + H]⁺). Elemental analysis for C₄₂H₃₈N₂: calc. C 88.38%; H 6.71%; N 4.91%; found: C 88.34%; H 6.69%; N 4.98%.

1,1-Bis{4-[*N*,*N***-bis(2-methoxyphenyl)]aminophenyl}cyclohexane (2).** Yellow crystals. Yield 1.04 g (50%). Mp: 179–180 °C. ¹H NMR (CDCl₃, 300 MHz) ppm: 1.36–1.57 (m, 6H, CH₂ cyclohexylidene), 2.04–2.20 (m, 4H, CH₂ cyclohexylidene), 3.61 (s, 12H, OCH₃), 6.55 (d, 4H, *p*-phenylene, J = 8.8 Hz), 6.83–6.92 (m, 8H, *o*-phenylene), 6.97 (d, 4H, *p*-phenylene, J = 8.8 Hz), 7.06–7.17 (m, 8H, *o*-phenylene). ¹³C NMR (CDCl₃, 300 MHz) ppm: 23.0, 26.6, 37.3, 44.9, 55.7, 112.8, 117.2, 121.0, 125.4, 127.1, 128.3, 135.9, 140.0, 145.3, 155.2. FT-IR (KBr) cm⁻¹: 3059, 3029, 2991 (*ν* C–H aromatic), 2936, 2849, 2834 (*ν* C–H aliphatic), 1612, 1591, 1500 (*ν* C=C aromatic), 1326 (*ν* C–N aromatic), 1271, 1237, 1024 (*ν* C–O–C), 820, 743, 697, 621 (*γ* C–H aromatic). MS (APCI⁺, 20 V) *m*/*z* 691.3 ([M + H]⁺). Elemental analysis for C₄₆H₄₆N₂O₄: calc. C 79.97%; H 6.71%; N 4.05%; found C 79.88%; H 6.69%; N 4.08%.

1,1-Bis{4-[N,N-bis(3-methoxyphenyl)]aminophenyl}cyclohexane (3). Pale vellow crystals. Yield 0.77 g (37%). Mp: 121-123 °C. ¹H NMR (CDCl₃, 300 MHz) ppm: 1.41-1.63 (m, 6H, CH₂ cyclohexylidene), 2.14-2.26 (m, 4H, CH₂ cyclohexylidene), 3.70 (s, 12H, OCH₃), 6.51-6.58 (m, 4H, *m*-phenylene), 6.62 (t, 4H, *m*-phenylene, J = 2.2 Hz), 6.63–6.69 (m, 4H, *m*-phenylene), 6.99 (d, 4H, p-phenylene, J = 8.8 Hz), 7.13 (d, 4H, p-phenylene, J =8.8 Hz), 7.13 (t, 4H, *m*-phenylene, J = 8.1 Hz). ¹³C NMR (CDCl₃, 300 MHz) ppm: 22.9, 26.4, 37.2, 45.5, 55.2, 107.8, 109.9, 116.6, 124.1, 127.9, 129.7, 143.3, 144.6, 149.0, 160.3. FT-IR (KBr) cm⁻¹: 3031, 2997 (v C-H aromatic), 2934, 2857, 2832 (v C-H aliphatic), 1596, 1506, 1487 (v C=C aromatic), 1318 (v C-N aromatic), 1208, 1043 (v C-O-C), 826, 769, 691 (v C-H aromatic). MS (APCI⁺, 20 V) m/z 691.4 ([M + H]⁺). Elemental analysis for C₄₆H₄₆N₂O₄: calc. C 79.97%; H 6.71%; N 4.05%; found C 80.00%; H 6.77%; N 4.11%.

1,1-Bis{4-[*N*,*N***-bis(4-methoxyphenyl)]aminophenyl}cyclohexane (4).** Pale yellow crystals. Yield 0.93 g (45%). Mp: 162–163 °C. ¹H NMR (CDCl₃, 300 MHz) ppm: 1.41–1.62 (m, 6H, CH₂ cyclohexylidene), 2.12–2.22 (m, 4H, CH₂ cyclohexylidene), 3.78 (s, 12H, OCH₃), 6.80 (d, 8H, *p*-phenylene, J = 9.2 Hz), 6.82 (d, 4H, *p*-phenylene, J = 9.2 Hz), 6.82 (d, 4H, *p*-phenylene, J = 8.8 Hz), 7.03 (d, 8H, *p*-phenylene, J = 9.2 Hz), 7.05 (d, 4H, *p*-phenylene, J = 8.8 Hz). ¹³C NMR (CDCl₃, 300 MHz) ppm: 22.9, 26.5, 37.2, 55.5, 114.5, 120.3, 120.4, 126.3, 126.3, 127.6. FT-IR (KBr) cm⁻¹: 3037, 2996 (*ν* C–H aromatic), 2933, 2857, 2832 (*ν* C–H aliphatic), 1604, 1504 (*ν* C=C aromatic), 1318 (*ν* C–N), 1239, 1036 (*ν* C–O–C), 826, 729 (*γ* C–H aromatic). MS (APCI⁺, 20 V) *m/z* 691.4 ([M + H]⁺). Elemental analysis for C₄₆H₄₆N₂O₄: calc. C 79.97%; H 6.71%; N 4.05%; found C 80.03%; H 6.67%; N 4.09%.

2.3 Computational methodology

DFT¹⁷ calculations employing the B3LYP^{23,24} functional were performed with the Gaussian 09 program.²⁵ The geometries of all

the molecules were optimized without symmetry constraints by using the $6-31G^{**}$ basis set, followed by frequency calculations to assure that real minima were obtained. The geometry optimizations of the cationic radical species were performed at the restricted open shell level.

The spectroscopic properties of the molecules were calculated by means of the time dependent density functional theory (TDDFT) method^{26–30} with the 6-31+G* basis set. Up to 20 excited states were calculated and the theoretical absorption bands were obtained by considering a band half-width of 0.33 eV at half-height (Gaussview 5 software).

The internal reorganization energies (λ_i) were calculated with the 6-31G** basis set by means of the following equation:³¹

$$\lambda_{i} = \lambda_{i}^{1} + \lambda_{i}^{2} = \left(E_{M}^{G-M^{+}} - E_{M}^{G-M}\right) + \left(E_{M^{+}}^{G-M} - E_{M^{+}}^{G-M^{+}}\right)$$
(2)

In this equation the quantity $E_{\rm M}^{\rm G-M^+}$ for instance corresponds to the energy of the neutral molecule (M) in the geometry of the cationic species (M⁺).

The calculation of the electronic couplings is based on the following approximations: (i) despite the irregular packing between adjacent molecules in the amorphous materials, dimers of different geometries can be established which are supposed to adopt local minima geometries. (ii) The hole is localized in only one molecule. (iii) Electronic coupling between the HOMO orbitals of adjacent monomers, also known as the "direct calculation" or "two state model,"32-35 is considered instead of the coupling between states. Detailed descriptions on different methods employed for the calculation of the transfer integrals can be found elsewhere.³¹⁻³⁵ The simplest but the more limited method is based on the Koopmans' theorem, in which the transfer integrals are determined as half of the energy splitting between the HOMO-1 (LUMO-1) and HOMO (LUMO) orbitals in the dimer. As this method is applicable only if the dimer possesses a perfect symmetry, the "direct calculation" of the transfer integrals in the frame of a "two state" model is commonly employed. Some more details on this method are given in the ESI[†], but we emphasize here that the HOMO (LUMO) orbitals of each monomer are generally considered, with the strict condition that the dimer HOMO (LUMO) contains contributions only from the monomer HOMO (LUMO) orbitals. As shown later in this study, this condition is satisfied for all compounds 1-4 which justifies the use of this method in our study. Finally, a general method evaluating the electronic coupling between electronic states (instead of frontier orbitals) has been proposed.³⁶ However, in our study the twostate model making use of the frontier orbitals for the calculation of the transfer integrals has been employed, which is commonly used and has proved to give correct results.

In order to correctly describe the π -stacking interactions, the geometries of the dimers formed by two identical molecules have been optimized by employing the ω B97X-D functional at the 6-31G** basis set.³⁷ Previous studies have shown that this functional provides good results on the description of weak interactions.^{38,39} The electronic couplings between the HOMO orbitals of two adjacent molecules have been calculated at the same level (ω B97X-D/6-31G**) according to the approach described by Valeev *et al.*³⁴ with the corresponding matrix elements evaluated with Gaussian 09 (ESI†). Note that the coupling values depend

on the functional used and generally increase with the increasing percentage of Hartree–Fock exchange in the functional.³⁸ The transfer integrals for **1–4** calculated by using two different functionals are thus expected to change by a roughly constant factor, but the trends obtained by both functionals should be the same.

The interaction energies of some optimized dimers were calculated with respect to the isolated monomers with the 6-311++G(3df,3pd) basis set and were corrected for the basis set superposition error (BSSE) by the counterpoise correction method of Boys and Bernardi.⁴⁰ The zero point energy (ZPE) correction has been also taken into account by using the value obtained at the 6-31G** basis set.

Finally, the vertical ionization potentials (I_p) were calculated at the B3LYP/6-31G** level by the energy difference between neutral and cation radical species at the neutral state geometry.

3. Results and discussion

3.1 Synthesis

Compounds **1–4** were obtained from primary aromatic diamine, 1,1-bis(4-aminophenyl)cyclohexane, and iodobenzene or respective iodoanisoles in one-step synthesis *via* the modified Ullmann method⁴¹ as shown in Scheme 1. The small amounts of biphenyl derivatives were also obtained due to dimerization of iodoarenes. The chemical structure of the compounds was proved by ¹H and ¹³C NMR, FT-IR, mass spectrometry and elemental analysis. The obtained data were in good agreement with the designed structures. The obtained materials are well-soluble in common organic solvents such as acetone, THF, chloroform, toluene, but almost insoluble in methanol and hexane.

3.2 Thermal characterization

Thermal behaviour of the materials was explored using DSC and TGA methods. Melting points (T_m) , glass transition temperatures (T_g) and 5% mass loss temperatures (T_D) were established. The data are summarized in Table 1. Thermal behaviour of **2** during DSC heating–cooling–heating scans is shown in Fig. 1. Such behaviour is typical for all other samples. In the first DSC heating scan sharp endothermic peaks of melting appeared showing the crystalline nature of the materials. During the cooling and the second heating scans only glass transitions were observed for all four samples. Although compound **1** can be

Table 1 Thermal characteristics of compounds 1-4

Compound	$T_{\rm m}/^{\circ}{\rm C}$	$T_{\rm m}{}^a/{}^{\circ}{\rm C}$	$T_{g}^{a}/^{\circ}C$	$T_{\rm D}/^{\circ}{\rm C}$
1	171	172	68	416
2	179	183	67	421
3	121	123	48	454
4	162	163	63	435
^a Established by	y DSC.			

transformed into the glassy state by fast cooling from the melt it readily crystallizes from solutions or from films prepared by spin coating. Thus incorporation of OCH₃ groups improves the morphological stability of the glasses without significant reduction of T_g , which is 68 °C, 67 °C and 63 °C for 1, 2 and 4 respectively. T_g of *meta*-substituted compound 3 was found to be considerably lower (48 °C).

TGA performed under nitrogen with a heating rate of 20 °C min⁻¹ revealed high thermal stability of the synthesized compounds. Their thermal degradation started above 400 °C. Methoxy-substituted derivatives showed slightly higher 5% mass loss temperatures than compound **1**. The highest thermal stability was observed for *meta*-substituted derivative **3**. Its 5% mass loss was observed at 454 °C.

3.3 Geometries

The geometries of compounds 1–4 have been determined theoretically as described in the Computational methodology. Some typical bond-lengths and dihedral angles are given in Fig. S1 (ESI[†]). Two possible geometries for compound 1 are shown in Fig. 2. The two geminal phenyl groups bonded to the cyclohexane moiety can adopt a face-to-face relative geometry (structure 1a) or can be positioned almost orthogonal to each other (structure 1b, which mostly resembles to a transition state structure). Structure 1b is roughly 0.5 kcal mol⁻¹ higher in energy than 1a, suggesting fluxional geometries for this compound. As for the cationic state, structure 1b is unstable and only structure 1a is obtained.

Geometries equivalent to 1a and 1b have been obtained for the methoxy substituted neutral compounds (2–4, Fig. S1, ESI†) while only structures similar to 1a have been obtained for the cationic species. Due to multiple relative orientations of the methoxy groups, compounds 2–4 can adopt different conformer geometries with energy differences less than 0.5 kcal mol⁻¹



Scheme 1 Synthesis of compounds 1-4.



Fig. 1 DSC of ortho-substituted compound 2.



Fig. 2 Two geometries for compound 1 obtained by gas phase calculations at the B3LYP/6-31G** level.

between them. It can be assumed consequently that for each compound (1–4) a mixture of different conformers of very similar energetical stability might be obtained. In the following only the conformers of the lowest energy are considered.

In good agreement with previous studies⁴²⁻⁴⁴ planar geometries around N atoms are found for all compounds (referred hereafter as "N-plane") which is due to the conjugation of the N lone-pair with the π (Ph) systems. The dihedral angles between the Ph rings and the "N-plane" are almost the same for 1 and 3 (~40 to 42°, absolute values). The N-C bond lengths (~1.421 Å) are also equivalent, meaning that the *meta*-substitutions do not noticeably modify the local geometry around the N atom. In the case of compound **4**, the Ph–"Nplane" dihedral angles are larger for the *para*-substituted Ph rings (~45°) than for the unsubstituted ones (~36 to 37°). Similarly, the N–C bond lengths are not equivalent for this compound (1.417 Å for the non-substituted ring and 1.423 Å for the substituted ones). In the case of compound **2** (Fig. S1, ESI†), the methoxy *ortho*-substitutions induce important repulsions with the adjacent Ph rings, resulting in Ph–"N-plane" dihedral angles ranging from ~24 to 26° for the non-substituted Ph rings to up to ~60 to 63° for the substituted ones.

The changes in the Ph–"N-plane" dihedral angles upon oxidation are more important for 2 (sum of all changes $\sim 36^{\circ}$) than for 1 ($\sim 28^{\circ}$), 3 ($\sim 26^{\circ}$), and 4 ($\sim 10^{\circ}$). It can be expected that upon oxidation this difference affects the efficiency of the π conjugation between Ph rings more importantly in the case of 2 than for 1, 3 and 4. Finally, from the geometrical parameters presented in Fig. S1[†], it can be deduced that in both states (neutral and radical cation), the Ph groups directly bonded to the cyclohexylidene bridge possess more quinoidal character than the external Ph groups (see also the values of Δd parameter, Table S1, ESI[†]).



Fig. 3 UV (3a) and PL (3b) spectra of dilute tetrahydrofuran solutions of compounds 1–4.

3.4 Optical properties

UV spectra of the dilute (10^{-5} M) THF solutions of compounds 1–4 are shown in Fig. 3a. The wavelengths of absorption maxima $(\lambda_{UV_{max}})$ and absorption edges are summarized in Table 2. The spectra of the compounds show wide and intensive absorption bands with the maxima in the range of 302–306 nm due to π – π * transitions. UV spectra of the dilute solutions of 1–4 are very similar to that of dilute solution of triphenylamine (TPA) in chloroform, which shows maximum at 300 nm.⁴⁵ The absorption edges of methoxy-substituted derivatives 2–4 are slightly red shifted with respect to compound 1.

PL spectra of the dilute solutions of compounds 1–4 are shown in Fig. 3b. PL maxima ($\lambda_{PL_{max}}$) of compounds 1–4 are in the region of 356–389 nm with the Stokes shifts ranging from 50 to 86 nm. The largest Stokes shifts are observed for compound 4 which emits in the violet light region (389 nm). These observations show that the position of OCH₃ group noticeably influences the fluorescent properties of methoxyphenyl-substituted 1,1-bis (4-aminophenyl)cyclohexane derivatives.

In order to get more insight on the nature of the absorption bands, TDDFT calculations were performed. The UV-VIS spectra for compounds 1–4 (Fig. S2, ESI†) indicate that $\lambda_{UV_{max}}$ of each absorption band results as a combination of electronic transitions toward several excited states (for the excitation energies and the oscillator strengths of the first ten excited states see Table S2, ESI†). It can be observed that the band maxima of 1 and 4 do not correspond exactly to the transition of the largest oscillator strength but mostly to a group of higher energy transitions of smaller oscillator strengths which are very close in energy. In the case of 4 for instance, the sum of the oscillator strengths corresponding to the transitions S₀ \rightarrow S_{7,8,11} (separated by ~0.1 eV, Table S2†) is larger than the oscillator strength of the strongest one (S₀ \rightarrow S₃) thus providing the major contribution to the absorption band maximum.

The theoretical $\lambda_{UV_{max}}$ values of each absorption band were deduced from Fig. S2⁺ and are shown in Table 2. While differences of ~20 nm roughly can be observed between the calculated and the experimental values, the negligible spread of the experimental $\lambda_{UV_{max}}$ values for compounds 1–4 (3 nm) is very well reproduced by the theoretical results (5 nm, Table 2).

It is worth remembering that due to the presence of multiple quasi-isoenergetic conformers for each compound (*vide supra*) the absorption spectra should contain similar contributions of wavelengths slightly different to those shown in Table 2. In Fig. S2 and Table S2[†] only one absorption spectrum for each compound is shown corresponding to the conformer of the lowest energy.

Table 2UV and PL spectral data for the dilute solutions of compounds1-4. In parentheses are shown the corresponding theoretical values

Compound	$\lambda_{\rm UV_{max}}/nm$	$\lambda_{PL_{max}}/nm$	Absorption edge/nm	Stokes shift/nm
1	303 (322)	363	335	60
2	302 (327)	368	340	66
3	306 (327)	356	345	50
4	303 (325)	389	340	86

The interpretation of the fluorescence spectra is not straightforward. All the excited states involved in the absorption bands (Fig. S2[†]) will relax and participate in the observed Stokes shifts. However, the analysis of the strongest transition for each compound might shed light on their PL spectra.

In the case of compound 4, the strongest transition $(S_0 \rightarrow S_3)$ corresponds principally to HOMO \rightarrow LUMO + 2 electronic transition (orbital pictograms shown in Fig. 4i and j). One can observe that during the $S_0 \rightarrow S_3$ transition some charge amount is transferred from the external phenyl groups of the TPA moieties toward the central part of the molecule (containing principally two phenyl rings bridged by the cyclohexylidene unit). It can be assumed consequently that the relaxation of this excited state involves important geometrical reorganizations in all the molecular backbone, giving rise to considerable Stokes shifts. The same effect should be produced for the other compounds when considering the same ground-to-excited state transition.

In order to get some insight on the differences between 1 and 4 we focus on the role of the methoxy groups. The HOMO orbital of compound 4 contains non-negligible anti-bonding contributions from the C(Ph)–O bonds (Fig. 4i) which are considerably reduced in the LUMO + 2 orbital (Fig. 4j). These contributions are absent in the case of compound 1 but also in the case of metasubstituted compound 3 (Fig. 4e). It can be then expected that during this electronic transition the C-O bonds will be much more affected by geometrical relaxations in the case of compound 4 than in compound 3 (and 1) which might be one of the reasons for the strongest Stokes shift observed for parasubstituted compound 4. This effect should be less pronounced for compound 2 due to the reduced contribution of the orthomethoxy groups in the HOMO orbital as compared to 4 suggesting consequently smaller relaxations upon excitation (Fig. 4c and d).

The same observations could be done for the transitions of lower oscillator strength ($S_0 \rightarrow S_7$ and $S_0 \rightarrow S_8$ for compound 4, Table S2†) which involve HOMO-1, HOMO, LUMO + 3, LUMO + 4, and LUMO + 5 orbitals (Fig. S3†) suggesting consequently that the contribution of the C–O bonds in the Stokes shifts works in the same sense for all the relevant transitions.

Admittedly, this analysis is not complete but points to one possible effect of the methoxy groups on the increasing Stokes shifts in the order 3 < 2 < 4. The smaller Stokes shift for 3 as compared to 1 seems to ask for more quantitative analysis and is out of the scope of this work.

3.5 Ionization potentials

The ionization potentials (I_p) of the solid amorphous samples of the materials are established from their electron photoemission spectra which are presented in Fig. 5. I_p values are summarized in Table 3. The introduction of OCH₃ groups leads to the decrease of I_p : methoxy-substituted compounds **2–4** show lower I_p than compound **1**. The I_p values also depend on the position of OCH₃ groups. The lowest I_p is observed for *para*-substituted compound **4**. Ortho-Substituted derivative **2** shows slightly higher I_p while *meta*-substituted compound **3** shows the highest I_p among methoxy-substituted derivatives.



Fig. 4 Pictograms of some relevant molecular orbitals involved in the strongest electronic transition for compounds **1–4**. Atoms in red, grey, blue, and white colors are oxygen, carbon, nitrogen, and hydrogen respectively. The encircled parts highlight the contribution of the C(Ph)–O(CH₃) bonds.

The theoretical vertical I_p values are presented in Table 3 and show the same trend as the experimental values. The differences between the theoretical and experimental values are in part due to the lack of the medium effects in calculations but also to the limited level of calculations employed.

The influence of the methoxy groups on the I_p values can be understood in the frame of the Koopmans' theorem relating for instance the I_p value to the energy of the HOMO orbital. The contribution of the methoxy groups to the HOMO energy of compounds 2-4 is principally related to the π -conjugation of the oxygen p orbitals (π -donor effect) with the HOMO of

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Fig. 5 Electron photoemission spectra of the solid samples of 1-4.

compound 1 (Fig. 4c, e, and i): the anti-bonding $\pi(OCH_3)-\pi$ (Ph) interaction increases the HOMO energy of compounds 2, 3 and 4 as compared to compound 1 which, according to Koopmans' theorem, corresponds to decreasing $I_{\rm p}$ values in the same order.46

This effect is more important for compounds 2 and 4 as compared to compound 3. This can be seen when comparing Fig. 4e and i; the contribution of the oxygen p orbital is much more important in the case of the para-substituted compound than for the meta-substituted compound (Fig. 4i and e). The case of *ortho*-substituted compound 2 is intermediate, probably due to the reduced contribution in the HOMO orbital from the ortho-substituted Ph rings (Fig. 4c). The increase of the HOMO levels and the decrease of the I_p values should be consequently more important for the para-substituted compound (and less important for the ortho one) than for the meta-substituted compound where the inductive effect remains dominant.

We finally remember that in some applications, such as dye sensitized solar cells, hole-transporting materials with low ionization potentials are required. The HOMO energies for compounds 1-4 increase in the order 1 < 3 < 2 < 4suggesting that based only on this factor, the efficiencies of devices using these materials should also increase in the order $1 < 3 < 2 < 4^{47}$

Table 3 Electronic and hole-transport parameters for compounds 1-4

3.6 Charge mobility

The solid amorphous layers of compounds 2-4 used for charge mobility measurements were homogeneous, transparent and stable. The morphological stability of the glassy layer of 1 was not sufficient due to its crystallization therefore its molecular mixture with inert polymer bisphenol-Z polycarbonate (PC-Z) (mass ratio of 1:1) was used for the time-of-flight measurements. In order to estimate the influence of OCH₃ groups on charge-transporting properties the layers of molecular mixtures of compounds 2-4 with PC-Z were also prepared and studied. Fig. 6 shows electric field dependence on hole mobilities for amorphous layers of 2-4 and molecular mixtures of 1-4 with PC-Z. The dependence of the square root of the applied electric field over the logarithm of mobility was found to be linear as expected for amorphous organic charge-transporting materials.⁴

The comparison of hole drift mobilities of PC-Z molecularly doped with the different derivatives of 1,1-bis(4-aminophenyl) cyclohexane 1-4 shows that methoxy-substituted derivatives 2-4 exhibit superior charge-transporting properties relative to those of non-substituted derivative 1. The best charge-transporting properties among methoxy-substituted derivatives (2-4) were observed for para-substituted compound 4. Hole mobility in the



Fig. 6 Electric field dependencies on hole mobilities for amorphous layers of 2-4 and for molecular mixtures of 1-4 with bisphenol-Z polycarbonate (PC-Z).

Compound	$I_{\rm p}{}^a$ /eV	$E_{\rm HOMO}^{b}/{\rm eV}$	λ_i^c/eV	<i>t^d</i> /meV	$k_{\rm HT}^{e}/10^{11}~{ m s}^{-1}$	$\mu_{\rm HT}^{f}/10^{-3}$ cm ² V ⁻¹ s ⁻¹
1	5.86, 5.64	-5.14	0.130	64	19	78
2	5.58, 5.43	-4.85	0.228	42 (13)	3 (0.3)	19 (2.0)
3	5.76, 5.55	-5.09	0.141	62 (10)	15 (0.4)	99 (2.5)
4	5.44, <i>5.34</i>	-4.78	0.142	40 (18)	6.4 (1.3)	41 (8.3)

^a Vertical ionization potentials calculated at the B3LYP/6-31G** level. The experimental ionization potentials are presented in italics. ^b Energies of the HOMO orbitals obtained at the B3LYP/6-31+G* level. ^c Intramolecular reorganization energy (λ_i) values for 1-4. ^d Examples of electronic couplings (absolute values) between the HOMO orbitals in model dimers 1c-4c (in parentheses values for 2b-4b) (Fig. 7) calculated at the ω B97X-D/6-31G** level. Hole-transport rate constants (at zero electric field) calculated from the Marcus–Levich–Jortner equation. Constant values of $\lambda_s = 0.3$ eV and $\Delta G^\circ =$ 0 are considered for all the compounds. ^f Hole mobility estimations calculated on the frame of a perfectly symmetric one dimensional model as described in ref. 12. A fixed distance of 4.5 Å between the monomers is considered in the case of 1 and 5.5 Å for 2-4. The value of the electric field used in these calculations is 10⁶ V cm⁻¹. In parentheses are reported the $k_{\rm HT}$ and $\mu_{\rm HT}$ values corresponding to t values shown in parentheses.

amorphous layer of **4** reaches 1.2×10^{-3} cm² V⁻¹ s⁻¹ at the electric field of 10^6 V cm⁻¹ (Table 4). *Ortho*-Substituted derivative **2** shows only slightly inferior charge-transporting properties, while the *meta*-substituted compound shows the lowest hole mobility among methoxy-substituted derivatives.

In order to understand the effect of the methoxy groups on the hole mobilities different factors could be evocated. In the following we focus only on some molecular parameters influencing the hole mobility in the amorphous bulk materials. These aspects will be discussed in terms of hole-transfer rate-constants (eqn (1)) and two parameters entering it, intramolecular reorganization energy (λ_i) and electronic coupling (*t*). Estimated mobilities, based on our $k_{\rm HT}$ values and a simple one dimensional model,¹² will also be presented. Other effects like morphological differences in the amorphous film, defects, and charge-traps are out of the scope of this work.

3.6.1 Intramolecular reorganization energies. The λ_i values for compounds 1-4 are presented in Table 3 and are found to increase in the order $1 < 3 \approx 4 < 2$. In order to get some insight on this trend we firstly compared the λ_i values of 1 (0.13 eV) and TPA (0.11 eV).⁴² The slightly larger λ_i value for 1 seems to be in disagreement with the idea that the larger space extension of the π system in 1 should correspond to reduced reorganization energy. One possible factor explaining this discrepancy may be due to the presence of the cyclohexylidene bridge in 1, as suggested by the greater λ_i value of TPA-CH₃⁶ (0.126 eV as compared to 0.11 eV for TPA). Replacing one H atom in TPA-CH₃ with a second TPA results in a model compound (TPA-CH₂-TPA) for which, in agreement with the common ideas, we found a smaller λ_i value (0.098 eV) as compared to TPA. However, going from TPA-CH₂-TPA to 1 (replacing the CH₂ bridge by the cyclohexylidene one) results in increased λ_i from 0.098 to 0.13 eV. This should be mainly due to the difference in the through-space interaction between the two TPA moieties in 1 and TPA-CH2-TPA. Indeed, the TPA...TPA interaction should be non-negligible as suggested by the shortest TPA…TPA distances (2.49 Å and 2.56 Å for 1 and TPA-CH2-TPA respectively). This assumption is also supported by the non-negligible splitting between HOMO-1 and HOMO orbitals (0.156 eV and 0.100 eV for 1 and TPA-CH2-TPA respectively), these last orbitals corresponding to the bonding and anti-bonding combinations of the local HOMO (TPA) orbitals (Fig. S3, ESI[†]). In the case of TPA-CH2-TPA model compound, this interaction is thus weaker as compared to 1 and the change in the TPA…TPA distance upon oxidation is also smaller (-0.035 A for TPA-CH₂-TPA as compared to -0.044 Å for 1), which can explain the smaller influence (smaller sensitivity upon oxidation) of this interaction on the λ_i value of TPA–CH₂–TPA.⁴⁸

As for the trend of the λ_i values for 1–4, multiple factors may be involved and clear explanation cannot be given. In the following only three factors will be considered: (i) the factor discussed above can influence the relative λ_i values for 1–4. The HOMO-HOMO-1 splitting (Table S1[†]) is the greatest for 2 (0.230 eV) and the smallest for 4 (0.140 eV). The change in the TPA…TPA distance upon oxidation also follows the same trend $(-0.074 \text{ Å and } -0.030 \text{ Å for } 2 \text{ and } 4 \text{ respectively. Fig. S1}^{\dagger})$ suggesting consequently stronger influence of this factor in the case of compound 2. (ii) The change in the Ph-"N-plane" dihedral angles upon oxidation is the largest for $2 (36^{\circ})$ and the smallest for 4 (10.5°). The change in the N–C bond-lengths, for instance, is consequently the most important for 2 (-0.046 Å) and the smallest for 4 (-0.015 Å), with the greatest contribution coming in each case from the N-C bond with the internal (nonsubstituted) phenyl ring (Fig. S1, ESI[†]). In the case of 1 and 3 this parameter exhibits intermediate values (-0.025 Å and -0.023 Å respectively). (iii) The anti-bonding contributions of the C(Ph)-O bonds in the HOMO orbitals are reduced upon oxidation. These contributions are absent in the case of 1, they are negligible in the case of 3 (negligible contribution from oxygen atoms in the HOMO, Fig. 4e), but are the strongest ones for 4 (Fig. 4i). The changes in the C-O bond-lengths upon oxidation seem to support this idea: the C-O bonds are shortened more importantly in the case of 4 (-0.015 Å) than for 3 (-0.011 Å). As for compound 2, smaller changes in the C-O bond lengths are found (-0.003 Å) probably due to the important O···Ph hindrance (Fig. S1[†]).

All these factors are expected to contribute to the increasing reorganization energy. The great importance of the first two factors for **2** gives a possible explanation for the largest λ_i value for this compound, whereas the smaller and roughly similar influence of these factors for **1**, **3**, and **4** could explain the corresponding smaller and similar λ_i values.

It is worth noting that the factors discussed above are considered as acting independently, thus ignoring the possible couplings between them and also with other factors not considered here. However, we remember that the aim of the above qualitative analysis is simply to identify some of the factors influencing the λ_i values.

We now turn to the correlation of the λ_i values with the experimental results. In view of eqn (1) and considering fixed identical values for the parameters t and λ_s , it can be expected that the k_{HT} values decrease in the order $1 > 3 \approx 4 > 2$, which is different from the experimental trend 4 > 2 > 3 > 1 of the mobility values (note that somewhat speculative parallel is made here between k_{HT} and the mobility values). This result also seems to be different from previous studies⁴³ having found that in a family of similar TPA compounds the hole mobilities follow the

Table 4 Hole mobility values in amorphous layers of 1-4. Magnitudes in parentheses are of mixtures with PC-Z (mass ratio 1:1)

Sample	Layer thickness/µm	$\mu_0/cm^2 V^{-1} s^{-1}$	$\mu/cm^2 V^{-1} s^{-1} at 10^6 V cm^{-1}$
1	(5.0)	(4.9×10^{-9})	$(2.0 imes 10^{-6})$
2	2.0 (5.6)	$6.5 \times 10^{-5} (7.8 \times 10^{-6})$	8.2×10^{-4}
3	2.8 (8.0)	$5.0 \times 10^{-6} (2.6 \times 10^{-9})$	$4.0 imes 10^{-4} (1.0 imes 10^{-5})$
4	4.0 (5.4)	$3.6 \times 10^{-5} (7.7 \times 10^{-7})$	$1.2 \times 10^{-3} (2.4 \times 10^{-5})$

same trend as the λ_i values. It seems that the definition "family of similar compounds" is subtle and could not apply to our compounds 1–4.

3.6.2 Electronic couplings. In order to shed light on this disagreement we focus on the electronic coupling properties of 1– 4. In this respect, different dimers were optimized for three model compounds: (i) dimers of *ortho-*, *meta-* and *para-*methoxy substituted aniline, referred hereafter as 2a, 3a, and 4a (Fig. 7), (ii) dimers of the *ortho-*, *meta-* and *para-*methoxy substituted TPA referred hereafter as 2b, 3b, and 4b (containing one non-substituted phenyl ring, Fig. 7). In both model compounds the optimized geometries show short C–H… π (Ph) contacts between a methoxy group of one monomer and the π (Ph)-system of the second one. These C–H… π (Ph) interactions seem to be sufficiently strong for retaining the dimers bonded, as suggested by the non-negligible interaction energies found in the case of **2a–4a** (6–7 kcal mol⁻¹). Similar C–H… π interactions have been previously calculated theoretically or have been observed in crystal structures.^{49–53} (iii) In the absence of the methoxy groups (compound **1**), the interactions between the phenyl groups of two adjacent monomers should involve C(Ph)–H… π (Ph) short contacts. The optimized structure for one dimer of this type is shown in Fig. 7 (model compound **1c**) where short H…C contacts ranging between ~2.6 and 2.9 Å were found. Starting from this geometry and introducing methoxy groups in *ortho*-, *meta*- and *para*-positions, geometries equivalent to **1c** were also optimized (referred hereafter as **2c–4c**), where C–H…O, C–H… π (Ph), and C(Ph)–H… π (Ph) short contacts can be observed (Fig. 7).

The electronic couplings between the monomer-HOMOs for each dimer were subsequently calculated. In the case of the



Fig. 7 Optimized geometries for some model dimers: (2a–4a) *ortho-*, *meta-* and *para-*methoxy substituted aniline dimers respectively; (2b–4b) *ortho-*, *meta-* and *para-*methoxy substituted TPA dimers respectively; (1c) TPA model dimer; (3c and 4c) dimers of *meta-* and *para-*methoxy substituted TPA corresponding to equivalent geometries as compared to TPA dimer 1c (see text for details). Some relevant C–H··· π (Ph), C–H···O, and C–H···N short contacts ranging from 2.6–2.8 Å are highlighted (dashed lines in black, red, and blue colours respectively). The d_{N-N} corresponds to the distance between the N atoms.

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aniline model dimers (2a-4a, Fig. 7) electronic couplings of 0.108 eV, 0.001 eV, and 0.077 eV respectively were found, indicating for the *meta*-substituted isomer (3a) a value of ~ 1 to 2 orders of magnitude smaller than for the ortho- and para-isomers. The smaller coupling value for the meta-substituted compound can be understood by considering the geometries of these model dimers. Indeed, the short contacts highlighted in Fig. 7 for 3a and 4a suggest that the only possible overlap between the monomer-HOMOs in these geometries can be established between the π (Ph) part of one monomer and the oxygen p atomic orbital of the other monomer. The contribution in the HOMO orbital from the oxygen atoms in the *meta*-position is negligible (Fig. 4e), resulting in smaller overlap and electronic coupling, as compared to the non-negligible contribution from the oxygen atoms in the case of para- and (to a lesser extent) ortho-isomers (encircled parts in Fig. 4i and c).

In the case of the TPA-based model compounds 2b-4b, the electronic couplings shown in Table 3 (values in parentheses) vary in a much smaller range as compared to 2a-4a, probably due to the larger space extent of the HOMO orbitals but also to the additional steric hindrance between monomers. However, the general trend is the same as in the case of 2a-4a, with the smallest t value found for **3b** (0.01 eV) and the largest one for **4b** (0.018) eV). As for model dimers 1c-4c (Fig. 7), much stronger electronic couplings ranging from 0.04-0.06 eV are found as compared to 2a-4a and 2b-4b. The values are however similar between 1c and 4c, probably due to the principal role of the TPA core in these dimer geometries. It is interesting to point out that the strongest couplings are calculated for non-substituted compound 1c, which seems to agree with previous observations.7 However, while this order might be reversed in the frame of a thorough study, the significant result is that the couplings for 1c-4c are of similar values.

It is worth noting that compounds 1-4 in the radical cationic state should exhibit mixed valence (MV) character. The intramolecular electronic couplings between the two TPA moieties, estimated as half of the energy difference between HOMO and HOMO-1 orbitals in the neutral species, range between 0.07 and 0.12 eV, thus being stronger than the intermolecular electronic couplings shown in Table 3. In these conditions we assume that among the intra- and intermolecular hole-transfer steps the ratelimiting one is the intermolecular step.⁵⁴

3.6.3 Hole-transfer rate constants. The intermolecular holetransfer rate constants ($k_{\rm HT}$, Table 3) have been calculated in the frame of Marcus–Levich–Jortner equation⁵⁵ by using the λ_i values for 1–4 and the electronic coupling values for 2b–4b and 1c–4c⁵⁶ (see ESI† for more details). Hole-mobility values estimated on the frame of a perfectly symmetric one dimensional model¹² are also presented in Table 3. As expected, higher mobility values are calculated as compared to the experimental ones, which is due to the limited and idealized frame of the model applied in this study. However, the significant result is that similar $k_{\rm HT}$ (and $\mu_{\rm HT}$) values are found for 2–4, differing in each case (2b–4b or 2c–4c) by less than one order of magnitude, which seems to correspond to the experimental results.

It is worth noting that the comparison of the experimental mobilities between 1 on the one hand and 2-4 on the other hand concerns only mixtures 1:1 with PC-Z, implying "dilute"

spacing between monomers. While model dimers **2b–4b** may correspond to this type of molecular packing, the geometries of **1c–4c** mostly correspond to a compact packing (Fig. 7). Indeed, the distance between the monomer centers in **1c–4c** is found to range between ~ 5 and 6 Å as compared to ~ 7 and 8 Å for **2b–4b**. It can be then assumed that in the case of "dilute" films for compound **1**, dimer geometries similar to **1c** cannot be established or should involve large mean distance, which suggests very small electronic couplings. On the contrary, despite the larger center-to-center mean distances, dimer geometries similar to **2b– 4b** (Fig. 7) should still be established between the methoxysubstituted compounds, giving consequently a possible explanation for the higher hole mobility values of **2–4** in "dilute" films as compared to **1**.

As for the films of pure compounds, one can reasonably assume that the packing mode between adjacent molecules in the amorphous materials cannot be entirely compact. The hole-path could then be figured out as an alternation of compact (similar to **2c-4c**) and dilute (similar to **2b-4b**) packed dimers. In this case we assume that the trend of the mobility values will be dominated by the dilute packed dimers, which suggests small spread of the mobility values with the best one expected for compound **4** (Table 3, values in parentheses).

Admittedly, only a small number of model dimers taken at idealized static geometries were considered and film morphology and other factors were ignored in this analysis, meaning that direct comparison between the calculated $k_{\rm HT}$ (and $\mu_{\rm HT}$) and the experimental mobilities cannot be proposed. However, these results point to the special role of the methoxy groups at the microscopic level, giving possible explanations on: (i) why methoxy substituted compounds **2**, **3**, and **4** show higher $k_{\rm HT}$ values in mixtures with PC-*Z* as compared to the non-substituted one; (ii) why the *para*-substituted compound shows the highest $k_{\rm HT}$ value and (iii) why the *meta*-substituted compound in "dilute" film shows lower $k_{\rm HT}$ value than the *para*-isomer.

Conclusions

In this work we have synthesized three new isomeric 1,1-bis(4aminophenyl)cyclohexane based triphenylamine containing methoxy groups in different positions and have studied their thermal, optical, photophysical and photoelectrical properties. Methoxy-substituted derivatives of 1,1-bis(4-(*N*,*N*-diphenyl) aminophenyl)cyclohexane show lower ionization potentials and higher hole drift mobilities than the compound containing no OCH₃ groups. Among methoxy-substituted derivatives the *para*substituted compound shows the lowest ionization potential (5.34 eV) and the highest hole mobility which reaches 1.2×10^{-3} cm² V⁻¹ s⁻¹ at the electric field of 10^6 V cm⁻¹.

The theoretical analysis is based on the influence of two factors: (i) the comparison of hole-transfer rate constants in the amorphous bulk material by considering the simultaneous influence of two electronic parameters, the intramolecular reorganization energy and the electronic coupling. Our results suggest that the trend of the $k_{\rm HT}$ values is dominated by the electronic coupling parameter whilst the use of λ_i values separately suggests in our case the wrong mobility trend. (ii) The comparison of the HOMO level energies, which are strongly

related to the efficiency of the film-electrode contacts in the DSSCs devices.

Both factors (electronic couplings and HOMO energies) work in concert, suggesting enhanced performances of the methoxysubstituted compounds with the highest one found for the methoxy-*para*-substituted compound.

In the frame of this study, the role of the methoxy groups is found to be related to two principal properties: the well-known mesomeric (π -donor) effect and the possibility to establish C-H··· π (Ph) and C-H···X (X = O, N) hydrogen bonds. The effects of these properties are multiple: (i) destabilize the HOMO orbital and decrease the I_p values of 2, 3, and 4 with respect to 1. (ii) Introduce anti-bonding interactions in the HOMO of para- and (to a lesser extent) ortho-substituted compounds which are reduced in the excited states. Due to this effect, the para- (and ortho-) substituted compounds undergo supplementary geometry-relaxation effects after photon absorption, suggesting one possible contribution to the increased Stokes shifts. The same effect is found to contribute to the increase of the intramolecular reorganization energies of para- (and ortho-) substituted compounds. (iii) In these amorphous materials, where compact and dilute packed contacts between monomers coexist, the methoxy groups introduce additional possibilities for establishing short contacts between adjacent molecules (at larger centerto-center distances as compared to the non-substituted compound) which seem to play a central role in the case of dilute packing. In this frame, the electronic couplings and $k_{\rm HT}$ for the methoxy-substituted compounds are enhanced as compared to the non-substituted one.

Finally, the absorption bands of these compounds are situated in the UV domain and the thermal properties are satisfying which makes them good candidates for DSSC applications.

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- 46 The effect of the *para*-methoxy substitutions on the Ph–"N–plane" dihedral angles and on the Ph–N–Ph π -conjugation should be cancelled out due to the opposite signs of these changes (see Section 3.3).
- 47 It is worth remembering that this explanation ignores the orbital level shift happening at the material–electrode interface. However, due to the structural similarity of these compounds no profound alteration of the above trend should be expected.
- 48 The contribution of the bridge in the relaxation energy should be negligible as suggested from the comparison between the λ_i values of TPA–CH₃ and TPA–C₆H₁₁ model compound (0.126 and 0.13 eV respectively, this work).
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- 54 The geometries of 1–4 are not symmetric and part of the energy difference between HOMO and HOMO-1 orbitals might be due to the mutual polarization between the two TPA moieties. However, the two geminal Ph rings in 1–4 are positioned almost

face-to-facebetween them and the role of the mutual polarization in the HOMO-HOMO-1 energy splitting should be small. Test calculations, where the two geminal groups are forced to be positioned as symmetrically between them as possible, result in practically the same HOMO-HOMO-1 energy splitting. Accordingly, we conclude that the intramolecular couplings in 1–4 are still more important than the intermolecular ones (see also the discussion in Section 3.6.3). For more details on the couplings in the M.V. compounds, see: V. Coropceanu, M. Malagoli, J. M. Andre and J. L. Bredas, *J. Am. Chem. Soc.*, 2002, **124**, 10519. 55 J. Jortner, *J. Chem. Phys.*, 1976, **64**, 4860.

56 Test calculations using the λ_i values of **2b–4b** (0.304 eV, 0.170 eV, and 0.271 eV respectively) do not modify the following discussion and conclusions. It is also assumed that adding the cyclohexylidene unit and the second TPA to model dimers **2b–4b** and **1c–4c** should not change the trends on the *t* values.