

A correlation between electrochemical properties and geometrical structure of some triarylamine used as hole transporting materials in organic electroluminescent devices

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Abstract

Two new compounds with four tertiary arylamine moieties connected in a fully *para*-conjugated system have been synthesised in order to obtain new molecules having low ionisation potentials, as required for hole transporting materials in Organic Light Emitting Diodes (OLEDs). Their electrochemical properties have been measured and compared to seven different commercial triarylamine tested in the same experimental conditions. Using the AM1 geometries and the statistical average of orbital potential method (SAOP), the redox potentials of the molecules have been estimated and found to be in good agreement with the experimental data. An evident correlation between the molecular geometry and the electrochemical potential of the first oxidation exists and shows that, for equal number of *para*-conjugated triarylamine moieties, the *starburst* configuration is more efficient than the linear one in lowering the oxidation potential and that the amine moieties of the inner sphere play a more important role than those of the outer sphere. Besides, amine moieties connected by a biphenyl bridge show generally higher ionisation potentials than those connected *via* one phenylene.

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I. INTRODUCTION

Since the discovery of electroluminescence in multilayer light emitting devices based on molecular organic compounds [1], triarylamine derivatives have been widely used as hole transporting material to be coupled with electron transporting and emitting materials. Much effort has been made to synthesise new molecules having high T_g and hence capability of forming amorphous and morphologically stable solids [2–4] in order to improve device durability [5–7]. Besides the morphological stability requirements, electronic aspects are key features for triarylamine as charge carrying materials. The energy barrier for hole injection from the anode, hole mobility inside the layer, good matching (or proper relation) of the electronic energy levels between the different active compounds in the device are other significant aspects to be considered in order to increase the overall device efficiency [8] or tune the emission wavelength of exciplex based organic light emitting diodes (OLEDs) [9–11]. Molecular engineering could be used to design molecules with suitable ionisation potentials, when a correlation between molecular structure and redox properties could be found. A route towards low oxidation potentials, as to match the indium tin oxide (ITO) work function, is the synthesis of complex molecular structures having many arylamine moieties connected through a *para*-conjugated system, as the *meta*-conjugation has been stated to be not so efficient [12, 13].

In the present work we have prepared two new compounds with four tertiary arylamine moieties connected in a fully *para*-conjugated system and have measured their electrochemical properties. We have also measured the electrochemical properties of seven different commercial triarylamine, which are used as hole transporting materials in OLEDs, in order to have a pretty large number of molecules with electrochemical parameters measured in exactly the same conditions. Besides, the redox potentials were compared with those calculated by a simple but rather accurate method, based on the vertical ionisation potential (VIP) obtained by the SAOP model potential [14] within the Density Functional Theory (DFT). The usage of the AM1 geometries allows a faster investigation of more complex triarylamine compounds with respect to those already considered in literature [15–17]. This will allow to understand the criteria useful to discriminate those triarylamine compounds, which among the others, show more promising characteristics for their application in electronic devices and can lead to a guideline to the synthesis of even more complex molecular

systems.

II. EXPERIMENTAL

In Fig. 1 are shown the molecular structures of the compounds we have considered. All of them are commercial ones except N,N'-diphenyl-N,N'-bis[N-phenyl-N-3-tolyl(4-aminophenyl)]benzidine (MDTAB) and N,N'-diphenyl-N,N'-bis[N-phenyl-N-3-tolyl(4-aminophenyl)]-1,4-phenylenediamine (MPTAB), which were synthesised by us by means of a two-step Ullmann reaction catalysed with activated copper bronze and purified by flash chromatography. Analytical characterisation of the synthesised compounds was performed by mass spectrometry.

The commercial materials have been used as supplied and their chemical purity was $\geq 99\%$. The voltammograms of the triphenylamines were carried out in dichloromethane (DM, Merck ACS product). DM was dehydrated with CaCl_2 for 12 hours, successively distilled in presence of P_2O_5 under argon flux and stored in dark under argon pressure. Tetrabutylammonium perchlorate (TBAP, Fluka AG "purum") was crystallised from methanol. The electrochemical measurements were carried out at 298 K under argon in a three electrode cell with an AMEL 5000 Multipurpose Apparatus. The reference was a saturated calomel electrode (SCE) separated from the cell by a bridge filled with the solution of the supporting electrolyte in the same solvent used in the electrolytic cell. All the potentials are referred to this electrode in this work. The counter electrode was a platinum wire. The working electrode was a platinum minidisc (0.003 cm^2). The geometry of the cell was accurately kept constant in all measurements and the concentration of triphenylamines was $1 \times 10^{-3} \text{ M}$, corresponding to peak currents of about $6\text{-}12 \mu\text{A}$. This accuracy was directed to minimise the difference in ohmic drop which affected the voltammetric curves of the compounds investigated.

III. THEORETICAL BACKGROUND

A long standing debate [18-21] about the reliability of molecular orbital energies evaluated using DFT in estimating the VIPs, was introduced by Perdew *et al.* [18]. Within this discussion about the physical interpretation of the Kohn-Sham (KS) [22] orbitals and ener-

gies it was established that the energy (ϵ_H) of the highest occupied KS orbital has a physical meaning and can be directly related to the lowest vertical ionisation potential (VIP), namely $\epsilon_H = -I_H$ [23-27]. Moreover, it was shown that the KS orbital energies, calculated using different approximations, exhibit a large but fairly uniform shift with respect to the experimental ionisation energies [28, 29]. It was pointed out that the difficulties in reproducing exactly these energies arises from the fact that the exchange-correlation (xc) potential should have the correct asymptotic behaviour of the exact KS potential to accurately estimate the needed downward shift for the calculated eigenvalues. The Δ_{xc} correction terms for an average ϵ_H obtained by GGA functionals, which improve the agreement with the experimental VIPs, were calculated for a wide set of small molecules[30]:

Recently, Chong *et al.* [31] have shown how the $-\epsilon_k$ of the occupied KS orbitals give a rather accurate approximation to the *referred* VIP I_k by using the asymptotically correct xc potential calculated with the statistical average of orbital potentials (SAOP). They compared their calculated VIPs of a meaningful set of atoms and small molecules with the experimental data obtained by molecular photoelectron spectroscopy. Moreover, an analogue of the Koopmans' theorem based on the exact relation between the energy (ϵ_H) of the highest occupied orbital (HOMO) and VIPs was demonstrated for the exact KS orbital energies [31, 32]. More recently, Gritsenko *et al.* [33] provided a further insight into the accuracy of this approximation, pointing out the possible difficulties in reproducing accurately the VIPs in case of systems characterised by a strong correlation in the ground state or in the ionised state.

The DFT calculations of the VIPs were performed using the Amsterdam Density Functional package (ADF2003.01 [34-36]), which uses Slater Type Orbitals (STOs). A good quality basis set with respect to the number of atoms present in the examined molecules, namely the valence double zeta polarised basis set (DZP) was used with the SAOP model. The effect of using even larger basis sets will also be discussed.

IV. RESULTS AND DISCUSSION

A. Electrochemical results

The voltammetric behaviour of the triphenylamine derivatives has been extensively investigated due to their importance as hole carriers in OLEDs preparation [6, 37–40]. These compounds often oxidise through reversible processes in cyclic voltammetry. It is known that when there are triphenylamine groups in a molecule and the redox centres interact, the relative oxidation peaks occur at different potentials, while in case of weak or negligible interactions the peaks overlap [37]. The same effect was described for the reduction of dicarboxylic diimide groups separated by an increasing number of perylene moieties [41]. Therefore, a relation linking the separation of the peaks with the interaction between the redox centres, which are mainly located at the nitrogen atoms, can be expected.

As examples of our measurements, in Fig. 2 are compared the cyclic voltammetries of MTDATA and TAPC measured up to 1.0 V, and in Fig. 3 is reported that of MPATAB measured up to 1.6 V. Fig. 2a shows the case when the first two peaks are well separated (about 250 mV), as those reported in Fig. 3, indicating two distinct redox processes due to the interacting redox sites, namely the N atoms connected by electron conjugation and successively involved in oxidative processes. The third and fourth peaks, which are very close and partially overlap, possibly involve the terminal nitrogen atoms, which are equivalent and separated by an oxidised moiety. In Fig. 2b too the peaks overlap, indicating that the N atoms are not, or they are scarcely connected by conjugation.

In Table I are reported the ratio I_{pc}/I_{pa} , where (I_{pc}) and (I_{pa}) are the peak current of the reverse and the forward peaks of the first oxidation process, respectively; the difference ΔE_p between the oxidation (E_{pa}) and the back-reduction (E_{pc}) potentials, and the E_{redox} potential, which is calculated as $E_{pa} - (E_{pa} - E_{pc})/2$. The data refer to the first oxidation process and to voltammetries performed at 20 $\text{mV}\cdot\text{s}^{-1}$. Under the last column is reported the comparable calculated energy $E_{calc.}$ obtained by subtracting to the calculated $-eH$ the value of 7.83, whose derivation will be discussed in the next Section. Since the peaks of MDTAB and TAPC overlap and cannot be measured with sufficient accuracy, though their oxidation processes are reversible, their I_{pc}/I_{pa} values are not reported. For all of the other examined compounds but TPA, the I_{pc}/I_{pa} value was ≈ 1 , revealing that successive chemical reactions

of the radical cation did not affect the voltammetric peaks. Therefore, the kinetics of the first oxidation process depends on the rate of the heterogeneous electron transfer and the peak current (I_p), in voltammetric conditions, depends on the diffusion of the electroactive species near the electrode. When the E_p values were not completely separated by the successive ones, they were taken on the flex connecting the two peaks (see Fig. 2b). Moreover, it should be pointed out that both I_{pa} and I_{pc} , at the investigated scan rates (v), linearly depend on $v^{1/2}$, which is a typical trend of diffusion controlled processes (inset in Fig. 2a). Hence, it can be inferred that ΔE_p mainly depends on the rate of the heterogeneous electron transfer, thought it can be slightly affected by the ohmic drop between the working and the reference electrodes. The "reversible" value of ΔE_p is expected to be $60/n$ (mV), where n is the number of exchanged electrons, but it can increase by decreasing the rate of the heterogeneous electron transfer and by increasing the ohmic drop. In every case, it was observed that the values of E_{redox} for the first oxidation processes, do not meaningfully change with v , and can be handled as thermodynamic parameters in the reaction medium.

Some considerations may be drawn about the variations of E_{redox} with the molecular structure (see Fig. 1). As already mentioned, the presence of a non-aromatic ring in TAPC heavily breaks the communication between the two arylamine moieties, which are comparable with TTA. The different substituents on the arylamine moieties only slightly affect their redox behaviour, as reported also by others [6] except for TTA where the three *para*-methyl substituents produces a 0.48 V decrease of its redox potential with respect to TPA, according to their Hammett parameter [40]. It should be pointed out that, when the nitrogen atoms of two amine moieties are connected through a biphenyl group, such as in TPD, NBDB, and NPB, the oxidation potential is decreased by only about 50 mV, while an average lowering of 240 mV is observed if the two N atoms are connected by a phenyl group [6]. The biphenyl effect is confirmed also by the higher oxidation potential of MDTAB with respect to MPATAB. As to the four-moiety amines, MPATAB, MDTAB and MTDATA, a strong dependence of the oxidation potential on the overall molecular structure is evident. The structure effect can be rationalised if we assume a strong stabilising action of amine groups surrounding the nitrogen atom carrying the positive charge (the redox centre) in the radical cation, only if connected by a single *para*-conjugated phenyl. We can envisage a first conjugation sphere of the positive charged nitrogen which can accept up to three amine moieties, each contributing to stabilise the radical cation, and hence to lower the redox potential. A second, outer, con-

jugation sphere can accept as much as six amine moieties connected by the same one-phenyl para-conjugated nitrogen atoms in a way similar to a dendrimeric structure. In Fig. 4 the redox potentials are reported vs the number of the amine moieties in the first sphere. In this picture TPD, TTA, TAPC, NBDB and NPB have no amine moieties in the first sphere, and in fact exhibit similar and high redox potentials. The lowest E_{redox} is obtained in the starburst structure where the central nitrogen atom is surrounded by three amine moieties and the first sphere is completed. The decreasing trend of the stabilising effect due to step by step filling of the conjugation sphere supports the idea that adding amine moieties in the second sphere would not provide much lower oxidation potentials.

Data by Strohrriegel *et al.* [39] for linear *para*-conjugated triphenylamines [the dimer (N,N,N',N'-tetraphenyl-1,4-phenylenediamine), the trimer (4,4'-di(phenylamino)triphenylamine) and the tetramer (MPTAB)] show that, while a 150 mV difference in E_{redox} is reported between the dimer and the trimer, the tetramer's E_{redox} is only 30 mV lower with respect to the trimer. Amine moieties in the second sphere only give a smaller stabilisation effect. The complete filling of the second sphere in a dendrimeric structure with 10 amine moieties, in fact, decreases E_{redox} of only 120 mV [42]. Besides its energy barrier at the hole injection anode interface, strictly related to the ionisation potential, the properties of a material as a hole carrier in OLEDs are determined by the kinetics of the self electron transfer in the bulk of the layer. This property will be investigated for the examined compounds in a further work.

B. Results of calculations

The most stable conformers of the TPA compounds were calculated, discriminating among the many possibilities allowed for each molecule by means of the AM1 semi-empirical method [43], which is known to give bond lengths and bending angles in satisfactory agreement for a large number of organic molecules. The optimized geometries of the investigated molecules are included as Electronic Supplementary Information.

The comparison among the bond lengths and angles calculated using the AM1 method with those reported in literature, obtained using the DFT B3LYP/6-31G** [16] and B3LYP/6-31G* [17] methods, evidences that the main discrepancies are observed for the torsional angles. In fact, limiting the comparison to those of the two building fragments of

the molecules under investigation, namely TPA and biphenyl, they turn out to be 34.7 and 28.6 with respect to 41.0 and 38.4 *degrees* [17], respectively. It should be pointed out that the 6-31G** basis set, which differs from the 6-31G* basis set only by the inclusion of the *p* orbital on the H atoms, calculates larger biphenyl torsions, namely 42.0 vs. 38.4 *degrees*. The same tendency to underestimate the torsional angles by the AM1 with respect to B3LYP is also observed by comparing with the other molecules reported in literature [16, 17], such as TPD [16, 17] and NPB [17], for all of the angles but those of biphenyl, which result overestimated by 3.8 and 2.8 *degrees*, respectively. An accurate calculation of the geometries of the neutral molecule and of the cation is crucial to calculate accurate IPs, though still expensive for large molecules, in cases when the relaxation phenomena play an important role. This has to be expected especially for those molecules containing the biphenyl fragment, which show a variation of 16.2 *degrees* in TPD in going from the neutral molecule to the radical cation [16]. The actual variation of the TPA torsional angle is expected to be much smaller and is calculated to be only 2.8 *degrees* by DFT [16]. Moreover, it should be pointed out that all the calculations discussed above refer to the isolated molecule model and should be compared with the data collected by gas phase experiments. In our case the comparison is with the data obtained by molecules in solution and it is known that the molecules in liquid phase are more planar than those in gas phase. Furthermore, we compare the calculated VIPs to the E_{redox} potentials focusing on the trend presented by the ensemble of the examined molecules.

Besides, preliminary tests performed on the basis set comparing the results obtained using SAOP with the DZP, TZP, and TZ2P basis sets indicated that in passing from the DZP to the TPZ basis set the calculated VIP is systematically lowered by 0.44-0.46 eV for the considered molecules, while a calculation performed on TPA showed that the VIP increases by only 0.05 eV in going from TZP to TZ2P basis set. Therefore, we can conclude that the SAOP model with the DZP basis set is already accurate enough to examine the trend followed by the calculated VIP of these molecules, though a comparison with the experimental data reported in literature (see Ref. [16, 17] and references therein) indicates that they are overestimated with respect to the IP measurements of TPA, TTA and TPD performed using different techniques. For the last molecule it should be noticed that the data of TPD reported for comparison in Table 10 of Ref. [17], actually refer to naphthalene.

In Fig. 5 are plotted the calculated VIPs of the considered molecules vs. the E_{redox} values

reported in Table I. The plotted $y = ax + b$ line is obtained by a linear least-squares fitting, where $a = 1.00$ ($\sigma_a = 0.07$), $b = 7.83$ ($\sigma_b = 0.03$), and $r = 0.93$. It should be pointed out the excellent agreement obtained in reproducing the trend of the measured ionisation potential, indicated by the slope coefficient value, particularly by TPA, TPD, MDTAB, MPTAB, and MTDATA. Under the E_{red} column of Table I were reported, for comparison with the experimental data, the ϵ_H energies calculated by the SAOP model, lowered by the b factor obtained by the least-squares fitting. The larger deviations from the fitted line are shown by TTA and TAPC, whose calculated VIPs are lower than the experimental ones, due to the overestimate of the stabilisation effect by the *para*-methyl substituents, and by NPB and NBDB, whose calculated VIPs result overestimated. A large part of the error, which affects the calculated VIP of these last two molecules, can be attributed to an overestimate of the biphenyl torsional angle by the isolated molecule model approximation. In fact, by forcing this torsional angle to planarity, one obtains a lowering of the calculated VIPs by 0.07 and 0.06 eV, respectively, significantly improving the agreement with the experimental data.

We can group the results of the plotted data into two subsets, i.e. those having an E_{red} up to 0.54 eV and those having an E_{red} over 0.75 eV. It turns out that the former group belong molecules with $N = 4$ with highly conjugated frames, confirming the idea that the interaction between the nitrogen lone pairs plays a major role in the stabilisation of the HOMO energy. The *starburst* structure of MTDATA, with a central nitrogen atom surrounded by three triphenylamines in a symmetrical way, favours these interactions, as the central phenyl unit of MPTAB, though to a lesser extent. The structure of MDTAB appears as a compromise between the good number of nitrogens and the presence of the biphenyl central unit. This latter has been indicated as a shortcoming for hole transport devices, as it implies a large reorganisation energy along the torsional angle between the two central phenyl groups [15]. In fact, all of the compounds presenting a relatively higher ionisation potential are characterised by the presence of the biphenyl central unit (TPD, NPB, NBDB, and MDTAB), while in TAPC the conjugation between the two moieties is interrupted by the presence of a saturated cyclic hydrocarbon. Moreover, the planar situation dictated by the central nitrogen atom has been indicated as a possible guideline in the building of these compounds [15]. Another factor to be considered is the stabilisation of the HOMO due to the methylation, which decreases the value of the VIP, especially in case of *para* substitution.

This effect is particularly evident in going from TPA to TTA, with a calculated decrease of 0.35 eV, overestimated with respect to that measured of 0.22 eV. Calculations on TPD, which has the methyls in *meta* position, show that in this case this stabilising effect amounts to only 0.07 eV.

The comparison with the experimental data suggests that the method adopted is accurate and fast enough to afford the study of the E_{red} of even larger TPA based compounds.

V. CONCLUSIONS

The electrochemistry of a series of TPA based molecules was examined and their oxidation potentials were correlated to their structural parameters.

The calculated VIPs by mean of the SAOP model (Amsterdam Density Functional package) based on molecular geometries obtained by the AMI method, result overestimated with respect to those already present in literature. Though, they show a good relationship with the experimental redox potentials, indicating that the proposed method can be safely used to investigate the electrochemistry of TPA based molecules.

From these results one can conclude that the guidelines to be taken into account when designing molecular structures with low ionisation potentials are: *i*) the *starburst* structure is more effective in lowering E_{red} with respect to the linear (or polymeric) one and, to this aim, the amine moieties of the inner sphere play a more important role than those of the outer sphere, *ii*) amine moieties connected by a biphenyl bridge show generally higher ionisation potentials. This feature, along with the energy necessary to reorganise the molecule in the cation geometry, renders this class of molecules less interesting as hole carriers in electronic devices.

VI. ACKNOWLEDGMENT

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TABLE I: Ratio I_{pc}/I_{pa} between the peak current of the reverse and forward oxidation processes along with the energy difference ΔE_p (eV) between the oxidation and the back-reduction potentials for voltammtries performed at 20 mV s^{-1} . The E_{redox} (V) is compared with the estimated redox energy E_{calc} . (eV).

Compound	I_{pc}/I_{pa}	ΔE_p	E_{redox}	E_{calc}
MTADATA	1.00	90	0.36	0.37
MPTAB	0.96	76	0.43	0.41
MDTAB	-	80	0.54	0.53
TTA	1.10	100	0.82	0.71
TAPC	-	100	0.81	0.68
TPD	0.98	100	0.75	0.78
NPB	0.84	90	0.77	0.90
NBDB	0.97	60	0.76	0.86
TPA	0.70	-	1.04	1.06

Fig. 1 Scheme of the molecular structures of the compounds studied.

Fig. 2 Cyclic voltammtries of MTADATA (a) and TAPC (b). The reference electrode is SCE. Inset: anodic peak current for the first oxidation process as a function of the square root of the scan rate.

Fig. 3 Cyclic voltammtry of MPTAB. The reference electrode is SCE.

Fig. 4 Redox potentials in Volt (first oxidation peak) vs. number of amine moieties sharing the positive charge in the cation radical. The line is a guide to the eye.

Fig. 5 Calculated VIPs (eV) vs. experimental E_{redox} (V) potentials. The drawn line is obtained by least-squares fitting.





