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Directional formation of microtubes by soft-template electropolymerization from fully conjugated triphenylamine-based monomers

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ABSTRACT

Microtubular structures have been prepared by soft-template electropolymerization of conjugated organic monomers with the aim to mimic the strong water-adhesive forces of gecko foot or rose petals. Water-saturated solvent of low water solubility (dichloromethane) was used to form a micellar solution stabilized by tetrabutylammonium perchlorate as the electrolyte and the surfactant, in which case the formation of nanotubes was particularly efficient. The studied monomers were built from a triphenylamine core conjugated with three arms differing by their structure and positions: (i) 2- or 3- positions in the thiophene arms or (ii) carbazole arms attached to *para*, *meta* or *ortho*-positions of the benzene ring of the core. The formation of microtubes is due to preferential growth of polymer films and an aggregation of formed polymers/oligolymers in one direction (1D) facilitated by π -stacking interactions. The key factors influencing on the surface morphologies (monomer structures and reactivity, electrodeposition conditions, etc) are discussed. Impressive results have been obtained in

studies of carbazole-containing monomers and the effect of regioisomerism in the monomers (the position of the carbazole attachment to the core). Extremely long microtubes (tens to >100 μ m length, diameter $\approx 1.0 - 1.5 \mu$ m) were formed on the electrode surface from the monomer **N-Ph-p-Cb** with the carbazole attachment in the *para*-position. Wettability analysis showed highly hydrophobic surfaces with apparent contact angles up to 154.0 ° and extremely strong water adhesion comparable to rose petals or gecko feet. Such coatings can find applications in water-harvesting systems, sensing platforms or electrochemical analyses.

Keywords: Adhesion, Conjugated polymers, Electropolymerization, Hydrophobicity, Surface structures, Triphenylamine, Thiophene, Carbazole, Regioisomerism.

1. Introduction

The control of surface structures at the nanoscale or microscale is fundamental for a huge number of applications such as in sensors, optics, catalysis, energy systems, biomaterials, cell culture [1,2,3,4], electrochemical analyses [5,6] or in wetting properties [7,8]. In nature, there are numerous species displaying extremely high hydrophobicity but also different water adhesive forces, such as lotus leaves, rose petals or gecko feet [9,10,11,12]. These surface wetting properties are highly dependent on both the surface energy and surface structures/features [13,14,15]. Different features were already investigated but the nanotubes are excellent candidates for their high surface area-to-volume ratio [16,17,18]. Jiang *et al.* also demonstrated stronger water adhesive forces compared to surfaces structures without pores [16].

There are few methods for forming well-defined nanotubes on a substrate. The electropolymerization is a very fast process while the tuning of non-porous structures (for instance nanofibers, nanosheets, nanospheres) is possible by changing the monomer or the electrochemical conditions [19]. Porous structures (for instance, nanotubes) are conceivable by electropolymerization on hard templates [20]. However, one hard template is necessary for each change in the nanotubes dimension (diameter, height or pitch). One of the most used hard templates are Anodic Aluminum Oxide (AAO) membranes but these membranes have to be removed after use. Strategies without hard templates are called templateless or soft-template electropolymerization. The soft template can be composed of gas bubbles or micelles in solution. When the electrode during electropolymerization because the potential of H_2O and the monomer oxidation potential are close [21,22,23,24,25]. Porous structures can be produced if the polymer growth around these gas bubbles. It is also possible to

produce hydrogen (H₂) bubbles by reducing H₂O using potentiodynamic electropolymerization such as cyclic voltammetry (CV) or pulse deposition. Most of the monomers are not soluble in H₂O, and low polarity solvents such as dichloromethane (CH₂Cl₂) or chloroform (CHCl₃) can be used as soon as trace H₂O is present in solution [26,27,28,29]. The process is completely different because micelles can be present in solution prior electropolymerization [27]. Micelles can be formed in solution if the electrolyte and/or the monomer play the role of a surfactant thus stabilizing these micelles. They will wet the substrate before electropolymerization.

To construct nanotubes on a substrate by electropolymerization, it is necessary to favor the polymerization in one direction (1D growth) [30]. The molecular structures that can induce strong π stacking interactions, such as 3,4-(1,2-naphthylenedioxy)thiophene (NaphDOT) [26, 27], 3,4phenylenedioxythiophenes (PheDOTs) [31,32,33] and some others [28], demonstrated exceptional preliminary results. The polymerization rate should not be also too fast because the 1D growth takes time as demonstrated by reducing the temperature [34]. Another proof of the importance of electropolymerization rate was demonstrated by comparing the surfaces obtained by electrodeposition of substituted PheDOT monomer and its dimer [31]. Whereas the monomer formed nice vertically aligned nanotubes, the dimer gave 3-dimensional spherical nanoparticles. The monomer and polymer solubilities are also important parameters influencing the process of electrodeposition [35,36,37]. The research group of Wang investigated tris(4-(thien-2yl)phenyl)amine (Chart 1, N-Ph-2-Th) as promising molecule for the formation of tubular structures by soft-template electropolymerization in similar electrochemical conditions [38]. Other cores (tetraphenylmethane, 9.9'-spirobifluorene) were also tested [39,40,41], while the effect of water on the electropolymerization and surface morphology was not investigated.

In this work, we have synthesized and investigated electropolymerization and the surface properties of electrodeposited films for two series of conjugated molecules based on the triphenylamine core differing by the fashion of the thiophene (2- or 3-positions, N-Ph-2-Th and N-Ph-3-Th) or carbazole arms attachment (*para-/meta-/ortho-*, N-Ph-p-Cb, N-Ph-m-Cb, N-Ph-o-Cb) (Chart 1). The monomers of high polymerization capacity (thiophene derivatives) and lower polymerization capacity (carbazole derivatives) were chosen. We studied the influence of the monomer structure, the effect of water presence in the solution during the electropolymerization, as well as the electrodeposition method on the resulting surface structures. The presence of reverse micelles was studied by transmission electron microscopy (TEM), the polymer films formation was investigated by cyclic voltammetry, and the surface structures was analyzed by scanning electron microscopy (SEM) and the surface wettability by goniometry.



Chart 1. Structures of monomers investigated by soft-template electropolymerization.

2. Results and discussion

2.1. Synthesis of monomers

Synthesis and characterization of monomers shown in Chart 1 have been presented in the Supporting Information (SI). Briefly, synthesis was done by Pd(0)-catalyzed Suzuki coupling of tris(4-bromophenyl)amine with corresponding arylboronic acids (Scheme S1, SI), and the products were purified by column chromatography.

2.2 DFT computational studies

The geometry and electronic structures of monomers were studied computationally by DFT method at the B3LYP/6-31G(d) level of theory. The optimized geometries of the monomers are shown in Figure S1, and the key dihedral angles between the conjugated fragments in the structures are presented in Table 1. The molecules are not flat because steric hindrances result in some distortion between the conjugated units. The dihedral angles at the central triphenylamine core (~ 41 °) and between the benzene rings and thiophene (26–30 °) or carbazole moieties (~ 55 °) are typical connections between these units. An exception is **N-Ph-o-Cb**, in which case large steric hindrance of *ortho*-substitution with carbazole moiety significantly distorts the structure and increases the dihedrals angles to 67.3 - 70.8 ° (Table 1).

Compound	Ph-N-Ph (°)	Ph-Th (°)	Ph-Ph (°)	Ph-Cb (°)
N-Ph-2-Th	41.0	25.7		
N-Ph-3-Th	41.1	30.1		
N-Ph-p-Cb	41.1		35.3	54.8
N-Ph-m-Cb	41.0		35.6	56.5
N-Ph-o-Cb ^b	38.7 / 42.4		46.0 / 48.1	70.8 / 67.3

Table 1. Key dihedral angles between the moieties in the studied monomers.^a

^a Ph-N-Ph are dihedrals in the central triphenylamine core; Ph-Th are dihedrals between the benzene and thiophene rings; Ph-Ph are dihedrals between benzene rings of the biphenyl fragment; Ph-Cb are dihedrals between the benzene and carbazole rings. ^b Bulky carbazole moiety in *ortho*-position in **N-Ph-o-Cb** results in different dihedral angles measured at different sides of the moieties.

Yet, one should consider that in conjugated polymers derived from these monomers, an extended conjugation and solid-state packing can make these building blocks a bit flatter. The effect should be the most pronounced in the case of **N-Ph-2-Th** due to extension of the conjugation length when coupling at the positions 5 of the thiophene rings occurs (producing fragment "N–Ph–Th–Th–Ph–N") and slightly smaller in **N-Ph-3-Th**. Electropolymerization of carbazole derivatives is known to occur at positions 3,6. Because carbazole rings significantly distorted from the triphenylamine plane, growing the polymer chains (especially for **N-Ph-o-Cb**) will likely occur near orthogonally to the triphenylamine plane (or, at least, far away from the extension along the triphenylamine plane).

The energies of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of the studied compounds together with HOMOs and LUMOs for thiophene, carbazole and triphenylamine molecules are given in Figure 1. It is seen that HOMO energies of studied compounds are close to that in triphenylamine, indicating significant contribution of the core. In contrast, substantial lowering their LUMOs (compared to Th, Cb or Ph3N building blocks) reflects an extension of the conjugation.



Figure 1. Frontier orbitals energy levels of studied monomers and subunits used in their structures.

Figure 2 shows delocalization of HOMOs and LUMOs in the molecules. HOMOs are mainly delocalized over the triphenylamine core, but with significant extension to the end thiophene rings in the arms (for **N-Ph-2Th** and **N-Ph-3-Th**) or (at less extent) to carbazole moieties in the case of parasubstituted **N-Ph-p-Cb**. HOMO orbital coefficients on carbazole moieties in **N-Ph-p-Cb** are small and are negligible in **N-Ph-m-Cb** and **N-Ph-o-Cb**, while lower energy levels (HOMO-1 to HOMO-3) sit on the carbazole moieties (Figure S2 in the SI; see also Figure 2 for HOMO-1 energies). LUMO orbitals also mainly sits on the triphenylamine core, extending to peripheral thiophene or phenylene moieties (Figure 1; keep in mind the degeneracy of the orbitals due to the C₃-symmetry of the studied molecules).

These results indicate that triphenylamine core should be significantly involved in the initial electron transfer process (oxidation) to form radical cations species during the electropolymerization process. Really, calculations of electronic structures of radical cation species from these molecules (intermediates in anodic electropolymerization process) at spin-unrestricted UB3LYP/6-31G(d) level of theory show significant spin delocalization over the central triphenylamine core with an extension to thiophene and carbazole end groups (Figure 3). As expected, in the arms, the largest spin coefficients are observed at positions 2,5 for the thiophene moieties and 3,6 for the carbazole moieties.



N-Ph-p-CbN-Ph-n-CbN-Ph-o-CbFigure 2. Frontier orbital coefficients distribution in studied monomersfrom DFT calculations atB3LYP/6-31G(d) level.



Figure 3. Spin density maps for radical cations of studied monomers, calculated at UB3LYP/6-31G(d) level in a gas phase. The cyan color surface corresponds to an excess of α -electron density and the red surface (negative spin density) corresponds to an excess of β -electron density. The isosurface value is 0.001.

2.3. Electrochemical deposition of polymer films from monomers onto the electrode surface

The polymer films were electrodeposited on gold-coated silicon wafer electrode by electropolymerization of monomers (0.005 M) in two solvents, i.e. dichloromethane (CH₂Cl₂) and dichloromethane saturated with water (CH₂Cl₂ + H₂O sat.), with 0.1 M of Bu₄NClO₄ as an electrolyte. Both potentiodynamic (by cyclic voltammetry) and potentiostatic deposition techniques were used.

As shown below, micellar solutions were produced by mixing $(CH_2Cl_2 + H_2O \text{ sat.})$ with the electrolyte tetrabutylammonium perchlorate (Bu₄NClO₄). We previously studied electropolymerization of another monomer, NaphDOT, in CH₂Cl₂ and (CH₂Cl₂ + H₂O sat.) with Bu₄NClO₄ as an electrolyte and found a relationship between the size of micelles formed in solution prior electropolymerization (by transmission electron microscopy, TEM) and the size of the resulting nanotubes formed on the surface (by SEM) [27]. While we tested many tetrabutylammonium salts with different counter anions, i.e. perchlorate (ClO_4^{-}) , tetrafluoroborate (BF_4^{-}) , hexafluorophosphate trifluoromethanesulfonate $(CF_{3}SO_{3}^{-}),$ perfluorobutanesulfonate $(C_4F_9SO_3^{-}),$ $(PF_{6}^{-}),$ perfluorooctanesulfonate ($C_8F_{17}SO_3^{-}$), and bis(trifluoromethane) sulfonimide (Tf_2N^{-}), nanotubes were formed only with ClO_4^- and BF_4^- [42]. Tetrabutylammonium perchlorate is not a typical amphiphilic surfactant having high critical micelle concentration values in water (CMC > 0.25 M) [43], and we did not investigate the influence of electrolyte concentration. Here, to confirm the

presence of micelles in the monomer solutions in Bu_4NClO_4 / (CH₂Cl₂ + H₂O sat.) prior electropolymerization, they have been studied by TEM. The obtained TEM images clearly demonstrate the formation of micelles of different sizes for different monomers (Figure 4).



Figure 4. TEM images of N-Ph-3-Th and N-Ph-m-Cb (0.005 M) in $(CH_2Cl_2 + H_2O \text{ sat.})$ with 0.1 M of Bu₄NClO₄.

 $(CH_2Cl_2 + H_2O \text{ sat.})$ solvent was also tested toward producing O_2 and/or H_2 gas bubbles from H_2O during the electropolymerization $(2H_2O \rightarrow O_2 + 4H^+ + 4e^-; 2H_2O + 2e^- \rightarrow H_2 + 2OH^-)$. Water oxidation potential lies in the range of oxidation potentials of studied monomers, while water reduction is close to -0.5 V. This means that H_2 bubbles can only be produced by potentiodynamic polymerization such as cyclic voltammetry (CV) or pulse deposition. Therefore, the effect of two different deposition methods, i.e. potentiodynamic (by CV) and potentiostatic (at constant potential) electropolymerization, have been tested.

Our proposed mechanism of vesicle/tube formation is as follows. The studied monomers are insoluble in H₂O, but soluble in CH₂Cl₂. In (CH₂Cl₂ + H₂O sat.) solution and in the presence of Bu₄NClO₄, inverse micelles (i.e. with H₂O inside the micelles) are formed and dispersed in CH₂Cl₂. Bu₄NClO₄ is an electrolyte soluble in CH₂Cl₂ but because it is a surfactant, it is present in large quantities at the CH₂Cl₂/H₂O interface. When the working electrode (here is gold) is inserted in solution, micelles will wet the substrate following the Young's theory: liquid (H₂O)/liquid (CH₂Cl₂)/solid (gold) interface. During electropolymerization, the electrodeposited polymer will grow from the substrate but only in the parts in contact to CH₂Cl₂ due to the absence of monomer in H₂O. On applied potential for redox process, H₂O present on the substrate is transformed into gas bubbles. O₂ bubbles are formed at constant (positive) potential and both O₂ and H₂ are formed in CV experiments. These bubbles also participate in the formation of specific surface structure. For the formation of nanotubes, it is important that the polymer grows in one direction.

First, the monomer oxidation potentials (E^{ox}) were determined by fast CV scans between 0 and 2.5 V vs SCE (Figure 5). For studied monomers, one or two intense peaks were observed in the potential range of $\approx 1.7 - 2.5$ V. For E^{ox} , we took the first intense peaks at $E^{\text{ox}} = 1.75 - 2.00$ V vs SCE (their $E^{\text{onset}} \approx 1.2 - 1.4$ V). Therefore, the electrodeposition of polymer films was performed at the first intense oxidation peaks (≈ 1.7 V) with each monomer giving thick films deposition at these potentials. We should also mention that the other oxidation peaks of much smaller intensitities were also observed for all monomers at lower potentials of ≈ 1 V vs SCE. These peaks correspond well to oxidation potentials of triphenylamine and its derivatives [44,45] and belong to the 1e oxidation of triphenylamine core in the monomers.



Figure 5. Cyclic voltammograms of studied monomers in CH_2Cl_2 with 0.1 M of Bu_4NClO_4 . The potential range sweep is from 0 to 2.5 V, scan rate is 100 mV s⁻¹. The first scans are shown.

Polymer films were electrodeposited by CV scanning in the range from -1 V to E^{ox} in order to release a large number of gas bubbles (Figure S3 in the SI). A scan rate of 20 mV s⁻¹ was used, as well as different numbers of deposition scans (1, 3, or 5 scans). The obtained films were then electrochemically characterized by CV in monomer-free solutions of 0.1 M Bu₄NClO₄ / CH₂Cl₂ (Figure 6).

All electrodeposited films show p-doping electrochemical response of several poorly resolved/overlapped peaks/shoulders in the range of ca. 1 - 2 V, i.e. close to that for starting monomers. This contrasts with the usual behavior of 1D conjugated polymers prepared by electropolymerization method (e.g. polythiophenes, polypyrroles, polyfluorenes etc) whose electroactivity is generally observed at significantly lower potentials than that for corresponding monomers. This difference can be explained by the fact that the conjugation length of the whole molecules is not increased significantly on coupling at the thiophene or carbazole sites.

The exception is polymerization of **N-Ph-2-Cb**, electrochemical coupling of which produces an extended conjugation in the fragment "N–Ph–Th–Th–Ph–N". This is particularly reflected by an appearance of an additional wave at low potential of ≈ 0.64 V (i.e. lower than that for triphenylamine oxidation in the monomer), which distinguishes it from other electrodepositions (Figure 6). For **N-Ph-3-Th** and carbazole-containing monomers (**N-Ph-p-Cb**, **N-Ph-m-Cb** and **N-Ph-p-Cb**), coupling of monomers only slightly increases the conjugation at coupled Th–Th or Cb–Cb fragments. It should also be taken into account that the used monomers are crowded trifunctional molecules of C₃ symmetry (see DFT section 2.2), so their electropolymerization can be stopped (or retarded) at the stage of rather short oligomers due to steric issues. Such oligomers, due to their low solubility, can aggregate and deposit on the surface. Thus, we have recently demonstrated that NaphDOT derivatives functionalized at position 2 of the thiophene ring (to prevent electropolymerization with the formation of conjugated polymers) form only dimers in CV experiments, which, due to their low solubility, are deposited on the surface forming growing unidirectional (1D) vertically aligned nanotubes, likely due to good π - π stacking of flat dimers [32].



Figure 6. Cyclic voltammograms of electrodeposited polymers in monomer-free solutions of CH_2Cl_2 with 0.1 M of Bu_4NClO_4 . The polymers were obtained by potendiodynamic polymerization (5 cycles) scanning from 0 to 2.5 V at the scan rate 20 mV s⁻¹.

2.4. Surface morphology and nanostructures

In CH₂Cl₂, the surfaces made from N-Ph-2-Th and N-Ph-p-Cb are extremely rough, but only non-porous cauliflower-like structures are observed, which means a classical three-dimension (3D) growth (Figure 7). However, some tubules (apart of spherical, likely hollow, structures) are present in the films made from N-Ph-3-Th, showing a higher capacity to form tubular structures due to preferential growth in one direction. The formation of porous structures in CH₂Cl₂ with increased number of tubules is possible if trace H₂O is present in solution.



Figure 7. SEM images of electrodeposited surfaces from each monomer by CV. The modified surfaces were obtained in CH₂Cl₂ or (CH₂Cl₂ + H₂O sat.) with 0.1 M of Bu₄NClO₄ for 3 scans in the potential range from -1 V to E^{ox} at the scan rate 20 mV s⁻¹. Magnification is ×10,000 (×5,000 for N-**Ph-p-Cb** in (CH₂Cl₂ + H₂O sat.)).

Therefore, more detailed studies have been performed in (CH₂Cl₂ + H₂O sat.) (Figure 7, right column). In the case of **N-Ph-2-Th**, both cauliflower-like structures and microtubes are formed, while in the case of **N-Ph-3-Th** densely -packed microtubes of a large diameter ($\approx 0.5 - 1 \mu m$) are observed. Such densely packed microtubules from **N-Ph-3-Th** are formed already after 1 scan, and with increasing the number of scans, the height of the tubes increases while the top of the tubes becomes close (Figure S4 in the SI). In the case of carbazole-containing monomers (**N-Ph-p-Cb**, **N-Ph-m-Cb**, and **N-Ph-o-Cb**), microtubular structures are formed for all regioisomers, but the position of carbazole attachment to the terminal benzene ring of the core (*para-*, *meta-*, or *ortho-*) has a huge impact on the resulting surface structures. These significant differences are even better seen from the SEM images with inclination angles of 45° (Figure 8).

The most impressive surface structures are observed for the compound with the carbazole moiety in *para*-position (**N-Ph-p-Cb**). In this case, ultra-long tubes ($\approx 1.0 - 1.5 \,\mu\text{m}$ in diameter with tens to >100 µm length) are growing, indicating the preferential polymer growth / packing along one direction (1D), although the formed tubes are not aligned along the single axis but form disordered wool-like / fiber-like high-surface structure. Better flatness of N-Ph-p-Cb (compared to N-Ph-m-Cb and N-Ph-o-Cb; Figure S1 in the SI) and less steric hindrance for coupling at both 3- and 6- positions of the carbazole moieties promote faster electropolymerization and the formation of more ordered structures, likely through some kind of π -stacking of deposited oligomers/polymers in a direction perpendicular to the triphenylamine plane, resulting in extremely long tubular structures. These results are in line with previous work on comparative electropolymerization of 3,4phenylenedioxythiphenes with 1-naphthyl or 2-naphthyl groups in the side chain (1Na-PheDOT and 2Na-PheDOT, respectively) [31]. Electropolymerization of 1Na-PheDOT, which has smaller steric hindranes from naphtyl groups (according to B3LYP/6-31G(d) studies of optimized geometries) gave uniform, vertically aligned nanotubes, whereas 2Na-PheDOT electrodeposition gave disordered nanoribbons. In the case of N-Ph-m-Cb, a two-step process of the surface development is observed. Initially (one CV scan), densely packed and almost uniformly vertically oriented microtubes are formed. The mean diameter of the tubes is rather small ($\approx 350 - 500$ nm) and most of the tubes have their top close. As the number of scans increases, large-diameter ($\approx 1.5 - 5 \,\mu m$) open spheres (tuliplike structures) are formed on the top of the tubes. In the case of N-Ph-o-Cb, the most sterically crowded monomer, the number of tubes is significantly less. After 1 scan, the surface structure mainly consist of hemi-spheres and rings (diameter $\approx 1 \,\mu$ m), while after 5 scans, cups of large diameter are formed (diameter $\approx 1.5 - 3 \,\mu\text{m}$, height $\approx 1.5 - 2 \,\mu\text{m}$).)



Figure 8. SEM images with an inclination angle of 45 ° of potentiodynamically (CV) electrodeposited surfaces from **N-Ph-p-Cb**, **N-Ph-m-Cb** and **N-Ph-o-Cb** by CV for 1, 3 and 5 scans. The modified surfaces were obtained in (CH₂Cl₂ + H₂O sat.) with 0.1 M of Bu₄NClO₄ by scanning in the potential range from -1 V to E^{ox} at the scan rate 20 mV s⁻¹. Magnifications are ×1,000, ×10,000 and ×10,000, respectively.

We also performed depositions under potentiostatic conditions at constant potential $E = E^{\text{ox}}$ (1.75 – 2.00 V, depending on the monomer) to investigate the effect of the deposition method (current-time curves are shown in Figure S5 in the SI). In these conditions, only O₂ bubbles are produced from H₂O (2H₂O \rightarrow O₂ + 4H⁺ + 4e⁻). The experiments were performed varying the deposition charges (12.5, 25, 50, 100, 200, 400 mC cm⁻²), and SEM images of surfaces prepared at 100 mC cm⁻² are shown in Figure 9. Here, the structures obtained at constant potential are relatively close to that obtained by CV method, but often at high deposition charges. For example, ultra-long and mostly horizontally oriented nanofibers have been observed with **N-Ph-p-Cb** in (CH₂Cl₂ + H₂O sat.), but only at a deposition charge of 400 mC cm⁻².



Figure 9. SEM images of potentiostatically electrodeposited surfaces from each monomer at constant potential of E^{ox} . The modified surfaces were obtained in CH₂Cl₂ or (CH₂Cl₂ + H₂O sat.) with 0.1 M of Bu₄NClO₄ at the deposition charge of 100 mC cm⁻². Magnification is ×10,000.

2.5 Surface wettability

The wettability of all surfaces, electrodeposited from studied monomers in both solvents, CH_2Cl_2 and $(CH_2Cl_2 + H_2O \text{ sat.})$, was also studied (Table 2). To better evaluate the effect of surface roughness, smooth surfaces have also been prepared (see SI for the details) to obtain the Young's contact angles (θ^{Y}) [46] and surface energy (γ_{SV}) [47] of each polymer (Table 3). The most intrinsically hydrophilic surface is that derived from **N-Ph-2-Th** ($\theta^{Y}_{w} = 60.5^{\circ}$) while the only intrinsically hydrophobic surface ($\theta^{Y}_{w} > 90^{\circ}$) is the surface derived from **N-Ph-p-Cb**.

The results obtained with **N-Ph-2-Th** in (CH₂Cl₂ + H₂O sat.) are impressive (θ_w up to 154.0 °, Table 2), especially considering that this is the most hydrophilic polymer ($\theta_w^Y = 60.5$ °, Table 3), and are due to the presence of both cauliflower-like structures and nanotubes. This transition from hydrophilic to hydrophobic state can only be explained by the Cassie-Baxter equation (1) [48] confirming the presence of an important air fraction between water droplet and the rough surface:

$$\cos\theta = r_{\rm f} f \cos\theta^{\rm Y} + f - 1 \tag{1}$$

where θ and θ^{Y} are apparent contact angles for rough and smooth surfaces, r_{f} is the roughness ratio of the substrate wetted by the liquid, *f* and (1 - f) are the solid and air fractions, respectively.

For densely packed large-diameter nanotubes obtained with **N-Ph-3-Th**, a maximum of $\theta^{Y} = 134.3^{\circ}$ was achieved. Even larger maxima $\theta^{Y} = 150.7^{\circ}$ and 146.8 ° were obtained for **N-Ph-p-Cb** and **N-Ph-m-Cb**, consisting of extremely long mostly horizontally oriented nanotubes and tulip-like structures, respectively. In the case of **N-Ph-o-Cb**, the surfaces are much less hydrophobic (θ_{w} up to 99.5 °) because their roughness is smaller. Moreover, these surfaces are also "sticky", like rose petals or gecko feet [12,49], so water droplets remain stuck on them whatever the tilting angle is.

As mentioned in the previous section, the structure/morphology of surfaces obtained in potentiostatic conditions at E^{ox} potentials is generally similar to (or not very different from) that obtained in potentiodynamic conditions by CV. However, the surfaces deposited under potentiostatic conditions are much more hydrophilic ($\theta_{\text{w}} < 100^{\circ}$; Table 4). Indeed, at a constant potential, the electrodeposited polymers are in the p-doped state, hence, with polar perchlorate (ClO₄⁻) counterions, which should also increase surface energy.

Monomer	Number of	So	olvent: CH	I_2Cl_2	Solvent	: (CH ₂ Cl ₂	+ H ₂ O sat.)
	scans	$ heta_{ m w}$	$ heta_{ ext{DIM}}$	$ heta_{ ext{HD}}$	$ heta_{ m w}$	$ heta_{ ext{DIM}}$	$ heta_{ ext{HD}}$
		(°)	(°)	(°)	(°)	(°)	(°)
N-Ph-2-Th	1 scan	93.1	<10	<10	123.2	<10	<10
	3 scans	109.6	<10	<10	154.0	<10	<10
	5 scans	114.2	<10	<10	151.4	<10	<10
N-Ph-3-Th	1 scan	71.0	23.3	<10	63.3	49.4	<10
	3 scans	72.0	18.8	<10	132.9	11.8	<10
	5 scans	47.0	17.7	<10	134.3	13.9	<10
N-Ph-p-Cb	1 scan	143.0	16.3	<10	138.0	<10	<10
	3 scans	142.6	<10	<10	145.5	<10	<10
	5 scans	137.0	<10	<10	150.7	<10	<10
N-Ph-m-Cb	1 scans	Х	Х	Х	146.8	<10	<10
	3 scans	Х	Х	Х	144.3	14.1	<10
	5 scans	Х	Х	Х	139.6	11.7	<10
N-Ph-o-Cb	1 scan	Х	Х	Х	69.7	23.8	<10
	3 scans	Х	Х	Х	77.3	15.8	<10
	5 scans	Х	Х	Х	99.5	11.6	<10

Table 2. Apparent contact angles for rough dedoped polymer films prepared by CV electrodeposition.^a

^a θ_{w} , θ_{DIM} and θ_{HD} are apparent contact angles of water, diiodomethane and hexadecane droplets, respectively, with the electrodeposited films surface.

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Monomer	$ heta_{ m w}^{ m Y}$ (°)	$ heta_{ ext{DIM}}^{ ext{Y}}$ (°)	$ heta_{ ext{HD}}^{ ext{Y}}$ (°)	γsv	γsv,d	γsv,p	
N-Ph-2-Th	60.5	23.5	<10	47.6	31.4	16.2	
N-Ph-3-Th	85.0	47.8	14.4	33.2	28.7	4.6	
N-Ph-p-Cb	94.2	41.0	12.0	32.9	31.4	1.5	
N-Ph-m-Cb	89.8	50.0	16.5	31.3	28.6	2.7	
N-Ph-o-Cb	85.1	44.5	12.7	33.6	29.7	3.9	

Table 3. Apparent contact angles and surface energy for smooth dedoped polymer films.^a

^a θ^{Y}_{w} , θ^{Y}_{DIM} and θ^{Y}_{HD} are apparent contact angles (Young's angles) of water, diiodomethane and hexadecane droplets, respectively, with smooth film surfaces. ^b γ_{SV} surface tensions between a solid and a gas; D and V superscripts denote disperse (apolar) and polar parts of surface energies calculated by Owens-Wendt equation [47].

Monomer	Deposition	Solvent	: CH ₂ Cl ₂		Solvent	: (CH ₂ Cl ₂	+ H ₂ O sat.)
	charge	$ heta_{ m w}$	$ heta_{ ext{DIM}}$	$ heta_{ ext{HD}}$	$ heta_{ m w}$	$ heta_{ ext{DIM}}$	$ heta_{ ext{HD}}$
	(mC cm^{-2})	(°)	(°)	(°)	(°)	(°)	(°)
N-Ph-2-Th	12.5	75.6	<10	<10	63.3	<10	<10
	25	72.5	<10	<10	60.4	<10	<10
	50	69.3	<10	<10	70.1	<10	<10
	100	75.8	<10	<10	90.7	<10	<10
	200	50.1	<10	<10	84.6	<10	<10
	400	59.4	<10	<10	69.8	<10	<10
N-Ph-3-Th	12.5	49.6	23.2	<10	76.7	22.7	<10
	25	42.3	13.2	<10	79.1	14.9	<10
	50	51.1	<10	<10	67.8	13.3	<10
	100	87.7	<10	<10	32.0	39.8	<10
	200	90.1	<10	<10	37.6	44.7	<10
	400	59.4	40.0	<10	43.1	62.1	<10
N-Ph-p-Cb	12.5	80.6	26.2	<10	66.0	22.1	<10
	25	54.2	31.4	<10	81.1	12.1	<10
	50	64.8	27.7	<10	72.9	25.5	<10
	100	55.5	<10	<10	55.7	17.9	<10
	200	64.3	<10	<10	71.4	12.4	<10
	400	67.6	<10	<10	60.0	<10	<10
N-Ph-m-Cb	12.5	63.1	27.0	<10	88.9	23.0	<10
	25	80.4	16.6	<10	93.2	21.1	<10
	50	76.2	23.6	<10	81.2	15.1	<10
	100	67.3	26.0	<10	79.7	18.3	<10
	200	84.9	24.4	<10	87.8	16.6	<10
	400	51.9	30.6	<10	82.5	21.1	<10
N-Ph-o-Cb	12.5	90.5	31.0	<10	80.7	25.4	<10
	25	79.1	26.0	<10	79.5	31.2	<10
	50	76.0	44.9	<10	81.1	26.9	<10
	100	60.1	45.7	<10	80.6	26.4	<10
	200	76.0	31.8	<10	71.3	20.4	<10
	400	98.5	29.4	<10	87.1	27.6	<10

Table 4. Apparent contact angles for the rough p-doped polymer films prepared at constant potential E^{ox} .

3. Conclusion

In this article, we used a soft-template electropolymerization approach to form microtubules on the surface of a substrate from electropolymerizable conjugated monomers. Low water-solubility solvent (dichloromethane) was saturated with water to form a micellar solution stabilized by Bu_4NClO_4 as the electrolyte and the surfactant. Under these conditions ($CH_2Cl_2 + H_2O$ sat.), the formation of nanotubes was especially straightforward process. Two series of monomers composed of a triphenylamine core conjugated with thiophene (2or 3-positions of thiophene attached to *para*-position of the benzene ring of triphenylamine) or carbazole arms (attached by its N atom to *para-*, *meta-* or *ortho*-positions of the benzene ring of the core) have been invewstigated. DFT calculations of the geometry and electronic structures (for both neutral and radical cation states) of the monomers have been performed to understand the coupling processes during the electropolymerization.

Except for the N-Ph-2-Th (with attached 2-thiophene monomer arms), coupling/electropolymerization of which extends the conjugation in the "N-Ph-Th-Th-Ph-N" fragment, resulting on lower oxidation potentials, oxidation potentials other monomers are comparable/overlapping with those for the monomers. The surface structures of the electrodeposited films are significantly influenced by the structure of the monomers, including the nature of the arms (thiophene or carbazole) and the regioisomerism (the place of an attachment of the arms), as well as the electrodeposition conditions. The formation of microtubes is induced by π -stacking interactions between the monomer moieties of polymer/oligomer chains during the electrodeposition, allowing a preferential growth in one direction (1D). Because the 1D growth takes time, the rate of the polymerization/deposition is also significant factor. Unique results have been demonstrated by simply changing the attachment position of the carbazole arms: in the case of the N-Ph-p-Cb monomer with carbazole arms in the *para*-position to the benzene ring of the triphenylamine ring, ultra-long microtubes were formed (tens to >100 μ m length and diameter $\approx 1 - 1.5 \mu$ m). The extremely strong water-adhesive forces, comparable to gecko foot or rose petals, with very high $\theta_w > 150^\circ$ have been demonstrated for electrodeposited surfaces from N-Ph-2-Th and N-Ph-p-Cb in $(CH_2Cl_2 + H_2O \text{ sat.})$. These results can be used in the future in a number of applications such as water-harvesting systems, electrochemical analysis or sensing platforms.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary data

Supporting Information to this article is available online at <u>https://doi.org/10.1016/j.jelechem.XXX</u> and contains: used materials and instruments, synthesis and characterization of monomers and their ¹H / ¹³C NMR copies, computational methodology and Cartesian coordinates of optimized geometries, methods of electropolymerization and surface characterizations.

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Graphical Abstract



10 µm

1 μm

Supporting Information

Directional formation of microtubes by soft-template electropolymerization from fully conjugated triphenylamine-based monomers

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Experimental section

Monomer synthesis and characterization.

Tris(4-(thiophen-2-yl)phenyl)amine(**N-Ph-2-Th**) was purchased from Sigma Aldrich. Tris(4bromophenyl)amine and all the used boronic acids were purchased from TCI. The other original monomers were synthesized from tris(4-bromophenyl)amine and by three Suzuki reactions as shown in Scheme S1. The components used for the Suzuki reaction were tris(4-bromophenyl)amine (2 mmol, 1.0 eq.), the corresponding boronic acid (7.0 mmol, 3.5 eq.), tetrakis(triphenylphosphine)- $\frac{26}{26}$ palladium(0) (0.1 mmol, 0.1 eq.) and sodium carbonate (4.0 g). These components were mixed to a solution containing 100 mL of toluene, 20 mL of ethanol and 10 mL of water, and were refluxed for 3 days. After solvent evaporation, the crude products were purified by column chromatography (silica gel; eluent: petroleum ether).

NMR spectra were obtained with a 400 MHz ultra blinded spectrometer equipped with an AVANCE III Nano HD electronic console. The proton and carbon frequencies were 400.13MHz and 100.63MHz, respectively.



Scheme S1. Synthesis of original monomers by Suzuki reaction.

Tris(4-(thiophen-3-yl)phenyl)amine (N-Ph-3-Th).

Yield: 23%.

¹<u>H NMR</u> (400MH_Z, CDCl₃); δ (ppm): 7.50 (d, J = 8.6 H_Z, 6H), 7.38 (m, 9H) 7.18 (d, J = 8.6 H_Z, 76H). ¹³<u>C NMR</u> (100 MHz, CDCl₃) δ 146.47, 141.82, 130.56, 127.28, 126.17, 126.13, 124.36, 119.38.

Tris(4'-(9*H*-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)amine(N-Ph-p-Cb).

Yield: 13%.

 $\frac{1}{11} \text{ NMR} (400 \text{ MHz, CDCl}_3) \delta (\text{ppm}): 8.17 (\text{d}, \text{J} = 7.5 \text{ Hz}, 6\text{H}), 7.91 (\text{d}, \text{J} = 8.5 \text{ Hz}, 6\text{H}), 7.80 (\text{m}, 3\text{H}), 7.71 (\text{d}, \text{J} = 8.5 \text{ Hz}, 6\text{H}), 7.62 (\text{m}, 6\text{H}), 7.51 (\text{m}, 6\text{H}), 7.46 (\text{m}, 9\text{H}), 7.32 (\text{m}, 6\text{H}).$

¹³<u>C NMR</u> (100 MHz, CDCl₃) δ 146.80, 140.82, 139.52, 139.28, 137.25, 136.60, 135.00, 132.46, 128.50, 128.00, 127.48, 126.01, 123.50, 120.37, 120.00, 109.82.

Tris(3'-(9*H*-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)amine (N-Ph-m-Cb).

Yield: 49%.

¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.17 (d, *J* = 7.7 Hz Hz, 6H), 7.80 (m, 3H), 7.65 (m, 6H), 7.57 (d, *J* = 8.6 Hz, 6H), 7.54 (m, 3H), 7.49 (m, 6H), 7.42 (m, 6H), 7.31 (m, 6H), 7.26 (d, *J* = 8.6 Hz, 6H).

¹³C NMR (100 MHz, CDCl₃) δ147.08, 142.40, 140.87, 138.23, 134.69, 130.25, 128.02, 125.95, 125.62, 125.54, 124.54, 123.39, 120.32, 120.00, 109.80.

Tris(2'-(9H-carbazol-9-yl)-[1,1'-biphenyl]-4-yl)amine (N-Ph-o-Cb).

Yield: 77%.

<u>¹H NMR</u> (400 MHz, CDCl₃*d*) δ(ppm): 7.98 (d, J = 7.7 Hz, 6H), 7.50 (m, 12H), 7.20 (m, 6H), 7.02 (m, 12H), 6.58 (d, J = 8.6 Hz, 6H), 5.95 (d, J = 8.6 Hz, 6H).

¹³<u>C NMR</u> (100 MHz, CDCl₃) δ 146.14, 140.88, 140.39, 134.75, 132.62, 130.81, 129.67, 128.64, 128.26, 125.49, 123.32, 123.00, 119.92, 119.34, 110.00.

Tris(4-(thiophen-3-yl)phenyl)amine (N-Ph-3-Th).

Yield: 23%.

¹<u>H NMR</u> (400MH_Z, CDCl₃); δ (ppm): 7.50 (d, J = 8.6 H_Z, 6H), 7.38 (m, 9H) 7.18 (d, J = 8.6 H_Z, 76H). ¹³<u>C NMR</u> (100 MHz, CDCl₃) δ 146.47, 141.82, 130.56, 127.28, 126.17, 126.13, 124.36, 119.38.

Computational methodology.

All the computational studies were performed with Gaussian 16 package of programs⁴⁹ using the density functional theory method (DFT). The hybrid functional B3LYP, which combines Becke's three-parameter hybrid exchange functional⁴⁹⁴⁹ and Lee–Yang–Paar's gradient-corrected correlation functional,⁴⁹ and 6-31G split valence basis set supplemented by d-polarization functions were used for geometry optimizations of isolated molecules in a gas phase. No constraints were used, and all structures were free to optimize. The force constants and vibrational frequency analysis for stationary points have been calculated after optimizations to check that they are true energy minima.

Electronic structure for the optimized geometries were calculated at the same level of theory. The restricted Hartree-Fock formalism was used for the neutral states of the molecules, and unrestricted Hartree-Fock formalism was used for radical cation calculations.

Visualization of the orbital coefficients and spin density distribution (in radical cations) were performed with GaussView 6.0 software.

Soft-template electropolymerization.

Two solvents were investigated: dichloromethane (CH₂Cl₂) and dichloromethane saturated with water (CH₂Cl₂ + H₂O sat.). Because the solubility of water in dichloromethane is ultra-low, the later was very easily prepared by mixing water and dichloromethane, and after decantation the aqueous phase was discarded. Tetrabutylammonium perchlorate (Bu₄NClO₄) (0.1 M) as the supporting electrolyte and monomer (0.005 M) were added to the solvent. Three electrodes were connected to an Autolab potentiostat-galvanostat model PGSTAT100 (Metrohm). 2 cm² gold-coated silicon wafer

as the working electrode, glassy carbon rod as the counter-electrode, and saturated calomel electrode (SCE) as the reference electrode. First, the oxidation potential for each monomer were determined by cyclic voltammetry. Then, two electrodeposition methods were investigated (by cyclic voltammetry and at constant potential). The experiments by cyclic voltammetry were performed from -1 V to E^{ox} , at a scan rate of 20 mV s⁻¹ with different numbers of scans (1, 3 and 5). The experiments at constant potential were performed with a potential $E = E^{\text{ox}}$, and with different deposition charges (12.5, 25, 50, 100, 200 and 400 mC cm⁻²). Then, the substrates were abundantly washed with CH₂Cl₂.

constant potential with a low deposition charge of 1 mC cm⁻². Then, in order to have polymers in the same state (i.e. dedoped state) as in cyclic voltammetry experiments, the deposits were reduced with one back scan from E^{ox} to -1 V in a solution free of monomer.

Surface characterization.

Samples were observed by transmission electron microscopy (TEM) prior to electrodeposition using a JEOL JSM-1400 TEM. For imaging, a drop of 0.45 μ m-filtered solution was deposited onto a 400 mesh TEM copper grid with a carbon support film and the exceeding liquid was absorbed with a paper filter to avoid excessive salt deposition onto the TEM grids.

The surface structures were imaged with a JEOL JSM-6700F scanning electron microscope (SEM). The surface wettability was characterized by measuring apparent contact angles (θ) using a KRÜSS DSA30 goniometer. Three probes of liquids of different surface tensions (γ_{LV}) were used: water (72.8 mN/m), diiodomethane (50.0 mN/m) and *n*-hexadecane (27.6 mN/m).

Each value is given here is a mean value of five measurements. For characterizing the water adhesion, a water droplet was placed on the substrate and the substrate was inclined until the droplet moved. If the droplet moved, that indicated extremely high water adhesion (parahydrophobic or sticky superhydrophobic). For smooth surfaces, the apparent contact angles are called Young' angles (θ^{Y}). Their surface energy γ_{SV} were calculated with the Owens-Wendt equation as well as their polar ($\gamma_{SV,P}$) and dispersive ($\gamma_{SV,D}$) parts.



Figure S1. B3LYP/6-31G(d) optimized geometries of studied monomers in a gas phase. For clarity, two views of each structure are shown, i.e. perpendicular to the triphenylamine plane and in the plane.



Figure S2. Orbital coefficients distribution in studied monomers, from HOMO–3 to LUMO+3 orbitals, calculated at B3LYP/6-31G(d) level in a gas phase.

Electrochemical characterization



Figure S3. Cyclic voltammograms of studied compounds on cycling. Electrodepositions were performed in CH_2Cl_2 or $(CH_2Cl_2 + H_2O \text{ sat.})$ as solvents and with 0.1 M of Bu_4NClO_4 as an

electrolyte. The range of potential scanes was from -1 V to E^{ox} , scan rate 20 mV s⁻¹. First five scans are shown.



Figure S4. SEM images of electrodeposited surfaces from **N-Ph-3-Th** by CV in (CH₂Cl₂ + H₂O sat.) with 0.1 M of Bu₄NClO₄ for 1, 3 and 5 scans in the potential range from -1 V to E^{ox} at the scan rate of 20 mV s⁻¹. Magnification is ×10,000.



Figure S5. Potentiostatic electrodeposition of studied monomers at applied potentials E^{ox} (currents *vs* time curves at constant potential E^{ox} are shown) in CH₂Cl₂ or (CH₂Cl₂ + H₂O sat.) as solvents, with 0.1 M of Bu₄NClO₄ as an electrolyte.



Figure S6.¹H NMR spectrum of N-Ph-3-Th in CDCl₃.



Figure S7.¹³C NMR spectrum of N-Ph-3-Th in CDCl₃.



Figure S8.¹H NMR spectrum of N-Ph-p-Cb in CDCl₃.



Figure S9.¹³C NMR spectrum of N-Ph-p-Cb in CDCl₃.



Figure S10.¹H NMR spectrum of N-Ph-m-Cb in CDCl₃.



Figure S11.¹³C NMR spectrum of N-Ph-m-Cb in CDCl₃.



Figure S12.¹H NMR spectrum of N-Ph-o-Cb in CDCl₃.





N-Ph-2-Th,	neutral	state
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 $\overline{E_{total}} = -2405.1372798$ Hartree // B3LYP/6-31G(d)

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$\frac{\textbf{N-Ph-3-Th, neutral state}}{E_{total} = -2405.1346219 \text{ Hartree } // \text{ B3LYP/6-31G(d)}$

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 $\frac{\mathbf{N}-\mathbf{Ph}-\mathbf{p}-\mathbf{Cb}, \text{ neutral state}}{E_{\text{total}} = -2991.6888124 \text{ Hartree } // \text{ B3LYP/6-31G(d)}$

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Н	-11,92299200	-7.78933600	1,21076200
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Н	-12.68851100	-5.27547300	-3.30048900
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	12.031/2300	-1.02230300	1.20403400
Н	10.91276700	-8.35239600	-3.29848800
Н	8.68520100	-7.45755000	-3.90918400
Н	7,51693900	-5,83435700	-2.44293700
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п 	0.03943800	-3.40333200	2.44343200
Н	10.85060800	-3.63674800	3.91157900
Н	12.76073700	-5.09180200	3.30329400
Н	12.70897500	-6.42766100	1.20993200
Н	-1.42568600	9.40456100	2.44467200
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Н	-1.96659100	13.59631900	3.30531600
Н	-0.78578300	14.21940600	1.21084000
Н	0.58527200	14.230411004 7	-1.20488900
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Н	1.77462800	13.62635900	-3.30009800
Н	2.11257100	11.24984600	-3.91137700
Н	1.29224800	9.42644600	-2.44453300

<u>N-Ph-m-Cb, neutral state</u> $E_{total} = -2991.688235$ Hartree // B3LYP/6-31G(d)

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C	3 57766900	-0 70104700	0 61864300
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C	-1.24898600	-1.96051500	0.62992700
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С	-4.64884900	-4,64182600	-0.06687100
C	-5 79796000	-5 /38/0000	-0 06236300
L	-3.79798000	-3.43849800	-0.06236300
С	-7.06182500	-4.84619500	-0.17108600
С	-7.15804600	-3,46008600	-0.28779000
C	-6 01364000	-2 66510500	_0 27671200
C	-0.01304900	-2.00510500	-0.2/0/1200
С	6.34615900	-1.70370200	-0.06791400
С	7.61080800	-2.30021400	-0.06322900
C	7 73019400	-3 69081400	-0 17252500
0	7.75019400	5.05001400	0.17232300
С	6.57811600	-4.46737300	-0.29007700
С	5.31727500	-3.87408300	-0.27914700
C	-1 69666600	6 34637400	-0 06873000
0	1.01007700	7 72077200	0.00075000
C	-1.81297700	1.13911300	-0.06431500
С	-0.66872700	8.53893700	-0.17416400
C	0 57998100	7 92995300	-0 29254300
0	0.00710000	C E 41 4 2 2 0 0	0.20170100
L	0.69/16900	6.54143200	-0.281/0100
N	-5.67838900	-6.85123500	0.04005400
N	-3.09660800	8.34159000	0.03953300
NT	0 77420000	1 40010700	0 02000700
IN	8.77430900	-1.49010700	0.03988700
С	-6.18438600	-7.78455200	-0.87240600
С	-5.85410600	-9.09013300	-0.42721900
C	-5 11817900	-8 93787500	0 81052600
°	5.1101/200		1 00000
C	-5.02819100	-/.54564400	1.0666/000
С	9.83566000	-1.46081800	-0.87243500
С	10.80125400	-0.52257600	-0.42618000
C C	10 20120400	0 02767700	0 01100500
	10.30120400	0.03/0//00	0.01190200
С	9.05044200	-0.58069600	1.06733300
С	-3.65377700	9.24585800	-0.87236200
C C	4 04020100	0 61107700	0 42520700
L	-4.94920100	9.01107700	-0.42556700
С	-5.18314200	8.89843600	0.81279200
С	-4.02151000	8.12525600	1.06744000
C	-4 5/8/1000	-9 8/310100	1 71350100
	4.54041000	9.04319100	T. / T. 3 3 0 T 0 0
C	-3.90995300	-9.35691900	2.85064900
С	-3.84297100	-7.97457900	3.09644000
C	-4 40051300	-7 05189900	2 21379100
		7.00109900	2.213/3100
C	-6.8//45000	-/.5/209300	-2.06/38000
С	-7.25439300	-8.69173400	-2.80598700
C	-6 94717100	-9 99326300	-2 37303400
- -	0.04564000	10 10774400	1 10050000
L	-0.24564900	-10.19//4400	-1.18820300
С	-3.12520200	9.73988500	-2.06820200
С	-3.90787300	10.62561400	-2.80584400
-		43	

C	5 10000700	11 00066400	2 27107400
L	-5.18822700	11.00966400	-2.3/10/400
C	-5./1419900	10.50423000	-1.185/8200
С	-6.25070600	8.85696600	1.71733900
С	-6.14661600	8.06109600	2.85442600
С	-4.98210200	7.31274800	3.09864700
C	-3 90555300	7 33/96800	2 21//3800
C	0.0011000	7.55490000	2.21445000
C	9.99811000	-2.16597000	-2.06819200
С	11.15627400	-1.93191100	-2.80648900
С	12.12992300	-1.01568800	-2.37245900
С	11.95630800	-0.30714600	-1.18718100
С	10.80009600	0.98317700	1.71563700
C	10 05936700	1 20232300	2 85272100
C	10.03930700	1.29252500	2.03272100
C	8.82867800	0.65898800	3.09///100
С	8.30870700	-0.28474700	2.21443500
Н	0.74786300	-2.14351500	-1.58379200
Н	2.96482800	-3.20156100	-1.58934800
Н	4.35606800	-0.29905900	1,26117300
ц	2 14061200	0 76136600	1 26167500
11	2.14001200	0.70100000	1.2010/300
H	-0.40985900	-2.23489200	1.26106100
H	-2.43668500	-3.62231200	1.26110400
Н	-4.25445900	-0.96483000	-1.58823200
Н	-2.22917100	0.42499800	-1.58343000
Н	1.48270100	1.71811000	-1.58546900
ч	1 29067800	4 16687100	-1 59179000
11	1 01602500	2 02172600	1 26000000
п	-1.91082300	3.921/3000	1.20000000
Н	-1./2/99/00	1.4/28/900	1.26186/00
H	-3.67742400	-5.12411900	-0.03102300
Н	-7.95083000	-5.46826600	-0.15083400
Н	-8.13687800	-2.99457000	-0.36379900
Н	-6.10957000	-1.58475300	-0.32922600
н	6 27797600	-0 62132300	-0 03192800
и и	8 71354400	-4 14946000	-0 15244900
п	0./1554400	-4.14940000	-0.13244900
Н	6.66469500	-5.54//4600	-0.36680500
H	4.42981900	-4.49754500	-0.33253400
Н	-2.59965700	5.74571300	-0.03184000
Н	-0.76357200	9.61980900	-0.15378200
Н	1.47207100	8.54542100	-0.36978700
н	1 68102900	6 08507400	-0 33566200
н	-4 60882400	-10 91287000	1 53008000
11	4.00002400	10.91207000	2.55000000
н	-3.46346100	-10.04999300	3.55/96800
Н	-3.34938300	-/.61453600	3.99518000
Н	-4.35573700	-5.98681600	2.41621100
Н	-7.11065300	-6.57023200	-2.41249000
Н	-7.79544400	-8.55193200	-3.73799800
Н	-7.25748200	-10.84511500	-2,97142500
ч	-6 00067500	-11 20433200	-0 85946700
11	2 14122400	0 44121200	2 41466000
п	-2.14132400	9.44131300	-2.41400000
Н	-3.51/8/800	11.02435100	-3./3849400
Н	-5.77204600	11.70387600	-2.96877100
Н	-6.70817900	10.79482800	-0.85555800
Н	-7.14757200	9.44342900	1.53515600
Н	-6.96906500	8.02044300	3,56290000
	-4 91538700	6 70535500	3 99732000
11	2 00101000 7.JLJJJU/000		0 A1EE1200
п	-3.00484900	0./0425500	2.41551300
Н	9.24696200	-2.86834600	-2.41410600
Н	11.30574100	-2.46935500	-3.73908900
Н	13.02282200	-0.85793100	-2.97067500
Н	12.70553400	0.40799500	-0.85742900
Н	11.75672300	1.46580200	1.53279000
н	10 43611000	2 02512800	3 56058500
 U	Q 26070200	0 00500000	3 99647100
11	0.209/0200	0.90390000	J. JJ04/100
н	/.36386/00	-0.//805100	2.41626500

 $\frac{\textbf{N-Ph-o-Cb, neutral state}}{E_{total} = -2991.6758183 \text{ Hartree } // \text{ B3LYP/6-31G(d)}}$

С	-0.85431400	1.13124200	-0.40025100
N	0.00054500	-0.00216100	-0.42881000
С	-0.55397400	-1.3090240044	-0.40092500

1 10917900	0 17138500	-0 40117000
1.40047000	0.1/150500	0.4011/000
0.01027100	-2.31502200	0.39861200
-0 54874400	-3 58846900	0 42240300
0.54074400	5.50040500	0.42240500
-1.69478500	-3.90289700	-0.32658500
-2 24901600	-2 88967900	-1 12688600
2.24901000	2.00907900	1.12000000
-1.68561600	-1.62004400	-1.17273000
2 24478600	-0 65409700	-1 17183400
2.244/0000	-0.03409700	-1.1/103400
3.62589300	-0.50552100	-1.12775900
4 22604000	0 40254000	0 22042000
4.22604800	0.48354900	-0.33042800
3,38064900	1,31925300	0.41799800
1 00040000	1 1 6 5 0 4 4 0 0	0 0000000
1.99843000	1.16504400	0.39604800
-0.55829500	2,26717300	-1.17160900
1 27705500	2 20020700	1 1050000
-1.3//05500	3.38922700	-1.12589000
-2 53210200	3 41471600	-0 32627100
2.00210200	5.111/1000	0.52027100
-2.83221200	2.26469300	0.42249500
-2 00788200	1 14455300	0 39898000
2.00700200	1.14455500	0.55050000
5.69823100	0.68514300	-0.29614800
-2 25853400	-5 27765500	-0 28902100
2.23033400	5.27705500	0.20902100
-3.44218200	4.58928900	-0.28993100
6 62200000	_0 37134700	_0 13339900
0.02200000	-0.3/134/00	-0.13220000
7.99973300	-0.11878100	-0.12941600
0 10775000	1 17644700	0 20116100
0.40775000	1.1/044/00	-0.28448400
7.58851000	2.23405900	-0.42569000
C 01007000	1 0055000	0 40706000
6.2182/800	1.98550200	-0.42/96200
-3,63638200	-5.54757200	-0.12571500
4 10707100	0.000	0 11055000
-4.10/9/100	-6.86555200	-0.11855200
-3.23170700	-7.93764100	-0.26891000
1 0 0 0 0 0 0 0 0		0.20092000
-1.86566200	-/.69020000	-0.40965300
-1 39389800	-6 37998300	-0 41599900
1.0000000	0.01005500	0.11000000
-2.98887000	5.91825500	-0.12/1/000
-3.89580300	6.98455800	-0.12256100
5.05000000	6.36100000	0.22200200
-5.26189900	6./5989400	-0.2/456200
-5.72881000	5,45241300	-0.41450700
0.72001000	0.10211000	0.1100700
-4.82868600	4.38983500	-0.41861800
6.18900100	-1.71812400	0.05850300
4 5045000	1 10012100	0.00000000
-4.58453000	-4.4964/800	0.06036200
-1 60518100	6 21592800	0 06054300
1.00010100	5.21552000	0.00001000
-0.85210100	5.93833600	1.20420100
0 45840800	6 45319900	1 03076200
0.10010000	0.10019900	1.0007.0200
0.49343300	1.0/669000	-0.2/598600
-0.79939100	6.91641300	-0.83946000
6 20170600	0.7000000	0.00050500
6.391/9600	-2.76803500	-0.83952500
5,88519800	-3,96669300	-0.27280200
5.0001000	2 60102000	1 02204700
5.36450/00	-3.62193800	1.03394/00
5.57373300	-2.22915400	1.20411400
E 0100000	2 2220200	1 00747600
-2.81868000	-2.82389300	1.02/4/600
-6.37819700	-3.10837100	-0.27774400
-5 59479500	-4 15020600	-0 03036000
5.59479500	4.13020000	0.03930900
4.76013800	-4.35702800	2.06096700
4 38086500	-3 70343900	3 22986900
1.90000900	5.70515500	5.22900900
4.60389100	-2.32342900	3.38306800
5 20299600	-1 56834000	2 37750900
0.2020000		2.3,,30000
0.96205400	-2./4134200	-2.11220800
7.02838100	-3.94218400	-2.81984600
	- 1 401 - 500	2.010000
6.53755600	-5.14017500	-2.27233300
5,96502800	-5.15807000	-1.00314900
7 440002000	0.000,000	1 01000000
-/.44928/00	-2.58411900	-1.01062300
-7,72071500	-3,09478700	-2.27731100
C 0000000	4 10007000	2.2,01000000
-0.92982000	-4.1223/800	-7.9TA88800
-5,85732700	-4.66317900	-2.11293800
4 21 22 7 200	2 00421 000	2 27/07/00
-4.3133/300	-2.80431600	3.3/62/400
-5.39591000	-1.92061300	3.21876700
C 1E17E700	1 00700100	2 0500700
-0.131/3/00	-1.92/28100	2.05000/00
-1.23613500	5.28674900	2.37848500
-0 28010500	5 14489500	3 38153100
0.20010300	5.14409000	J.JUTJJT00
1.02625500	5.64146700	3.22507500
1 39978300	6 29690800	2 05535700
1.0000	0.29090000	2.000000/00
1.48360000	/./4126900	-1.00883800
1,17880200	8,22811900	-2.27731200
1.1/000200	0.22011900	2.21101200
	8.U543/400 15	-2.82164100

C	-1 11066500	7 39682700	-2 11473100
H	0 88117400	-2 09509200	1 00734400
Н	-0 10595200	-4 34483400	1 06501800
Н	-3 11564000	-3 10224200	-1 74451100
н	-2 12147400	-0 85905500	-1 81195600
ц	1 80391400	-1 /1367200	_1 80929000
11 U	1.00391400	-1 15030400	-1 7//79100
11 U	1 372/8700	1 81011000	1 0039/900
11 U	1.37240700	2 26486700	-1 81054900
11 U	_1 12020700	2.20400700	_1 7/222700
п	-1.12029700	4.24034000	-1.74323700
п	-3.70913700	2.23031300	1.00442000
п	-2.23232100	0.27900000	1.00/21900
н	8.6/920300	-0.95406600	0.01174200
H	9.55883600	1.35/3/300	-0.28234800
H	7.95227400	3.25100400	-0.54456000
H	5.52302600	2.80818800	-0.56/91400
H	-5.1/146100	-7.03430700	0.02218500
H	-3.61206600	-8.95511300	-0.26361000
H	-1.16/94100	-8.51514900	-0.52485600
H	-0.33334500	-6.19134/00	-0.55524100
H	-3.51164900	7.99057800	0.01763900
H	-5.95393200	7.59716600	-0.27104600
Н	-6.79169500	5.25920600	-0.53099200
Н	-5.19409900	3.37646800	-0.55758600
Н	4.59407400	-5.42541200	1.94767600
Н	3.91215200	-4.26327400	4.03435600
Н	4.30457300	-1.83306700	4.30553100
Н	5.37378600	-0.50400800	2.50019400
Н	7.34397400	-1.81841200	-2.54048500
Н	7.46899900	-3.94916700	-3.81319400
Н	6.60533300	-6.05954800	-2.84703600
Н	5.58358200	-6.08583200	-0.58421400
Н	-8.06104300	-1.78709300	-0.59559900
Н	-8.55034700	-2.69563300	-2.85394400
Н	-7.15660900	-4.50499300	-3.81140600
Н	-5.24984100	-5.45804300	-2.53413600
Н	-3.73880900	-2.78627500	4.29851100
Н	-5.64532200	-1.23029400	4.01974800
Н	-6.99309500	-1.24875000	1.93341700
Н	-2.24306800	4.90280300	2.50374100
Н	-0.55288300	4.64038200	4.30459300
Н	1.74746600	5.51514900	4.02769900
Н	2.40784300	6.68714100	1.93963400
Н	2.47885900	7.87458800	-0.59240300
Н	1.93978700	8.74628500	-2.85396200
Н	-0.32213200	8.43937100	-3.81450200
Н	-2.10195500	7.26621000	-2.53725600
Н	3.81409600	2.08296300	1.05829300
С	-4.71830700	-3.70215600	1.20197800
С	-3.96046100	-3.70636200	2.37527000
Н	-3.12493900	-4.38680200	2.50141300

N-Ph-2-Th, radical cation

$E_{ t total}$	= -2404.923962	Hartree	// UB3LYF	°∕6-31G(d)
С	1.01211	437 -0.98	8410846 0.	.07111476
N	-0.00012	629 -0.00	0.012318	.07181746
С	0.34592	864 1.3	6849409 0.	.07107759
С	-1.35839	461 -0.38	8470308 0.	.07115832
С	-0.39670	824 2.29	9555222 0.	.83172165
С	-0.04982	187 3.63	3340169 0.	.83305659
С	1.04084	804 4.13	1723363 0.	.07022421
С	1.77125	772 3.1	7233626 -0.	.68872419
С	1.44026	616 1.82	2975608 -0.	.68826838
С	-2.30509	420 0.33	3238062 -0.	.68813955
С	-3.63330	092 -0.05	5222022 -0.	.68847739
С	-4.08639	264 -1.15	5715396 0.	.07057411
С	-3.12200	224 -1.85	5973554 16 0.	.83341283
			10	

С	-1.78993521	-1.49129423	0.83193737
С	0.86444446	-2.16249409	-0.68821369
С	1.86173108	-3.12034392	-0.68876212
С	3.04529964	-2.96014731	0.07005635
С	3.17157580	-1.77369874	0.83293081
С	2.18632625	-0.80444263	0.83170762
С	1.38508549	5.52783005	0.07597168
С	-5.48011784	-1.56431961	0.07638694
С	4.09497315	-3.96336356	0.07548131
С	0.64234133	6.59296553	0.56229684
С	1.27623326	7.84869626	0.40442106
С	2.50542509	7.74755837	-0.19961707
S	2.90531974	6.11328117	-0.58534366
С	-6.03135934	-2.73949031	0.56407339
С	-7.43573168	-2.81861153	0.40581914
С	-7.96254023	-1.70434704	-0.19990819
S	-6.74703861	-0.54142769	-0.58683498
С	5.38868718	-3.85267509	0.56206286
С	6.15956444	-5.02919751	0.40355029
С	5.45774671	-6.04292525	-0.20127899
S	3.84241681	-5.57228004	-0.58696253
Н	-1.22062473	1.94948547	1.44655499
Н	-0.61183574	4.31617847	1.46059828
Н	2.59525194	3.50363788	-1.31310687
Н	2.00201888	1.13342566	-1.30149893
Н	-1.98298621	1.16698931	-1.30145854
Н	-4.33223314	0.49576058	-1.31281089
Н	-3.43225887	-2.68781495	1.46100742
Н	-1.07825593	-2.03178339	1.44675904
Н	-0.01947882	-2.30092327	-1.30140203
Н	1.73665893	-3.99959098	-1.31315348
Н	4.04398634	-1.62825761	1.46031137
Н	2.29863215	0.08214769	1.44649094
Н	-0.34216517	6.48027379	1.00171925
Н	0.84212054	8.79039549	0.71987621
Н	3.20130125	8.54174626	-0.43577764
Н	-5.44170296	-3.53512275	1.00488374
Н	-8.03431344	-3.66498083	0.72223885
Н	-8.99818170	-1.49913652	-0.43673112
Н	5.78304684	-2.94390091	1.00211571
Н	7.19213097	-5.12402649	0.71910771
Н	5.79790635	-7.04241212	-0.43806432

 $\frac{\mathbf{N}-\mathbf{Ph}-\mathbf{3}-\mathbf{Th}, \text{ radical cation}}{E_{\text{total}} = -2404.917917 \text{ hartree } // \text{ B3LYP/6-31G(d)}$

С	1.01912747	-0.97885513	-0.01115028
Ν	-0.00767586	-0.00928737	0.01995663
С	0.31853969	1.36514104	0.03552285
С	-1.36087102	-0.41403731	0.03529482
С	-0.42209985	2.26599649	0.82662464
С	-0.09429834	3.61091648	0.83984167
С	0.97264633	4.12079757	0.06659068
С	1.70368569	3.20105697	-0.71945008
С	1.39101214	1.85380584	-0.73885926
С	-2.32904983	0.30129463	-0.69944863
С	-3.65204502	-0.10170647	-0.68061258
С	-4.07454427	-1.22542140	0.06571697
С	-3.09088122	-1.92527578	0.79983229
С	-1.76225782	-1.53680532	0.78661827
С	0.87735769	-2.14503721	-0.78963440
С	1.88955180	-3.08899480	-0.81794162
С	3.07842239	-2.92274615	-0.07281610
С	3.20176783	-1.74609324	0.70084678
С	2.20111016	-0.79183783	0.73503709
С	1.30261792	5.54734235	0.08103535
С	-5.47493926	-1.65284160	0.07934187
С	4.13724569	-3.9336891747	-0.10291673
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С	0.92385482	6.46538910	1.12481861
С	1.34769284	7.73985323	0.89752628
S	2.21117044	7.87057504	-0.60460210
С	2.01277767	6.19242127	-0.91775120
С	-6.06873720	-2.48204839	1.09698781
С	-7.38717681	-2.74230355	0.87445164
S	-7.94944912	-1.99851364	-0.59175027
С	-6.40031151	-1.31926409	-0.89559850
С	4.30112428	-4.91787176	-1.14228512
С	5.36045218	-5.74806018	-0.93213631
S	6.18807714	-5.37008681	0.54815931
С	5.10778134	-4.07407216	0.87505771
Н	-1.23643822	1.89920511	1.44214262
Н	-0.68193915	4.28403693	1.45460137
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Н	1.95858247	1.17296597	-1.36401989
Н	-2.03010254	1.15762918	-1.29424090
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Н	-0.01821393	-2.29093203	-1.38390934
Н	1.75444143	-3.97927545	-1.42249613
Н	4.10548768	-1.57477218	1.27625906
Н	2.31556639	0.09394318	1.35047286
Н	0.39092693	6.17726875	2.02332837
Н	1.21772560	8.61049411	1.52591850
Н	2.38978656	5.77442342	-1.84101816
Н	-5.54235268	-2.83641988	1.97544647
Н	-8.06906414	-3.31543360	1.48791317
Н	-6.23743065	-0.74617659	-1.79799804
Н	3.67701449	-4.97764482	-2.02617957
Н	5.71563749	-6.55240843	-1.56193674
Н	5.21434954	-3.50974852	1.79127341

 $\frac{\mathbf{N}-\mathbf{Ph}-\mathbf{p}-\mathbf{Cb}, \text{ radical cation}}{E_{\text{total}} = -2991.476981 \text{ Hartree } // \text{ B3LYP/6-31G(d)}}$

С	-1.41079438	0.11767234	-0.00247618
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С	0.60274056	-1.27996516	-0.00234844
С	0.80634443	1.16260562	-0.00256890
С	1.75442860	-1.52901504	0.76738799
С	2.34118129	-2.78495632	0.76248368
С	1.81218626	-3.84624648	-0.00160795
С	0.65711411	-3.57906948	-0.76609194
С	0.06194239	-2.32709498	-0.77173329
С	1.98328835	1.21786510	-0.77238417
С	2.77005462	2.35919702	-0.76682505
С	2.42437046	3.49297712	-0.00194089
С	1.24099225	3.42045979	0.76251879
С	0.44654741	2.28443515	0.76746705
С	-2.20242187	-0.75465945	0.76775731
С	-3.58347209	-0.63468613	0.76275617
С	-4.23797773	0.35364976	-0.00200379
С	-3.42894051	1.21979632	-0.76702031
С	-2.04712475	1.10915700	-0.77248936
С	3.26498734	4.70322861	-0.00140971
С	2.44036432	-5.17917682	-0.00113566
С	-5.70640752	0.47626435	-0.00166441
С	4.65959835	4.62534559	-0.18837774
С	5.45661708	5.76146556	-0.18329223
С	4.88162116	7.03024400	0.00000406
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С	2.26178162	-7.60641087	-0.18227144
С	3.64826004	-7.74226813	0.00008731
С	4.42597376	-6.5863302348	0.18177400

С		
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Н Н		
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н Н		

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4.84857774	9.34175839 10.47725391	2.09898544
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-10.29315891 -10.51517163	2.20914475 -0.47184055	-2.09832616 2.09871321
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-1.72520505 -4.16580369	-1.50414272 -1.29144143	1.39026432 1.40116529
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Н	8.71762488	11.24004820	-1.15655136
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Н	-14.09414469	1.92684109	-1.15835462
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Н	-10.98720393	3.33246999	-3.78733613
Н	-9.24877951	2.26709794	-2.38409166
Н	-9.49461753	-0.70226310	2.38353717
Н	-11.38443501	-1.46463467	3.78840744
Н	-13.72213223	-0.91603122	3.18539908
Н	-14.21751120	0.43718580	1.16216551
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Н	6.96458052	-9.12312970	3.78656279
Н	7.65808111	-11.42218519	3.18420778
Н	6.73200722	-12.52915012	1.16255895
Н	5.37794324	-13.16867718	-1.15635437
Н	3.93576988	-13.18026531	-3.17873881
Н	2.60428154	-11.18259908	-3.78366176
Н	2.65882530	-9.14361215	-2.38151476

N-Ph-	m-Cb, radical cati	on	
$E_{ total}$	= -2991.469723 Har	rtree // B3I	LYP/6-31G(d)
С	-1.18128938	0.78288443	-0.17469516
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С	1.26703832	0.63131467	-0.17513201
С	-0.08839679	-1.41325155	-0.17419248

C	1.20/03032	0.03131407	0.1/313201
С	-0.08839679	-1.41325155	-0.17419248
С	2.32230533	0.11626895	-0.94970074
С	3.56234889	0.73878685	-0.94460483
С	3.80360832	1.89412274	-0.17584264
С	2.73643611	2.39844443	0.59280017
С	1.49261953	1.78388023	0.59952326
С	0.79714037	-2.18436983	0.60079729
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С	-1.26325368	1.95414114	-0.94944937
С	-2.42253462	2.71660092	-0.94412867
С	-3.54336365	2.34787258	-0.17482967
С	-3.44614892	1.17171011	0.59401939
С	-2.29186276	0.40202737	0.60051826
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7.08685819	8.18119108	-0.39586637
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5 98839036	6 76755603	1 05568767
-9 54499886	2 83711361	-0 84947001
-10 62934755	2.03/11301	-0 39630272
-10 19078793	1 38526373	0.81963595
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4 96363630	-0 61217120	1 71/001/04
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2.88000972	-7.73977682	2.1810/639
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2.3302/339	-11.13/9/004	-2.74207042
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-11.906/8984	2.77505820	-2.29988633
-11.81/62316	2.02040038	-1.13009352
-10.80/93518	0.511051/8	1./1/58310
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8.47900304	7.59437854	-2.74246516
8.36048136	8.92123895	-2.29848332
7.66154595	9.22182015	-1.12929178
5.84796964	9.10299552	1.71755762
5.11164224	8.70683575	2.83393857
4.83080564	7.35025537	3.06264991
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4.34750956	0.34594314	-1.58298775
2.89568702	3.26457049	1.22775741
0.69664484	2.17570356	1.22391749
1.53429467	-1.69040721	1.22495198
1.37836606	-4.13942263	1.22992121
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-0.42520825	2.24500747	-1.57396020
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-4.27565643	0.87655671	1.22923599
-2.23271674	-0.48303885	1.22512334
1.78581731	-6.03537691	-0.02656128
-0.57184143	-9.61642101	-0.17515803
-2.63571189	-8.24679810	-0.39757941
-2.50348144	-5.78238933	-0.36274263
4.33468962	4.56469652	-0.02782751
8.61463106	4.31081159	-0.17781227
8.45874015	1.83899866	-0.40227405
6.25772042	0.72265024	-0.36745662
-6.12123306	1.47149189	-0.02688865
-8.04300814	5.30409893	-0.17900602
-5.82476415	6.40590814	-0.40269404
-3.75688526	5.05880207	-0.36656082
5.75876750	-10.33477495	1.54950510
5.81355121	-8.84485174	3.53512093
3.98634546	-7.22591782	3.94504311
2.07447372	-7.03916159	2.37431563
0.78085335	-9.68213525	-2.38624844
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4.01458205	-12.48964625	-2.87823339
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-8.77749663	4.16241530	-2.38913255
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Н	-11.83052645	0.18315170	1.55301567
Н	-10.56687627	-0.60705336	3.53901919
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Н	8.81305120	9.72180306	-2.87571185
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Н	5.06124328	5.31372498	2.37338187

N-Ph-o-Cb, radical cation

E_{total}	=	-2991.	460	755	Har	tree	//	в3	LYP	/6-	-31	.G ((d)
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N			-0.	00244	1643	0.0	0176	645	- (.43	3257	684	
С			-1.	27839	9701	-0.6	0517	678	- (0.41	.792	2032	
C			1.	16147	7716	-0.7	9943	669	- (.41	.573	3710	
С			-1.	51096	5169	-1.7	6023	862	(0.35	6413	3283	
С			-2.	77992	2296	-2.3	1714	879	().39	535	5878	
С			-3.	85694	4460	-1.7	51492	253	- (0.31	637	059	
С			-3.	59866	5973	-0.6	16623	369	- 2	L.11	209	018	
С			-2.	33610	5147	-0.0	4962	195	- 2	1.10	5401	805	
С			1.	21142	2071	-1.9	9291	507	-1	1.16	5218	8089	
С			2.	33411	1843	-2.8	02093	155	-1	1.10	834	1385	
С			3.	44426	5911	-2.4	5805	653	- (0.31	.021	.090	
С			3.	39341	1830	-1.2	4286	415	().40)197	/506	
C			2.	27632	2/69	-0.4	2288	302	(1.35	860	842	
C			1.	11969	9534	2.0	4839:	5/4		L.10	429	1569	
C			1.	20103 41043	9989	3.4	23014 16009	4/6 5//		L•11 \ 21	210.	0000	
C			_0.	41043 6180/	1916	4.2	10000 6647'	544 525	-() 30 1.21	243	211	
C			-0.	77221	1579	2.1	8929'	162	() 35) 35	641	770	
C			٥. م	64306	5560		2374	197	- (1 22	270	064	
C			-5.	20645	5906	-2.3	56170	127	- ().23	3241	513	
C			0.	56445	5869	5.6	8657	110	- ().22	2543	3093	
C			4.	55926	5712	-4.7	29312	210	- (0.08	3444	158	
С			5.	72277	7503	-5.5	0660	649	- (0.06	5007	7500	
С			6.	97673	3625	-4.9	0978	146	- (0.10	5321	772	
С			7.	07631	L222	-3.5	2083	968	- (0.27	401	212	
С			5.	92302	2406	-2.7	43354	436	- (0.29	9629	9484	
С			-6.	38134	4516	-1.5	8056	134	- (0.08	3943	3717	
С			-7.	63657	7789	-2.1	9895	402	- (0.06	638	3576	
С			-7.	74748	3561	-3.5	8293	925	- (0.17	377	276	
С			-6.	5949(0660	-4.3	6394	005	- (0.28	3747	7554	
C			-5.	34461	18/2	-3.7	5454: 1 2 4 E I	592	-().30	0824	1030	
C			⊥. 1	8230.	1507	6.3 77	1345:	527 702	-(J.U8	314	1221	
C			1.	91981 77005	16/5	/./	0948 0002.	103	-(J.U3	000	3246	
C			-0	17590. 47590	5985	7 8	9506'	±24 558	-() 25	1991 1983	2622	
C			-0	57601	1982	65	0781	779	- (1 20	200	1493	
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С			5.	13759	9069	4.7	5353'	745	- (0.31	.160	825	
С			4.	10329	9368	5.5	7673	957	- (0.82	2475	5288	
С			2.	78465	5967	-6.3	3692	153	- (0.82	2608	8161	
С			1.	55761	1862	-6.8	26272	247	- ().31	.059	843	
С			1.	33524	1884	-6.1	5222	930	().95	386	5299	
C			2.	43393	3334	-5.2	7936	573	-	L.15	540)148	
С			-5.	9985	/417	1.9	20034	438	(J.95	/90	117	
C			-6.	09422	2354	2.0	68204	491 200	-(1.30	15/3	5Z45	
C			-6.	8853 2201	1258 1510	0.7	62333 2500	902 101-	-(J.82	:433	593	
C			υ.	32814	7 D T Q	-6.2	2006	^{4 o} 45	2 -	1.92	249	0ZU	

â	0 401 50 700	F 42071001	2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2
C	0.43150/93	-5.439/1801	3.06865206
C	1 536/81//	-1 59198400	3 25856071
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C	2.55813808	-7.71925961	-2.75944097
-	1.00010000		
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9	7 07011420	1 ([[0 0 1 0 7	0 75460050
L	-/.9/011439	1.0552913/	-2./5460359
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C	1 02020605	2 24021024	2 07217710
L	-4.92020005	2.34031034	5.0/51//10
C	-5 55685007	2 82586620	1 92856071
-		2.0200020	1.02000011
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H	6.00418159	-1.66670270	-0.41418826
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H	-6.6/120931	-5.44409108	-0.36802958
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H	4.92291175	2.98129578	1.78157249
H H	4.92291175 6.22796526 7.12888317	2.98129578 3.98425936	1.78157249 -0.66168320
H H H	4.92291175 6.22796526 7.12888317 7.37315557	2.98129578 3.98425936 5.16726868	1.78157249 -0.66168320 -2.83006075
н Н Н	4.92291175 6.22796526 7.12888317 7.37315557	2.98129578 3.98425936 5.16726868	1.78157249 -0.66168320 -2.83006075
н Н Н Н	4.92291175 6.22796526 7.12888317 7.37315557 5.54145647	2.98129578 3.98425936 5.16726868 6.58139639	1.78157249 -0.66168320 -2.83006075 -3.70790035
н Н Н Н	4.92291175 6.22796526 7.12888317 7.37315557 5.54145647 3.42636725	2.93075043 2.98129578 3.98425936 5.16726868 6.58139639 6.86182222	1.78157249 -0.66168320 -2.83006075 -3.70790035 -2.43800940
н Н Н Н Н	4.92291175 6.22796526 7.12888317 7.37315557 5.54145647 3.42636725	2.98129578 3.98425936 5.16726868 6.58139639 6.86182223	1.78157249 -0.66168320 -2.83006075 -3.70790035 -2.43800940
н Н Н Н Н Н	4.92291175 6.22796526 7.12888317 7.37315557 5.54145647 3.42636725 4.22628455	2.98129578 3.98425936 5.16726868 6.58139639 6.86182223 -0.96132930	1.78157249 -0.66168320 -2.83006075 -3.70790035 -2.43800940 1.03877965
н н н н н С	4.92291175 6.22796526 7.12888317 7.37315557 5.54145647 3.42636725 4.22628455 -5.79309724	2.93073043 2.98129578 3.98425936 5.16726868 6.58139639 6.86182223 -0.96132930 0.5314188 5 2	1.78157249 -0.66168320 -2.83006075 -3.70790035 -2.43800940 1.03877965 1.15589413

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