

## The electron transfer rate of large TPA based compounds: a joint theoretical and electrochemical approach

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### Abstract

A series of triphenylamine (TPA) based compounds is investigated by means of density functional theory and cyclic voltammetry. Using the Nicholson's formalism, the measured  $\Delta E_p$  are correlated with B3LYP/6-31G\* calculated reorganisation energies ( $\lambda$ ), elucidating the trend followed by the electron transfer rate of these compounds. Besides the direct dependency upon the dimension of the cationic fragment contributing to the hole stabilisation, the  $\lambda$ s are tuned by the symmetry local to the TPA units, as evidenced by the structural relaxation of the cations. MDTAB shows the interesting combination of low ionisation potential (IP) and low  $\lambda$ . This can make this compound interesting for practical applications in organic light emitting diodes (OLEDs) devices, due to the direct correlation of the IP and  $\lambda$  with the hole transfer efficiency to the anode, along with the hole mobility.

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## I. INTRODUCTION

The widespread interest in triphenylamine (TPA) derivatives is due to their actual use as hole transporting materials in electroluminescent multilayer light emitting devices based on molecular organic compounds [1–4]. Their electronic properties are key features to understand their behaviour as charge carrying materials. To increase the overall device efficiency[5] or tune the emission wavelength of exciplex based organic light emitting diodes (OLEDs)[6–8] one has to know the energy barrier for hole injection from the anode, the hole mobility inside the layer and find a good matching of the electronic energy levels between the different active compounds in the device. Moreover, to gain a deep insight into the electron-transfer mechanism it is necessary to know the reorganisation energies associated with this process[9].

A recent review of the status of research on charge transfer at the nanoscale dimensional level elucidates the present understanding of this process and suggests the future research needs for progress in nanoscience and nanotechnologies [10]. Besides, the strong connection between basic and applied research while investigating the charge-transfer processes in organic systems was underlined in a recent review article by Brédas and coworkers[11]. The interest in obtaining accurate information by molecular modelling is due to the fact that, molecular engineering could be used to design molecules with suitable properties to fabricate OLEDs, once a correlation between the molecular structure and its electronic properties is established.

Particularly valuable is the correlation of the molecular structures with the ionisation potentials and electron affinities, defining the energy levels involved in charge injection, and with the electron transfer rate, determining the charge mobility. In their pioneering work on TPA based compounds Sakanoue *et al.*[12] pointed out that the reorganisation energy is one of the most important factors to determine the hole transport mobility, and a good hole transporting material must have a small reorganisation energy ( $\lambda$ ) in an ionisation process. They calculated the  $\lambda$  of TPA taken as model system to investigate the hole mobility of higher homologous molecules. Malagoli and Brédas[13] considering the reorganisation energy of TPD discussed the substantial difference between the relaxation processes taking place in this molecule with respect to TPA. They evidenced the important role played by the central biphenyl moiety in case of TPD and pointed out that the properties of this kind of compounds cannot be derived on the basis of TPA properties alone. Lin *et al.*[14]

extended the investigation considering one more molecule with two substituted TPA units, concluding that values of  $\lambda < 0.2$  eV can be obtained only for molecules which contain a single TPA unit, and that the  $\lambda$  value is mainly determined by the moiety which contribute predominantly to the HOMO. Recently, Szeghalmi *et al.*[15] showed that the radical cation of the smallest bis(triarylamine) adopts a symmetrical delocalised structure both in solid state and solution. Besides, the TPA based compounds are also widely investigated for their potential technological applications in mixed-valence systems containing two or more redox states in the same molecule or molecular unit [16]. We have already investigated the electrochemical properties of a series of TPA based compounds[17] having up to four units by means of AM1 + SAOP model, evidencing a correlation between the molecular geometry and the electrochemical potential of the first oxidation process. The trend shown by the calculated oxidation potentials obtained by vertical ionisation energies (VIPs) was in good agreement with voltammetric measurements encouraging further investigation.

## II. EXPERIMENTAL

The examined TPA based compounds are shown in Fig.1. Here the actual structure of TAPC incorrectly drawn in Ref.[17] is reported, along with those of TTA, NDB, NBDB, and MTDATA. Among the investigated compounds 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-phenyldiamine (MPTAB), 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. All the other considered molecules are commercial ones and have been used as supplied with a chemical purity  $\geq 99\%$ . The voltammetries of the triphenylamines were carried out in dichloromethane (DM, Merck ACS product). DM was dehydrated with  $\text{CaCl}_2$  for 12 hours, successively distilled in presence of  $\text{P}_2\text{O}_5$  under argon flux and stored in dark under argon pressure. Tetrabutylammonium perchlorate (TBAP, Fluka AG "purum") was purified by recrystallisation 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

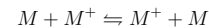
in the electrolytic cell. All the potentials are referred to this electrode in this work. The counter electrode was a platinum wire. The working electrode was a platinum minidisc ( $0.003 \text{ cm}^2$ ). The geometry of the cell was accurately kept constant in all measurements and the concentration of triphenylamines was  $1 \times 10^{-3} \text{ M}$ , corresponding to peak currents of about 6-12  $\mu\text{A}$ . This accuracy was directed to minimise the ohmic drop which affected the voltammetric curves of the investigated compounds.

## III. CALCULATIONS

The calculations of the structures and energies of TAPC, NBDB, MDTAB, MPTAB, and MTDATA (see Fig. 1) were performed using the B3LYP/6-31G\*[18-21] density functional theory (DFT) method with the GAUSSIAN 03 software package[22]. The geometries of both the molecule and the cation were fully optimised, using as initial guess the AM1 geometries[17]. The UB3LYP/6-31G\* calculation of the energy is almost free of any spin contamination ( $S^2 = 0.76$ ) for all considered cations. All the calculated energy derivatives were less than  $1 \cdot 10^{-3}$  a.u. and the energies were converged down to  $5 \cdot 10^{-5}$  eV.

## IV. THEORETICAL BACKGROUND

The transport of a hole/electron in organic solids can be viewed as an electron hopping process, which can be accounted for by the semiclassical Marcus theory[10, 23-25]. The rate of the electron transfer (ET) between the molecule M and its cation  $\text{M}^+$ :



is given by[10, 25]:

$$k_{ET} = A \cdot \exp(-\lambda/4k_B T) \quad (4.1)$$

where  $\lambda$  is the reorganisation energy,  $k_B$  and T are the Boltzmann constant and the temperature, respectively. The activation energy of this kind of processes depends, therefore, only on  $\lambda$ . Using  $\hbar$  for the Planck constant, the prefactor A, depending upon the electronic coupling term  $H_{DA}$  between the donor ( $\text{D} = \text{M}$ ) and acceptor sites ( $\text{A} = \text{M}^+$ ), is written as:

$$A = H_{DA}^2 / \hbar \cdot (\pi / \lambda k_B T)^{\frac{1}{2}} \quad (4.2)$$

Both  $\lambda$  and  $H_{DA}$  determine the relative hole/electron transfer rate. Since the intermolecular charge transfer processes considered in OLEDs involve molecules in an amorphous solid state phase a limited range of  $H_{DA}$  is expected within a series of homologous molecules, and the electron transfer process should be dominated by the reorganisation energy term[11, 14]. The reorganisation energy  $\lambda$  is usually expressed as the sum of inner, or intramolecular, and outer contributions[10]. This last arises from the nuclear polarisation and relaxation of the surrounding medium. In case of solid state systems the separation between the two terms is reasonable, due to the weakness of the van der Waals interactions among the organic molecules. Within the Franck-Condon approximation the inner reorganisation energy  $\lambda$  is largely defined as the sum of the two contributions indicated in Fig.2, where it is schematised the energy of the reorganisation process that a molecule M undergoes in passing to its cationic form  $M^+$ , then back to its neutral form.  $\lambda_1$  and  $\lambda_2$  arise from the stabilisation energy due to geometry relaxation of the radical cation in the oxidative and in the electron attaching processes, respectively. Therefore,  $\lambda_1$  can be calculated as the difference between the vertical ionisation potential (VIP) and the adiabatic ionisation potential (IP), while  $\lambda_2$  as the energy difference between the vertical electron affinity and the adiabatic electron affinity of the radical cation. The energies of the two step reaction can be correlated with those of the direct and reverse reactions of the molecule in an electrochemical cell. In fact, a relationship between the  $k_{ET}$  of homogeneous phase reactions and the standard electron-transfer rate constant  $k^0$  of electrochemical reactions under equilibrium conditions can be established [10, 26, 27], provided the electronic coupling element  $H_{DA}$  for the heterogeneous reaction is independent of the electrode energy. An estimate of  $k^0$  can be obtained by cyclic voltammetry (CV), which rapidly gives valuable information about the kinetics of electron-transfer reactions. A precise evaluation of the voltage splitting for the direct and reverse peaks,  $\Delta E_p$ , giving information about  $k^0$  in an electrodic reaction, needs experimental conditions avoiding the ohmic drop between the work and the reference electrodes. The case of interest is the so-called quasi-reversible process, when  $k^0$  is within the range from  $0.3 v^{\frac{1}{2}}$  down to  $2 \cdot 10^{-5} v^{\frac{1}{2}}$ , where  $v$  is the voltage scan rate. Outside this range, at larger  $k^0$  values,  $\Delta E_p$  becomes a constant ( $\approx 60$  mV for the transfer of one electron) indicating a reversible electron transfer process while, at lower  $k^0$ ,  $\Delta E_p$  cannot be determined due to the lowering of the reverse peak (irreversible process). The dimensionless equation derived by Nicholson[28]

for an electron transfer process defines  $k^0$  as a function of  $\Delta E_p$  in the following manner:

$$k^0 = (\pi F D v / RT)^{\frac{1}{2}} \cdot \Psi(\Delta E_p) \quad (4.3)$$

where  $D$  is the diffusion coefficient,  $F$ , and  $R$  are the Faraday and gas constants, respectively, and  $T$  is the temperature. The function  $\Psi$  of  $\Delta E_p$  was empirically derived by Nicholson and is used by electrochemists. In the range of high  $\Delta E_p$  values ( $\geq 140$  mV), a suitable relationship was found by Klingler and Kochi[29]. For  $60 \leq \Delta E_p \leq 140$  mV Lavagnini *et al.*[30] proposed the following function of  $\Psi(\Delta E_p)$ , which fits Nicholson's data, for practical usage:

$$\Psi = (-0.6288 + 0.021\Delta E_p)/(1 - 0.017\Delta E_p) \quad (4.4)$$

Moreover, Nicholson pointed out the dependence of  $\Psi$  on a charge transfer coefficient  $\alpha$ , which can affect the symmetry of the voltammetric curves by modifying their shape and position. However, in his original formula,  $\alpha$  appears as an exponent of a quantity ( $\gamma$ ) related to the diffusion coefficients ratio of the oxidised and reduced species in solution, which is assumed to be  $\approx 1$ . Therefore, except for unusual cases of very large differences between the diffusion coefficients of the reduced and oxidised species, this coefficient is not expected to sensibly affect the empirical relation found between  $\Psi$  and  $\Delta E_p$ . Information about the  $k_{ET}$  defined by Eq. 4.1 can, therefore, be related to CV measurements of  $\Delta E_p$ , since  $k_{ET} \propto k^0 \propto \Psi(\Delta E_p)$ .

## V. RESULTS AND DISCUSSION

The voltammetric behaviour of triphenylamine based compounds is widely investigated due to the role that they can play as hole carriers in the preparation of OLEDs[31–35]. The present study means to contribute to this investigation by correlating measured  $\Delta E_p$  obtained by CV with estimates of  $\lambda$  obtained by DFT calculations for a set of compounds containing up to four TPA units by means of calculated reorganisation energies. The results of previous calculations on TPA based systems[12–14] will be taken into account and discussed within this context. Besides, the trend presented by the  $k_{ET}$  of these compounds will be related to their molecular and cationic parameters. Moreover, a comparison with previously calculated IPs[17] will be performed and the behaviour of two different theoretical approaches will be discussed.

### A. Electrochemistry.

CV is not routinely used to study the electron transfer processes, because of the difficulties in achieving all the conditions which must be fulfilled to obtain an accurate correlation between the oxidation and the back-reduction potential difference,  $\Delta E_p$ , and the process kinetics parameters. Unfortunately, some of these compounds oxidise through irreversible processes or participate to homogeneous chemical reactions, which are competitive with the electron transfer process. Besides, the recorded cyclic voltamogram must show well defined and symmetric direct and reverse peaks, and the first oxidation peak must be accurately discriminated from the second oxidation process[32]. Moreover, the ohmic drop between the work and reference electrodes, also causing a variation of  $\Delta E_p$  which could be wrongly attributed to slow electron transfer, must be negligible, and parallel reactions or absorption processes must be ruled out. For these reasons, a careful setup of the experimental conditions was performed, in such a way to rule out or minimise the disturbing effects. For all the compounds, but TPA itself, the radical cations do not undergo successive chemical reactions, and the first oxidation process occurs in quasi-reversible conditions.

In Fig.3 are shown, as an example of the trend followed by the considered TPA based compounds, the voltammograms of MTDATA while varying the scan velocity  $v$ . The cathodic and anodic peaks' symmetrical shift, occurring while increasing  $v$  from 5 up to 100 mV/s, indicates that the charge transfer coefficient  $\alpha$  can be assumed to be equal to 0.5. Hence the symmetry conditions required by Eq. 4.3 are fulfilled. In these conditions, the  $\Delta E_p$  splittings of a set of analogous TPA based amines are expected to have the same correlation with their  $k^0$  when derived from CVs obtained in identical experimental conditions. Therefore,  $\Delta E_p$  (see Table I in the following) were derived from CVs taken at same scan rate of 20 mV/s, and concentration ( $1 \cdot 10^{-3}$  M). Moreover, the  $\Delta E_p$  of TPA and TTA will not be reported, because of the physical dishomogeneity of these compounds with respect to the higher homologous. In fact, different solvent interactions and diffusion rates are expected to affect the CV of these small molecules with respect to the others, specially those of the radical cation. Furthermore, it must be pointed out a problem encountered in evaluating the  $\Delta E_p$  of both TAPC and MDTAB, which show two electron transfer with very similar *redox* potentials separated only by less than 200 mV by a current flex. In these cases, the  $\Delta E_p$  values were obtained by digital simulation of the CVs[32].

### B. Results of the Calculations

In Table I are compared the experimental ionisation potentials (IP) estimated by adding to the measured *redox* potentials  $E_{redox}$ , obtained by cyclic voltammetry in solution[17], the value of 4.68 eV as the absolute potential of the reference electrode[36]. For comparison the calculated data of DTAB, PTAB, and TDATA, which refer to the non-methylated compounds corresponding to MDTAB, MPTAB, and MTDATA reported in Fig.1, are also reported. The value of 5.43 eV, obtained for TPD, well agrees with those of 5.38 eV and 6.69 eV obtained by UPS spectroscopy in thin film and gas phase[37, 38], respectively. As expected experimentally, the trend:  $IP_{gas} > IP_{solution} > IP_{solid}$  is observed. Under column II are reported the IPs calculated by taking the relaxed geometries of both molecule and cation. For sake of completeness, the data of TPA, TTA, TPD, NPB previously calculated with the same method and level of accuracy by Lin *et al.*[14] are also reported. An excellent agreement is observed among the experimental and calculated data for all the examined compounds. In fact, the largest differences are those of 0.57 eV and 0.46 eV calculated for TPA and TTA, respectively. Previous calculations[13] on the TPA and TPD molecules used the same hybrid functional but a larger basis set (6-31G\*\*), which includes  $p$  polarisation functions on the hydrogen atoms, giving IP values larger by 0.13 and 0.28 eV, respectively, than those obtained with the basis set presently used. It should be evidenced that, the previous comparison[13] among calculated and experimental IPs, obtained by REMPI[39] and UPS[37] spectroscopies in gas phase, evidenced a difference of 0.46 eV and 0.96 eV between the two sets of data for TPA and TPD, respectively. This indicates the level of agreement among experimental and calculated IPs, which can be expected for this kind of molecules using different experimental techniques and theoretical methods. Moreover, when discussing the accuracy with which the IPs are estimated, one has to remind that the calculations refer to an isolated molecule and, therefore, should better compare with the data obtained by gas phase measurements. Nevertheless, B3LYP/6-31G\* shows an excellent agreement with the liquid phase measurements performed by cyclic voltammetry, especially for those compounds containing more than one TPA unit. The IP value of MTDATA obtained in solid state is 5.1 eV[40] and well agrees with that of 5.04 eV measured by cyclic voltammetry and its calculated value of 5.06 eV. It should be mentioned that the calculated IP values of DTAB, PTAB, and TDATA evidence, as expected for these large molecules, the very low

effect (0.03-0.04 eV) of the *meta* methyl groups in tuning the IP of these compounds. Under column III is reported the ratio of  $\lambda_1/\lambda_2$ , which indicates the relative weight with which the two relaxation processes (see Fig.2) contribute to the total reorganisation energy. Apart from TPA and MDTAB, which show an equal contribution by both reorganisation processes, the considered molecules can be divided into two subsets: TPD, NPB, and NBDB, containing the biphenyl central unit, having  $\lambda_1 < \lambda_2$ , and TTA, TAPC, MPTAB, and MTDATA, having  $\lambda_1 > \lambda_2$ . Under column IV are reported the calculated total reorganisation energies  $\lambda$ . With respect to these last, the molecules can be divided into three subsets: TPA, TTA, and TAPC having, or behaving as having, a single TPA unit and  $\lambda < 0.2$ , TPD, NPB, NBDB, and MDTAB having a biphenyl bridge and  $0.2 < \lambda < 0.3$ , and MPTAB and MTDATA having  $\lambda > 0.3$ . A comparison with previously calculated  $\lambda$  of TPA[12, 13] and TPD[13] does not evidence a large difference among the results obtained by using different basis sets with the B3LYP hybrid functional. In fact, the  $\lambda$  value of TPA is equal to 0.10 eV when calculated with the 3-21G\* basis set, while a value of 0.12 eV is calculated by both 6-31G\* and 6-31G\*\* basis sets. The  $\lambda$  values of TPD calculated by 6-31G\* and 6-31G\*\* basis sets are 0.28 and 0.29 eV, respectively. Besides, comparing the results calculated for the three largest TPA based compounds, one observes that the effect of the *meta* methyl group is to increase the  $\lambda$  of MTDATA, while it lowers that of MPTAB and MDTAB. The  $\lambda_1/\lambda_2$  ratio is close to 1 for all the amines and states again the symmetry of the forward and backward *redox* processes for this set of compounds. Under the last column are reported the measured  $\Delta E_p$ .

### C. The $k_{ET}$ trend

In order to investigate the trend followed by the  $k_{ET}$  (Eq. 4.1) within the series of the examined TPA based compounds, the  $\Delta E_p$  measured by CV were correlated to the activation energy of these processes by means of the calculated  $\lambda$ s. The Nicholson's  $\Psi(\Delta E_p)$  function[28] ( $\Psi(\Delta E_p) \propto k_0 \propto k_{ET}$ ) of heterogeneous charge transfer in CV measurements is expected to be well characterised by Eq. 4.4 within the range of measured  $\Delta E_p$  (70 mV  $\leq \Delta E_p \leq$  110 mV) reported in Table I. In Fig.4 are plotted the natural logarithms of  $\Psi(\Delta E_p)$  vs. the calculated  $\lambda$ s ( $k_{ET} \propto \exp\{-\lambda\}$ ) along with the least squares fitted line,  $\log y = a x + b$ , with  $a = -5.44$  ( $\sigma_a = 1.0$ ),  $b = 1.34$  ( $\sigma_b = 0.36$ ), and  $r = -0.83$ . It should be

emphasised that, for  $\lambda = 0$ , indicating a process in which no molecular rearrangement takes place in going from the molecule to the cation and *vice versa*, the extrapolated value of  $\Delta E_p$  (= 66 mV) well approximates the limiting value of  $\approx 60$  mV expected for reversible *redox* processes. Moreover, the calculated slope coefficient value of -5.44 is reasonably close to that expected by Marcus theory for an electrode reaction, where only one molecule is reorganising as compared to two in a self exchange reaction, and the slope of the line should, therefore, be  $-1/(8 k_B T)$ , i.e. -4.86 at 298 K for  $\lambda$  in eV. The good correlation found among the calculated activation energy, by means of the exponential containing  $\lambda$ , of the two steps process[11] schematised in Fig. 2, and the measured  $\Delta E_p$  indicates the adequacy of the CV technique to investigate the trend followed by the  $k_{ET}$  of this series of homologous compounds. In fact, the larger differences of the measured  $\Delta E_p$  from those calculated using the fitted line are observed for NBDB (+12 mV) and MDTAB (-8 mV), for both of which the interpolated value of  $\Delta E_p = 84$  mV was calculated. With respect to the examined parameters, the four N atoms compound MDTAB shows a behaviour similar to that of the two N atom molecules with a central biphenyl moiety such as TPD, NPB and NBDB. This indicates that the central TPD like fragment of this molecule largely influences the charge transfer process of this compound[41]. It was already discussed that the  $\lambda$ s largely depends upon the HOMO shape[11, 14], hence on the molecular fragment over which the hole/electron is delocalised. Moreover, a comparison among the partial charges  $\delta$  of the neutral molecule and cation performed using the Mulliken population analysis evidences how the charge redistribution affects a large part of the cation, though it is largely localised at the N atoms. In fact, their calculated value for all the N atoms in the neutral molecules is  $\delta \approx -0.65 e^-$ , as in TPA, while in the cation the inner N atoms have  $\delta = +0.22 e^-$ ,  $+0.18 e^-$ ,  $+0.17 e^-$ ,  $+0.16 e^-$ , and  $+0.12 e^-$  for MTDATA, TAPC, NBDB, MPTAB, and MDTAB, respectively, less than that of TPA which is  $\delta = +0.37 e^-$ . In case of MPTAB, MDTAB, and MTDATA, also the outer N atoms acquire a partial positive charge  $\delta = +0.09 e^-$ , evidencing the wide range of charge delocalisation of these large compounds. Furthermore, a comparative analysis of the changes which occur in the bond lengths, along with in the planar and dihedral angles, shows how these molecules relax after the hole is created, and evidences which fragments of these compounds are largely involved in the hole stabilisation and those which do not contribute to this process. The HOMO electron density contouring of the investigated molecules, indicating how the  $+1 e^-$  charge can be delocalised within the cation, along with

the significant calculated geometrical parameters of both the neutral and cationic species of all the examined compounds are included as Supplementary Information. The main changes within the molecular fragment delocalizing the charge are observed in the shortening of the N-C bond length, along with the shortening of the biphenyl interring distance in case of NBDB, and MDTAB. The rings participating to the same relaxation process become more planar with respect to the molecular skeleton. The external molecular fragments show longer N-C bond lengths when passing to the cation, and larger dihedral angles between two rings, indicating a minor participation to the electron delocalisation within each TPA unit. Besides, a lowering of the symmetry within each TPA unit present in these compounds contributes to a lowering of the calculated  $\lambda$ s. The simplest example of this behaviour is given by TAPC, whose inner phenyl ring largely participates to the charge delocalisation with respect to the outer rings, which are left almost unchanged, hence lowering the symmetry of the TPA unit with respect to that of TPA itself or TTA.

## VI. COMPARISON WITH PREVIOUSLY CALCULATED IP

In Fig.5 are plotted the calculated IPs *vs.* those obtained by cyclic voltammetry for all of the considered molecules. For comparison the VIPs previously obtained[17] using the AM1 + SAOP method are also reported. The drawn lines  $y = a x + b$  are obtained by a least-squares fitting of the data. In case of AM1 + SAOP, reported in the upper part of Fig.5, it was shown that  $a = 1.00$  ( $\sigma_a = 0.07$ ) and  $b = 3.15$  ( $\sigma_b = 0.03$ ), when referred to the electrochemical IPs ( $E_{redox} + 4.68$  V). The IPs calculated using the B3LYP/6-31G\* method of GAUSSIAN 03 evidence how TPA and TTA largely deviate from the trend followed by the heavier TPA based compounds. It should be mentioned that the VIP of TPA calculated by using the AM1 geometry and the B3LYP/6-31G\* method, closely reproduce those presently calculated, being 6.34 and 6.35 eV, respectively. This indicates that the calculated IP mainly depends on the DFT method employed, being the AM1 optimised structure a compromise between the molecular and cationic structures obtained by B3LYP/6-31G\*. A linear least-squares fitting of all the IP calculated data gives a slope coefficient of  $a = 1.7$  ( $\sigma_a = 0.2$ ). A better agreement with the experimental data is obtained by discarding TPA and TTA from the set of data. In fact, in this way, the calculated least-squares parameters are  $a = 1.17$  ( $\sigma_a = 0.08$ ) and  $b = -0.86$  ( $\sigma_b = 0.05$ ) with  $r = 0.98$ , when referred to the electrochemical IP. It

should be pointed out that, in case the experimental data are obtained by cyclic voltammetry, the molecular relaxation phenomena, whose energetic effect is particularly evident for the MPTAB and MDTAB compounds, should be taken into account. The calculated slope coefficients in the case of the B3LYP/6-31G\* method evidence how properly accounting for relaxation improves the agreement among calculated and experimental data, though the amount of relaxation could be overestimated by the isolated molecule model. Nevertheless, as already mentioned, also the comparison with the available REMPI[39] and UPS[37] for TPA and TPD in gas phase evidences how the VIPs calculated by the AM1+SAOP model overestimate the experimental IPs of this class of compounds, while the B3LYP/6-31G\* method, underestimating them, gives energy values in better agreement with the IPs obtained in liquid phase. It was already evidenced[17] that the fast AM1 + SAOP method allows to obtain accurate information about the trend followed by the IPs of this class of compounds, through the calculated VIPs of the neutral species. This fact is especially valuable for large molecules. In case the relaxation processes have to be taken into account, as in the present investigation, the calculation of the cationic relaxed geometry is necessary. We found a faster convergence in calculating the relaxed geometries of both molecule and cation by using the GAUSSIAN 03 geometry optimisation routine.

## VII. CONCLUSIONS

A joint theoretical and experimental approach allowed to investigate the trend of the electron transfer rate ( $k_{ET}$ ) followed by a series of TPA based compounds by mean of a relation among the  $\Delta E_p$ , obtained by cyclic voltammetry, and the B3LYP/6-31G\* calculated reorganisation energies ( $\lambda$ ). Moreover, the comparison with previously calculated model systems[12–14] allowed to show that the proposed theoretical modelling well behaves while increasing the number of TPA units up to four. Furthermore, the adequacy of the molecular modelling to be used to investigate the *redox* processes of this series of compounds was discussed based on a balance between accuracy and computational time, comparing with the results obtained by a different theoretical approach[17]. The  $\lambda$ s largely depend upon the dimension of the cationic fragment, which mainly contributes to the hole stabilisation, and increase while increasing it. In fact, compounds containing four N atoms, such as MDTAB and MPTAB show  $\lambda$ s larger than 0.3 eV. TAPC shows the lowest  $\lambda$  (= 0.11 eV), comparable

with that calculated for the model systems TPA ( $\lambda = 0.12$  eV) and TTA ( $\lambda = 0.13$  eV)[14], since its TPA units reorganise independently the one from the other. Compounds having the biphenyl bridge, such as NBDB and MDTAB, are characterised by  $\lambda = 0.22$  eV, lower than those previously calculated for TPD ( $\lambda = 0.28$  eV) and NPB ( $\lambda = 0.29$  eV)[14] using the same DFT method. Among the compounds made by four TPA units, MDTAB shows the lowest calculated activation energy and measured  $\Delta E_p$ . This feature, along with its low IP with respect to the other examined compounds, could make it interesting for practical applications in organic electroluminescent devices (OLEDs) due to the direct correlation of the above parameters, IP and  $\lambda$ , respectively, with the electron transfer efficiency to the anode and with the hole mobility inside the bulk material. In conclusion, we feel that the combination of electrochemical data and structural investigations can provide a predictive pattern on a series of TPA based compounds as hole transporting materials for high efficient OLEDs.

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## Figure Captions

- Fig.1: Structures of the molecules under investigation.
- Fig.2: Scheme of the reorganisation energy process of the M molecule and  $M^+$  cation. The indexes refer to the geometry.
- Fig.3: Cyclic voltammetry of MTDATA at different scan rates  $v$  (mV/s) as indicated above the arrows. The reference electrode is SCE.
- Fig.4:  $\log \Psi(\Delta E_p)$  vs. calculated  $\lambda$  (eV). The line drawn is obtained by least-squares fitting.
- Fig.5: IPs ( $\bullet$ ) and VIPs ( $\Delta$ ) calculated by B3LYP/6-31G\* and VIPs ( $\star$ ) by AM1 + SAOP vs. measured  $E_{redox}$  of TPA(1), TTA(2), TPD(3), NPB(4), TAPC(5), NBDB(6), MDTAB(7), MPTAB(8), MTDATA(9). The drawn lines are obtained by least-squares fitting.



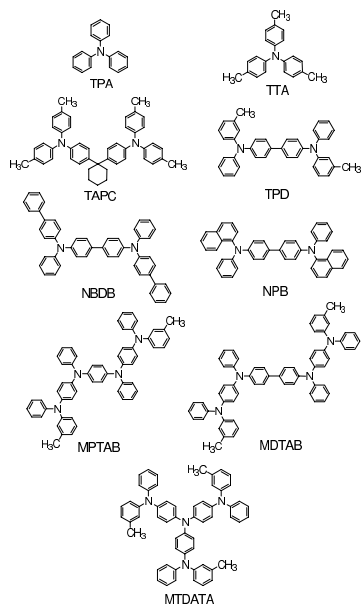


FIG. 1: Structures of the molecules under investigation.

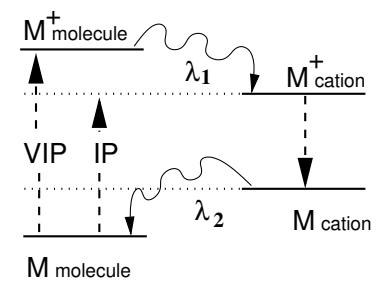


FIG. 2: Scheme of the reorganisation energy process of the  $M$  molecule and  $M^+$  cation. The indexes refer to the geometry.

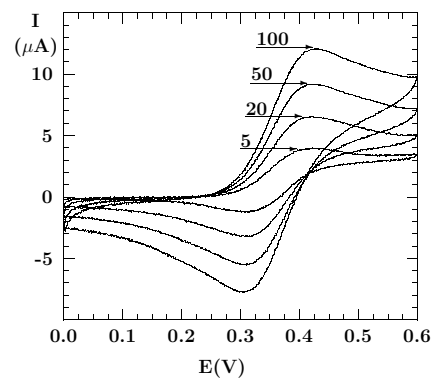


FIG. 3: Cyclic voltammetry of MTDATA at different scan rates  $v$  (mV/s) as indicated above the arrows. The reference electrode is SCE.

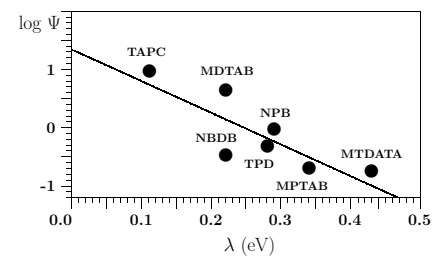


FIG. 4:  $\log \Psi(\Delta E_p)$  vs.  $\lambda$  (eV). The line drawn is obtained by least-squares fitting.

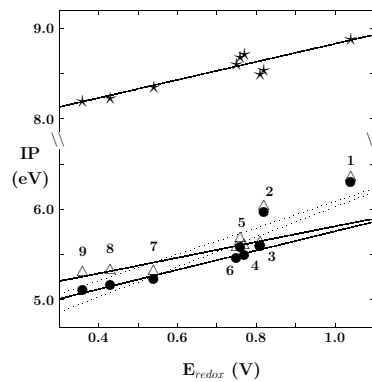


FIG. 5: IPs (●) and VIPs ( $\Delta$ ) calculated by B3LYP/6-31G\* and VIPs ( $\star$ ) by AM1 + SAOP vs. measured  $E_{redox}$  of TPA(1), TTA(2), TPD(3), NPB(4), TAPC(5), NBDB(6), MDTAB(7), MPTAB(8), MTDATA(9). The drawn lines are obtained by least-squares fitting.

TABLE I: Comparison among I) experimental and II) calculated IPs (eV). Calculated III)  $\lambda_1/\lambda_2$  and IV)  $\lambda$  (eV). The calculated values indicated by *a* are those of Ref. 14. Under column V are reported the  $\Delta E_p$  (mV) obtained by cyclic voltammetry.

	I	II	III	IV	V	VI
TPA	5.72	6.29 <sup>a</sup>	1.00	0.12 <sup>a</sup>	-	
TTA	5.50	5.96 <sup>a</sup>	1.17	0.13 <sup>a</sup>	-	
TPD	5.43	5.45 <sup>a</sup>	0.87	0.28 <sup>a</sup>	95	
NPB	5.45	5.47 <sup>a</sup>	0.81	0.29 <sup>a</sup>	87	
TAPC	5.49	5.58	1.22	0.11	70	
NBDB	5.44	5.57	0.88	0.22	100	
MDTAB	5.22	5.18	1.00	0.22	74	
MPTAB	5.11	5.12	1.10	0.34	108	
MTDATA	5.04	5.06	1.09	0.43	110	
DTAB		5.21	1.04	0.23		
PTAB		5.15	0.93	0.37		
TDATA		5.10	1.26	0.35		