Supplementary Information

Wavy Graphene Sheets from Electrochemical Sewing of Corannulene

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Molecular Orbital calculations of Corannulene

DFT calculations, carried out at the B3LYP/cc-pVTZ level of theory, show a MO energy diagram (Figure S1, Supporting Information) and MO isosurfaces (Figure S2) in which the two highest occupied MO's are degenerate, as are the two lowest unoccupied MO's, thus showing a tight agreement with the experimental results. Moreover, the separation of about 0.6 eV is also a value compatible with the interaction energy between two electrons in the same MO or two MO's occupying the same molecular region in aromatic systems.¹



Corannulene B3LYP/cc-pVTZ

Figure S1. Energy diagram for the molecular orbitals of corannulene (left) and corannulene radical cation (right) calculated at the B3LYP/cc-pVTZ level of theory.



Figure S2. (a) Isosurfaces of the two degenerate HOMOs of Corannulene at the B3LYP/cc-pVTZ level of theory; (b) Isosurfaces of the two Highest in energy Occupied Molecular Orbitals of Corannulene radical cation, with energy values E = -10.24 eV (left), E = -10.30 eV (right), calculated at UB3LYP/cc-pVTZ level of theory.

Supplementary Voltammetric Results

Cyclic voltammetric curves in *liq*-SO₂



Figure S3. Cyclic voltammetric curves of corannulene 1 mM in a 0.07 M TBAAsF₆/*liq*-SO₂ solution. Working electrode Pt disk 0.5 mm (diameter); reference electrode SCE; T= -65 °C; scan rate=200 V/s.

It is worth noting that the corannulenium carbocation is much more reactive than the tri-cation of the fullerene C_{60}^{3+} , which is known to be a highly electrophilic carbocation. As matter fact, the cyclic voltammetric behaviour of third oxidation process of C_{60} is reversible at a scan rate of 100 V/s under similar experimental conditions (in DCM solution at -55 °C).²

Cyclic voltammetric curves in DCM



Figure S4. Multiscan cyclic voltammetric curves of corannulene 1 mM in a 0.08 M TBAH/DCM solution. Working electrode Pt disk 125 μ m (diameter); reference electrode SCE; scan rate=1 V/s, T= 25 °C. Red trace: last set of 10 cycles with a reversing sweep potential E_r=2.00 V; blue, light blue, green, orange and black lines correspond to the 1st, 2nd, 3rd, 4th, and 5th, respectively, subsequent scans of a 5-cycles set with potential sweep limits between an anodic E_r= +2.00 V and a cathodic E_r= -1.85 V value.

The electropolymerization process of corannulene in DCM, carried out by cycling the potential scan from 0 V to 2 V, continues also when the scans are extended in the region of negative potential window down to -1.9 V, as shown in Figure S4 above. In such a case it is possible to observe a further process centered at about -0.75 V attributed to the negative doping of the film. Note that the film can be both positively doped (p-doped) and negatively doped (n-doped). It is also worth noting that in the first cycle (blue line) the peak potential of the forward scan is 100 mV negatively shifted with respect to the subsequent cycles and that the cathodic-anodic peak separation is at least 200 mV a larger value than those relative to the p-doping processes. This can be due to the higher resistance for inserting the tetrabutylammonium (TBA⁺) cation during the n-doping to balance the charge on the film, as the TBA⁺ is much larger than the anion PF_6^- . Moreover, once the film has been completely undoped, the rearranging of layers of the film itself leads to a drop of ions permeability, and this is particularly important for the TBA⁺ cations (for their size) involved in the first scan, thus undergoing a larger shift.

Replacing the Electrolyte TBAH with TBAAsF₆

The electropolymerization of corannulene in the solvent DCM has also been investigated by replacing the electrolyte TBAH with the less nucleophilic one TBAAsF₆, which has been used to deal with very reactive and electrophilic carbocation systems.³ The voltammetric pattern of the first few cycles is basically the same as with the electrolyte TBAH (compare Figure S4 or Figure 1c and Figure S5). However, as the number of potential scans increases (see red traces in Figure S5) the processes related to the doping of material, both p- and n-doping, starts to be shifted towards higher potentials (more positive for the p-doping and more negative for the n-doping), as highlighted by the red arrows. In particular, this is observed for the anodic voltammetric wave (p-doping) and the cathodic one (n-doping), with a much more evident shift at the negative potentials.



Figure S5. Multiscan cyclic voltammetric curves of corannulene 1 mM in a 0.08 M TBAAsF₆/DCM solution. Working electrode Pt disk 125 μ m (diameter); reference electrode SCE; scan rate=1 V/s, T= 25 °C. Black trace: first set of 3 cycles with a reversing sweep potential E_r=1.90 V; blue lines: subsequent set of 5 cycles; red lines: further set of 5 cycles with reversing sweep potential E_r=2.00 V.

Electropolymerization of Corannulene in the presence of Decamethylferrocene and Ferrocene

In Figure S6 (Supporting Information) is shown the evolution of the cyclic voltammetric curves upon several scans for a solution of corannulene and decamethylferrocene (dMeFC) in DCM. It is possible to observe that the electropolymerization of corannulene proceeds in a similar way as for a pure corannulene solution under the same conditions. This can be seen by comparing the multiscan voltammetric curve of a mixture of Corannulene and dMeFC with that of pure corannulene (multicycle voltammetric curve of Figure 1c in the main text) and basically the same voltammetric features can be recognized.

It is, however, worth noting that when the electropolymerization of corannulene is carried out in the presence of dMeFC as redox probe to test the electron transfer, in Figure S6 (panel a) it is possible to see that after the third cycle, and hence when the thickness of the polycorannulene film is still very small (estimated to be from few nanometers to a maximum of 10 nm) the electron transfer constant becomes very small, and the dMeFC oxidation peak is no longer visually observed. Conversely, when the same experiment is repeated with ferrocene (FC) instead of dMeFC, as shown in Figure S7, the oxidation of FC can still be observed (although it is convoluted with the doping process of the polycorannulene film) even with a larger number of voltammetric cycles, thus indicating that ferrocene on this material maintains a rather high electron transfer constant.



Figure S6. Multiscan cyclic voltammetric curves of corannulene 1 mM and decamethylferrocene 0.5 mM in a 0.08 M TBAH/DCM solution. Working electrode Pt disk 125 µm (diameter); reference electrode SCE; scan rate=1 V/s, T= 25 °C. (a) First set of 5 voltammetric cycles: 1st (grey); 2nd (blue); 3rd (light blue); 4th (light green); 5th (orange). (b) Subsequent set of 12 voltammetric cycles: red trace (4 cycles); green trace (8 cycles).



Figure S7. Multiscan cyclic voltammetric curves of corannulene 1 mM and ferrocene 1.2 mM in a 0.08 M TBAH/DCM solution. Working electrode Pt disk 125 µm (diameter); reference electrode SCE; scan rate=1 V/s, T= 25 °C. First set of 2 voltammetric cycles (black trace); second set of 2 cycles (blue); third set of 5 cycles (red); fourth set of 10 cycles (green).

Morphology Results



Figure S8. Optical microscope (magnification: 4X) pictures of polycorannulene film electrochemically deposited on ITO electrode from 1mM of corannulene in 0.08 M TBAH/DCM electrolyte solution. In pictures (a) and (b) it is possible to see the smooth film surface together with the <u>chipped edges of the ITO glass</u> slide; in picture (c) it is shown the cracked polycorannulene film and its partially peeling from the ITO surface.

Thus, the film electrochemically grown is mechanically quite stable, although at the edges of the electrode, in some cases, can partially detach from the surface.

Detachment of the film was also occasionally observed upon rinsing the film with DCM, to remove the electrolyte and the starting corannulene from the deposited surface, after the electrode has taken out from the cell. Most probably, this is due to the fast evaporation rate of DCM in air and the capillary forces established as a consequence of the formation of a wet layer.

Oxidation of Corannulene in ACN and Trapping of Corannulene Cation by Pyridine

The reactivity of corannulenium carbocation has been probed also by trapping the electrogenerated highly electrophilic species with a nucleophile such as pyridine, following the strategy reported in literature for the cations of anthracene derivatives.⁴ The voltammetric investigation, reported in Figure S9, shows that after the first scan, with an anodic peak at +1.86 V, the current decreases with the subsequent cycles. It is worth noting that the oxidation peak almost disappears on the second cycle indicating that the electrode surface is progressively passivated by the formation of an insulating film, which is deposited when the oxidation is performed. The formation and growth of the insulating film is clearly evident even at negative potentials, as it also affects the current and potential peak of the reduction process.

More in detail, in Figure S9a the 3-cycles voltammetric curve (blue trace) shows the initial evolution of the voltammetric pattern due to the polycorannulene conducting film deposition on the electrode. It is also possible to observe that the first reduction of corannulene (black trace) is irreversible in DCM with a peak potential E_p = -2.06 V (vs SCE).

Supporting Information Figure S9b reports the cyclic voltammetric curves of pyridine (green trace) and the multiscan voltammetric curve of corannulene $(1^{st}, 2^{nd} \text{ and } 3^{rd} \text{ scans: blue, light blue and red,}$ respectively) in the presence of pyridine. It should be noted that within the explored potential window (between -2.4 V and +2.1 V), pyridine does not show any redox process; its oxidation redox potential is at 2.2 V vs SCE.⁵ Thus, the interaction of pyridine with the radical cation of corannulene can be investigated, as in the case of the radical cations of anthracene derivatives.⁶

The comparison of the voltammetric curves in the upper and bottom panels of Figure S9 highlights the huge effect played by the presence of a nucleophile such as pyridine in scavenging the highly electrophilic corannulenium radical cation. As a matter of fact, both the oxidation and the reduction processes (Figure S9b) show a strong decrease (blue arrows) of the peaks current, leading to a complete disappearing for the oxidation, due to the formation of a passivating film on the electrode surface, produced by the reaction product between corannulene cation and pyridine (not further investigated). This behavior is quite similar to that observed in Figure S10, relative to the electrochemical experiments performed in acetonitrile (ACN), which are in agreement with the results so far reported in literature. Corannulene in ACN has an irreversible oxidation process with a peak potential of 1.90 V, similarly to the voltammetric behavior in DCM. Cycling repeatedly the potential up to include the oxidation, the process itself disappears stepwise, and no other electron transfer can be observed within the explored potential window. Subsequent electrochemical investigation of the electrode used above in a clean solution indicates the presence of a passivating thin film that was not further investigated.

Finally, comparison between the voltammetric results in acetonitrile (Figure S10) and DCM, together with those in the presence of pyridine, reflects the kinetics of the process for formation of the insulating film, initiated by the corannulenium carbocation in the presence of a nucleophile, which might be the solvent itself or even some impurities of the electrolyte. Water might be another nucleophile that can scavenge the electrogenerated corannulene radical cation. In fact, the oxidation of corannulene performed in the same solvent/electrolyte system (i.e., TBAH/DCM), without any drying purification procedure (i.e., not in ultra-dry conditions), leads to observation of an electrochemical behavior very similar to that in ACN, with fouling of the electrode surface within very few voltammetric scans.



Figure S9. (a) Cyclic voltammetric curves of corannulene 0.8 mM in a 0.08 M TBAH/DCM electrolyte solution. Blue trace: multiscan (3 cycles) curve that includes the irreversible oxidation process of Corannulene; Black line: single voltammetric cycle showing the first reduction of corannulene.

(b) Voltammetric curve of pyridine (3 mM; green line) and multiscan voltammetric curve of 1mM corannulene in presence of 3mM pyridine in 0.08M TBAH/DCM solution (blue line: 1st cycle; light blue line: 2nd cycle; red line: 3rd cycle).

All the voltammetric curves have been recorded at a scan rate of 1 V/s, by using a Pt disk (diameter=125 μ m) as working electrode; T= 25 °C and reference electrode: SCE.

It is worth noting in Figure S10 that the decrease of the irreversible oxidation peak current of corannulene is much slower than the corresponding one in the presence of pyridine (Figure S9a and S9b), both because in ACN the scan rate is 10-times higher than in DCM containing pyridine and also because pyridine is a stronger nucleophile in comparison to ACN.



Figure S10. Cyclic voltammetric curves of corannulene 1 mM in a 0.08M TBAH/ACN electrolyte solution recorded at a scan rate of 10 V/s, T= 25 °C, by using Pt disk (diameter=125 μ m) as working electrode; reference electrode: SCE.

Black line: 1st cycle; green line: 2nd cycle; red line: 3rd cycle. Blue and light blue traces: subsequent multiscan (8 cycles - first and last one are in blue) curves. Magenta lines: further set of multiscan (6 cycles) curves.



LDITOF-Mass Spectra and Hypothetical dimeric structures of Corannulene

Figure S11. Laser desorption-ionization mass spectra (LDITOF-MS) of the electrochemically deposited polycorannulene film onto a *uflat*-ITO substrate from a 1 mM corannulene in 0.08 M TBAH/DCM solution, by repeatedly scanning the potential between 0 V and 2.1 V (vs SCE). (a) Lower intensity spectrum recorded in the m/z range 1300–2000; (b) Zoomed region of the mass spectrum shown in Figure 2 (main text), relative to the m/z range 830-1060.



Figure S11-1. LDITOF mass spectra of the electrochemically deposited polycorannulene film onto a *uflat*-ITO substrate: zoomed region of the mass spectrum shown in Fig. 2a (main text), in the m/z range 672-758 together with the relevant mass losses of 12, 13 and 24 units.



Figure S11-2. (a) LDITOF mass spectra of the electrochemically deposited polycorannulene film onto a *uflat*-ITO substrate in the m/z range 736-746; (b) calculated isotopic pattern for $C_{60}H_{20}$ trimer of corannulene, (i.e., $3 \times C_{20}H_{10}$ -10H).

The possible dimeric structures, as the initial step of oligomerization of Corannulene, can be seen below in Figure S12.

In particular, the dimeric corannulene **1**, inspired by the *zig-zag chain* structure of the C₆₀-polymer, as reported by Riccò,⁷ might be expected as corannulene represents the polar cap of fullerene. The corannulene dimers **2** and **3** can be hypothesized considering the reactivity of the rim carbon atoms of the corannulene units that can lead either to one-bond or two-bonds structures, respectively.

As reported in literature, the reactivity of corannulene mainly occurs on the rim carbons,^{8,9} since the reactions involving the inner ring carbons (those in the pentagon) would implicate a large reorganization energy.



Figure S12. Sketch of possible structures of dicorannulene as initial step for the electrochemical oligomerization of corannulene

Electrochemical Oligomerization Mechanism

The hypothesized mechanism concerning the anodic oligomerization of corannulene is sketched below, in Figure S13 (Supporting Information). The corannulenium radical cations generated by electrochemical oxidation of corannulene undergo a rapid coupling, to give a dimer by forming a carbon-carbon bond between the atoms of the rim of two corannulene units. As consequence (step 2 of Figure 3) the dimeric dicationic species has partially loss the aromaticity which is readily regained with the deprotonation of the ipso carbon atoms. The single-bonded dicorannulene thus obtained is expected to be oxidized even more easily than corannulene (see Table S-I and Table S-II, Supporting Information), moreover, the two moieties are almost independent by each other, as the dihedral angle is about 65°, and hence it can undergo a two closely spaced oxidation processes (step 3 on Figure S13, with a global 2-electron process) at less positive potentials. The resulting two-electrons oxidized species is a diradical and the DFT calculations indicate a high spin density (Figure S14) at the rim-carbons adjacent to the new established C-C bond, in the step 2. This makes possible the prompt formation of a second C-C bond between the two corannulene units (step 4 in Figure S13), that the subsequent deprotonation leads to the *double-bonded* dicorannulene. It is noteworthy that this further C-C bond builds up a hexagonal ring. Such a mechanism can basically be divided into two parts: the first two steps follow a classical polymerization processes, while the second two steps represent an intramolecular oxidative cyclodehydrogenation of an aromatic hydrocarbon, also known as a Scholl reaction,^{10,11} which has been electrochemically induced.

The mechanism can be straightforwardly extended to the formation of trimer, tetramer and so on, with the possibility to establish even three single C-C bonds between the corannulene units, as sketched in Figure 2b.



Figure S13. Sketch of the hypothesized electrochemical mechanism, restricted to the dimeric structure of corannulene oligomerization process.

Regarding the electrochemically triggered Scholl reaction (i.e., the second part of the whole mechanism, steps 3 and 4, in Figure S13), it is worth pointing out that an alternative route can be hypothesized as shown below in the Supporting Information Figure S13bis, on the basis of studies by King¹⁰ and Rathore.¹² The *single-bonded* dicorannulene, obtained in step 2 (Figure S13), can be one-electron oxidized to produce the radical cation, which undergoes a rapid intramolecular C-C bond formation. Such a species thus generated can either give a partial rearomatization of the structure by a proton loss (not shown in the sketch of Figure S13bis) or undergo a further one electron oxidation at the electrode surface with a subsequent deprotonation that leads to the *double-bonded* dicorannulene.



Figure S13bis. Sketch of the alternative route for the hypothesized electrochemically triggered Scholl reaction (i.e., the steps 3 and 4 of the mechanism in Supporting Information Figure S13).

DFT calculations of Corannulene and hypothesized oligomers

	IP values: B3LYP/6-31G* (in red); B3LYP/cc-pVTZ		
Species	Structure	IP (eV)	
Corannulene		7.49 7.73	
<u>diCorannulene</u> <u>single-bonded</u> (diCoran-1B)		<mark>6.90</mark> 7.16	
<u>diCorannulene</u> <u>double-bonded</u> (diCoran-2B)		<mark>6.77</mark> 7.01	
Trimer		6.47 6.72	
Tetramer		6.18 6.44	

Table S-I. Theoretical ionization potentials (IP), calculated at the B3LYP/cc-pVTZ level of theory for the oneelectron oxidation of corannulene and the first four hypothesized oligomers. **Table S-II.** Theoretical standard potentials (versus SCE), calculated at the B3LYP/cc-pVTZ level of theory for the one-electron oxidation of the corannulene and the first four oligomers and experimental oxidation potential of corannulene compound.

	Experimental V vs SCE	B3LYP/cc-pVTZ V vs SCE
Corannulene	1.86 ^a	1.934
diCoran-1B		1.721
diCoran-2B		1.516
Trimer		1.371
Tetramer		1.184

^a irreversible process; peak potential value at scan rate=1 V/s



Figure S14. DFT results of optimized dicorannulene *single bonded* (diCoran-1B) at B3LYP/6-31G*: (a) Isosurface of the HOMO(-1) with an energy value E=-6.2 eV, which is very close to the HOMO energy of corannulene; (b) spin density plot of doubly oxidized species diCoran-1B in its triplet state.

Reduction of $\boldsymbol{H}^{\!\!\!+}$ produced by the oligomerization

As required by the oligomerization mechanism (Figure S13), a release of protons occur, and this has been verified both by voltammetry and theoretically by calculating the standard potential of H^+ reduction in dichloromethane (Figure S15).



Figure S15. Multiscan cyclic voltammetric curves of corannulene 1 mM in a 0.08 M TBAAsF₆/DCM solution. Working electrode Pt disk 125 μ m (diameter); reference electrode SCE; scan rate=1 V/s, T= 25 °C. Black trace: first set of 3 cycles; blue trace: subsequent set of 5 cycles.

Inset: magnification of the orange dashed oval for the first 5 cycles in the region close to the reversing potential; black, orange, green, light blue, blue lines correspond to the 1st, 2nd, 3rd, 4th, and 5th cycle, respectively.

The electrodeposition of the corannulene-based film is always coupled to a shrinking of the useful potential window at the negative values, upon running subsequent voltammetric cycles. This is

observed when the process is performed scanning the potential up to include the negative potential side with a reversing value at about -1.9 V, that is at the onset of the irreversible reduction process of corannulene. As shown in the Figure S15, after scanning the potential first on the negative values and then to positive potentials, which initiates the oligomerization process, it is possible to observe during the subsequent scan on the negative side that at the reversing potential the current has increased (see on the inset of the Figure S15 the lines black and orange). Such an effect is attributed to the reduction of H^+ in DCM.

As a matter of fact, the reduction potential of H^+ in DCM, considered explicitly as proton coordinated by the chlorine lone pairs of DCM (as sketched below) has been calculated by DFT at the B3LYP/cc-pVTZ level of theory, and its value is -2.19 V (vs SCE), in satisfactory agreement with the experimental findings.



XPS and NEXAFS Analysis

The C 1s XPS peak of the measurements performed on the electrochemically grown film is shown in Figure S16a. The spectrum has been fitted using three Doniach-Sunjic components, resulting at 284.8 eV (sp²), 286.3 eV (sp³) and 288.6 eV (CO contamination), superimposed to a Shirley background. The binding energy value of the main C 1s component (284.8 eV) is close, but shifted to higher binding energy by about 0.6 eV, to that reported for the anodically obtained C_{60} polymer.³ The reason for that must stem from the presence of mainly sp²-hybridized carbon atoms in the film, with very few detectable sp³-hybridized carbon atoms, which renders the binding energy close to that of graphite/graphene (284.5 eV), and to the better screening of the core hole for the anodically obtained C_{60} polymer. Indeed, contrary to the XPS spectrum of the C_{60} polymer, in the C 1s peak of polycorannulene, the asymmetry in the high binding energy side of the lineshape is not very large. The observed high-energy lineshape can be simply obtained mainly with the Shirley background. In any case, a small asymmetry of the peak is needed. This may imply that the system has a small density of states at the Fermi level. On the other hand, it may equally well result from superposition of different C 1s peaks corresponding to carbon atoms in different environments, as expected for the electrochemically deposited film, or from oxygen adventitious carbon contamination.

Near edge x-ray absorption (NEXAFS) was measured in s- and p- geometry in correspondence of the Carbon K-edge adsorption, with the electric field either parallel to the substrate plane or nearly perpendicular to it (8° with respect to the normal to the substrate plane). The two spectra are shown in Figure S16b. Characteristic spectral features are observed that can be assigned to typical π^* resonances and σ^* transitions of aromatic carbons in the polycorannulene.¹³ The structure at about 288 eV can be associated with C-H bonds, but also with some level of surface contamination,¹⁴ in agreement with XPS. The absence of linear dichroic effects in s- and p- spectra suggests that, over the footprint area of the impinging beam, the polycorannulene units have random average

orientation. Alternatively, small aligned domains of polycorannulene units may be present, but these do not present a preferential common orientation with respect to the substrate plane. This is consistent with TEM observations (*vide infra*).



Figure S16. a) XPS C 1s photoemission spectrum of electrochemically deposited film of polycorannulene on ITO, obtained from corannulene 1 mM in a 0.08 M TBAH/DCM solution. The background (dashed line) is also shown together with the fitting results (red dots), revealing the presence of three deconvoluted components (sp², sp³ and CO); b) NEXAFS acquired in s- and in p- scattering conditions on the same polycorannulene film on ITO as above.

FTIR and Raman Spectroscopy



Figure S17. FT-IR spectrum of the electrochemically deposited film of polycorannulene on Pt foil, obtained from corannulene 1 mM in a 0.08 M TBAH/DCM solution.

In Figure S18 is shown the Raman spectrum of polycorannulene (red lines) together with that of corannulene (black lines). The spectrum of the polymeric film is obtained by subtracting the strong fluorescence background observed exciting both at 633 and at 488 nm. Such a strong fluorescence of the thin film can be understood looking at the UV-Vis spectrum (see Supporting Information Figure S19) in which electronic transitions at the exciting laser wavelengths are now present. The spectrum of a corannulene drop-casted film shows a fluorescence background only when exciting at 488 nm, and it is reported in Figure S18, after subtraction of this background.



Figure S18. Raman spectra of (a) corannulene polymer as deposited on a platinum electrode (red lines) and corannulene drop-casted on Pt (black lines) excited at 633 nm; (b) corresponding theoretical spectra for the tetramer of corannulene (see Figure 2b) as a model for polycorannulene (red) and corannulene (black) calculated at the B3LYP/cc-pVTZ level; (c) experimental results as in (a) but using excitation at 488 nm.

UV-Vis-NIR Spectroscopy and Spectroelectrochemistry

The film electrochemically deposited on ITO electrode as reported in the main text and under the same experimental conditions of Figure 1, was transferred into a spectroelectrochemical cell containing only the blank electrolyte (i.e., a monomer-free electrolyte solution) as above. The surface of the film covering the ITO substrate is 6x10 mm². A multiscan cyclic voltammetry curve of polycorannulene film on ITO in the blank DCM/electrolyte solution was also recorded at different scan rates, spanning from 0.02 to 1 V/s (Figure S19b). No appreciable loss or degradation of the film was observed by analyzing the electrochemical signal.

The UV-Vis-NIR spectrum of the polycorannulene film (black trace, Figure S19a), which is similar to that recently reported for some graphene nanoribbons, has an absorption peak at about 500 nm.¹⁵ The film was seen to be strongly electrochromic upon positive doping, even during its electrochemical deposition (Figure S20a). The four spectra reported in Figure S19a, recorded at three different positive potentials (0.95 V, 1.50 V and 1.80 V) and at 0 V (spectrum of pristine polycorannulene film), show a stepwise decrease in the absorption band at about 500 nm and a corresponding growth of a strong band at about 630 nm that makes less evident the bleaching of the undoped polymeric film absorption. Moreover, a weaker and broad band in the NIR region, centered at about 1200 nm, also develops upon positive doping. These optical changes upon oxidation are reversible and, in fact, going back to 0 V the oxidized layer returns to its neutral state, recovering the original spectrum.

It is noteworthy that despite the very small thickness of the film, which is at maximum 300 nm, as determined by AFM, the absorption is rather high, and this, together with the very strong electrochromic effect, can make this material also very interesting for optoelectronic applications.



Figure S19. (a) UV-Vis-NIR spectra of the polycorannulene film (absoption of ITO substrate electrode subtracted) at different doping potentials, as indicated by the coloured arrows on the (b) multiscan cyclic voltammetry, recorded in a 0.08M TBAH/DCM electrolyte blank solution (i.e., monomer-free solution). Surface of the polycorannulene film on ITO substrate is 6x10 mm². T= 25 °C. scan rate of the multiscan cyclic voltammetric curve is 1 V/s.

A double step chronoamperometric investigation of the polycorannulene film has also been performed, stepping the potential between 0V and 1V, and the results (Figure S20b) show that the film has a fast electrical response with the faradaic current dropping to zero in a time interval shorter than 200 ms, according to the very thin deposit. Thus, only a single spectrum per each doping potential step was possible to record. The reversibility check of each process was obtained by recovering the spectrum to the original one (i.e, that before the oxidation or doping step) upon stepping the potential down to the value of the corresponding original spectrum.



Figure S20. (a) Pictures of undoped (E=0 V vs SCE) and doped (E=1.5 V vs SCE) polycorannulene film electrochemically deposited on ITO electrode in a blank TBAH/DCM electrolyte solution. (b) Double step potential chronoamperometry (E_1 =0 V, E_2 =1.0 V) of the polycorannulene film (9 weeks aged) in a blank TBAH/DCM electrolyte solution.

Supplementary Electron Microscopy and X-ray Results

Scanning Electron Microscopy



Figure S21. Further SEM images of electrochemically deposited polycorannulene on uflat-ITO by cyclic voltammetry at T=25°C from corannulene 1 mM in a 0.08 M TBAH/DCM solution.

Transmission Electron Microscopy (suspended in ethanol)

A further series of TEM images is shown below in Figure S22 of this Supporting Information. Such images have been obtained by scratching the electrode surface deposit and suspending the film flakes in ethanol. The suspension was then drop-casted onto a TEM grid.

In the images below, it is possible to observe that some fragments of the film are very thin and transparent to the electron beam, whereas others are thicker; thus, the film has not a uniform thickness. The thin film fragments present dark lines which are not breaking lines of the film itself, as evidenced by higher magnification images, but represent grains borders similarly to those of polycrystalline materials.



Figure S22. TEM images of polycorannulene electrochemically deposited on uflat-ITO (from corannulene 1 mM in a 0.08 M TBAH/DCM solution at T=25°C), mechanically scratched, suspended in ethanol and drop-casted onto a TEM grid.

In Figure S23, further TEM images show the lamellar structure of the as electrochemically deposited film; it is also possible to see the presence of nanometric filamentous structures on the border.



Figure S23. Supplementary TEM images at higher magnification of fragments of polycorannulene electrochemically deposited on uflat-ITO (from corannulene 1 mM in a 0.08 M TBAH/DCM solution at T=25°C), drop-casted onto a TEM grid after having mechanically scratched and suspended in ethanol.

X-ray Analysis



Figure S24. Diffraction patterns of (red trace) polycorannulene film electrochemically deposited on *uflat*-ITO substrate; (blue trace) drop-casted film of polycorannulene from a TCB solution/suspension of the electrochemically obtained film on *uflat*-ITO; (green) pristine *uflat*-ITO substrate. The splitting of the additional peak observed in the case of the drop-casted polycorannulene film can be due to a non-uniform thickness of the film.

Transmission Electron Microscopy (suspended in TCB and TCE)

In Figure S25 it is possible to observe some further examples of single and multiple layers of polycorannulene when the electrochemically obtained deposit was treated and suspended in solvent 1,2,4-trichlorobenzene (TCB).



Figure S25. TEM images of polycorannulene film obtained by drop-casting on a TEM carbon covered grid a TCB solution/suspension of the electrochemically deposited film (on uflat-ITO from corannulene 1 mM in a 0.08 M TBAH/DCM solution, at T=25°C). The solution/suspension was obtained by treating the deposited film with TCB solvent (see Experimental Section details).

The images below in Figure S26 report the TEM of the electrochemically obtained film, dissolved/suspended in 1,1,1,2-tetrachloroethane (TCE) and then drop-casted onto a grid. They show a very similar picture as in the case of polycorannulene suspended in TCB. Some crystalline platelets are visible, that are randomly distributed among a quite amorphous matrix. The platelets have a thickness between two and several atomic planes with an interlayer distance of about 10.2 Å.



Figure S26. Supplementary TEM images of polycorannulene film obtained by drop-casting on a TEM carbon covered grid a TCE solution/suspension of the electrochemically deposited film (on uflat-ITO from corannulene 1 mM in a 0.08 M TBAH/DCM solution, at T=25°C). The solution/suspension was obtained by treating the deposited film with TCE solvent (see Experimental Section details)

DFT Interlayer separation of Corannulene oligomers



Figure S27. DFT calculated bilayer structures of tetracorannulene oligomers at the M06/3-21G* level of the theory, to determine the interlayer separation in the absence and in the presence of solvents such as TCE and TCB, which are able to dissolve and intercalate solvent molecules in between the corannulene oligomers, thus leading to a cooperative action of van der Waals forces to keep stacked together the various polycorannulene layers even at a distance as large as 10 Å. (a) The separation in the absence of solvent intercalated is about 6.5 Å, a distance at which the dispersive forces are too weak to keep the layers stacked. (b) In the case of TCE, the interlayer distance is in average 10.2 Å while (c) with TCB, such a separation increases up to 10.6 Å.

Materials and Experimental Methods

Chemicals and Electrochemical Measurements. Tetrabutylammonium bromide (TBABr), lithium hexafluoroarsenate (LiAsF₆) and lithium tetrakis(perfluoroaryl)borate (containing 2 tetrahydrofuran solvent molecules; LiFAB), were used as received, and all were electrochemical or analytical grade from Fluka. The electrolyte tetrabutylammonium hexafluoroarsenate (TBAAsF₆) was synthesized by metathesis reactions from tetrabutylammonium bromide with lithium hexafluoroarseniate and twice re-crystallized following the procedures reported in the literature.¹⁶ Tetrabutylammonium tetrakis(perfluoroaryl)borate (TBAFAB) was obtained by the metathesis reaction between TBABr in ethanol and LiFAB in water and purified twice by recrystallization with ethanol and water, following the procedures previously reported,^{18,2} stored in a specially designed Schlenk flask and protected from light. Sulfur dioxide (SO₂) was purified and dried by bubbling through concentrated sulfuric acid, refluxing over activated basic alumina super I (ICN Biomedicals) at the corresponding boiling temperature and then percolated through an activated basic alumina super I column under reduced pressure, just before condensing the vapor into the electrochemical cell.

All the halfwave potentials ($E_{\frac{1}{2}}$) have been directly obtained from cyclic voltammetric curves as averages of the cathodic and anodic peak potentials and by digital simulation for those processes, which are not Nernstian, or for processes closely spaced in multielectron voltammetric peaks. The $E_{\frac{1}{2}}$ values, referenced to the aqueous saturated calomel electrode (SCE, which is 0.241 V vs NHE, i.e., the normal hydrogen electrode ¹⁹), have been determined by adding ferrocene at the end of each experiment as an internal standard and measuring them with respect to the ferrocinium/ferrocene couple standard potential. The temperature-dependent ferrocinium/ferrocene couple standard potential. The temperature-dependent ferrocinium/ferrocene couple standard potential was measured with respect to SCE by a non-isothermal arrangement according to the method outlined by Weaver et al.²⁰ The potentials thus obtained were not corrected for the two unknown contributions: (i) the liquid junction potential between the organic phase and the aqueous SCE solution, and (ii) the potential due to the thermal gradient existing between the SCE, at room

temperature, and the low temperature test solution.

The cell containing the supporting electrolyte and the electroactive compound was dried under vacuum for at least 60 hours. The pressure measured in the electrochemical cell prior to performing the trap-to-trap distillation of the solvent was typically 1x10⁻⁵ mbar. The electrochemical station was interfaced to a Nicolet Mod. 3091 digital oscilloscope and the data transferred to a personal computer by the program Antigona.²¹ Minimization of the uncompensated resistance effect in the voltammetric measurements was achieved by the positive-feedback circuit of the potentiostat. The determination of the potentials, for the irreversible processes, was obtained by digital simulation of the cyclic voltammetric curves,²² carried out either by Antigona or DigiSim 3.0, utilizing a best fitting procedure of the experimental curves recorded at different scan rates spanning over, at least, two orders of magnitude.

Laser Desorption-Ionization Time of Flight Mass Spectra (LDITOF-MS). The laser desorptionionization mass spectra experiments were performed with an Applied Biosystems/MDS SCIEX 4800 MALDI TOF/TOF[™] Analyzer, to record Laser Desorption-Ionization Time of Flight Mass Spectra (LDITOF-MS), using a Nd:YAG laser (355 nm wavelength, 3 to 7 ns pulse width, 200 Hz firing rate) and deflecting ions outside the mass range of m/z 300-3000 for higher sensitivity. The LDITOF analysis was conducted directly on the original ITO/glass or platinum support on which the film was initially deposited by electrochemistry. The transfer of the film from the originally deposition support onto the LDITOF-MS target holder was prevented by the overall low amount of material. The original substrate was fixed to the LDITOF sample holder using double-sided adhesive tape. The laser intensity was changed over a reasonable range to ascertain that no photoprocesses occur and then appropriately adjusted to a low value which allows a good detection of ions.

XPS. Photoemission spectra were measured at room temperature in ultra-high-vacuum (UHV) conditions (10^{-10} mbar) in a modified VG ESCALAB MKII experimental chamber. Photoelectrons were excited by means of Mg K α photons and collected using a 150 mm hemispherical analyzer in

normal emission geometry with an overall energy resolution of about 0.8 eV. The samples deposited either on ITO/glass or Platinum were directly inserted in UHV using a fast-entry air lock and measured as received as well as after a mild annealing (50 °C) to remove the adsorbed contaminants from air. The binding energies are referred and calibrated to the Fermi edge of Au plate in electrical contact with the sample.

NEXAFS. Near edge x-ray absorption spectra at the carbon K edge were measured at the BEAR beamline^{23,24} at Elettra (Sincrotrone, Trieste – Italy). Photon energy resolution was set to 0.2 eV. Spectra were acquired in total yield mode, measuring the drain current from the sample. To correct for the optics transmission at the carbon K edge, spectra were normalized to the signal recorded in the same energy region on a carbon-free clean Au surface. The spectra were taken at a grazing incidence of 20°, with linear polarized light (linear polarization degree 94%) in s- and p- scattering geometries (with the electric field vector perpendicular and parallel to the scattering plane.

FTIR and Raman spectroscopy. Micro-FTIR spectra of the deposited films were recorded by a Nicolet Magna 560 spectrometer, coupled with a Spectra-Tech Continuum microscope. The instrument operates in the 4000-650 cm-1 infrared region and is equipped with a mercury cadmium telluride (MCT) detector cooled to liquid nitrogen temperature.

Raman spectra were recorded with an inVia microRaman spectrometer using a 20x objective and exciting at 633 nm (He-Ne Laser) and at 488 nm (Ar laser). Power on the samples was kept as low as possible (between some tenths of mW to few mW) to avoid laser induced damages.

UV-Vis-NIR spectroscopy. UV-Vis-NIR adsorption spectra were measured on a Varian Cary 5 spectrophotometer and were baseline corrected.

SEM and TEM Microscopy. Scanning Electron Microscopy (SEM) observations were carried out by a Zeiss Supra 40 field emission scanning electron microscope (SEM) equipped with a Bruker Z200 EDX microanalysis.

Transmission Electron Microscopy (TEM) analysis was performed by using a Philips CM200 microscope operating at 200 kV and equipped with a LaB6 filament. Samples for TEM

observations were prepared using the two following procedures. a) Small portions of the electrochemically deposited polycorannulene film were scratched from the electrode, by using a tweezer, and simply deposited on a commercial TEM grid covered with a thin carbon film and where a drop of ethyl alcohol was preventively added. Afterward, the grid was kept in air until complete ethyl alcohol evaporation. The alcohol assists the adhesion and dispersion of the sample on the carbon film. b) The polycorannulene film deposited on the electrodes were dipped one in 1,2,4-trichlorobenezene (TCB) and the other in tetrachloroethane (TCE) solvent, either shortly sonicating or heating up to 80°C. Portions of the film were detached from the electrode and dissolved/suspended in both solvents. A drop of such a suspension was deposited on a commercial TEM grid covered with a thin carbon film and kept in air until complete solvent evaporation.

Atomic Force Microscopy (AFM). AFM imaging and analysis were performed in air with a Digital NanoScope 3D Multimode microscope (Veeco, USA) using phosphorus n-doped Silicon probes (spring constant, 20-80 N/m; resonance frequency 250-300 kHz; nominal tip radius either <10 nm or supersharp ones <4 nm) and operating in tapping mode. Samples for the AFM experiments were prepared either by electrochemically induced polymerization, as described above, or by spin-coating a saturated solution of the dissolved film previously obtained by electrochemical deposition. The substrates used for the AFM experiments were ultra-flat indium tin oxide (*uflat*-ITO, with a root mean square (RMS) roughness of about 0.5 nm for a pitch of $1 \times 1 \mu m^2$; supplied by Kuramoto, Japan),²⁵ flame annealed gold on glass (by Arrandee, NL), highly oriented pyrolytic graphite (HOPG) and freshly cleaved mica sheets. The phase imaging was obtained by optimizing the setpoint tapping amplitude with respect to the free amplitude of the probe, near the resonance frequency of the probe itself.

X-ray diffraction (XRD). X-ray powder diffraction patterns of the samples were collected by using a PanAnalytical X'Pert Pro equipped with X'Celerator detector powder diffractometer and the Cu K_a radiation generated at 40 kV and 40 mA. The diffraction patterns were collected within the 20 range from 5° to 75° with a step size ($\Delta 2\theta$) of 0.05° and a counting time of 150 s. The X-ray

powder diffraction patterns were analyzed using the X'Pert HighScore Plus software (PANalytical).

Computational Details. All the ab-initio and DFT molecular orbital calculations were performed using the Firefly Quantum Chemistry package,²⁶ which is partially based on the GAMESS (US) source code, and GAMESS in itself.²⁷ First, the geometries of the molecules involved in the redox processes were fully optimized at the B3LYP/6-31G* level checking for the positive semidefinite character of the hessian in order to ensure that the located stationary point was a true local minimum. Starting from these optimized structures, the vertical ionization potential (IPv) and the vertical electron affinity (EAv) were obtained (for each system) both at the B3LYP/6-31G* level and also at the B3LYP/cc-pvtz level. Aiming at theoretical evaluation of redox potentials for the various species, the IPv and EAv were combined with the solvation free energies using the thermodynamic cycle proposed by Cramer and Truhlar.²⁸ It is worthwhile to note that the solvation energy, calculated at the B3LYP/6-31g* level, was obtained in the C-PCM framework^{29,30,31} only considering the electrostatic contribution. For the sake of comparison with experimental values, the parameters selected for the evaluation of the solvent effect correspond to dichloromethane (DCM). Supporting Information Scheme S1 shows the detail of the elementary steps taken into account to reckon the Redox Standard Potential values for the Corannulene oxidation process. The same strategy has been applied to calculate the redox potentials for the oxidation relevant to some hypothesized Corannulene oligomers.

The gas-phase Gibbs energies of both reactants and products, as well as the relevant solvation energy, are the quantities involved in the calculation of the redox potential. The standard reduction potential of the redox couple in solution is calculated as the sum of elementary step contributions. The standard Gibbs energy variation of the whole oxidation process is determined as the sum of the two contributions due to the C/C⁺ couple and hydrogen reduction half-reactions; thus, ΔG°_{ox} (C/C⁺ vs NHE) = $\Delta G^{\circ}(IV) + \Delta G^{\circ}(H)$. In Scheme S1, the step IV is the half-reaction Gibbs energy variation of the oxidation process in solution: $\Delta G^{\circ}(IV) = \Delta G^{\circ}(I) + \Delta G^{0}(III)_{(solv)} - \Delta G^{0}(II)_{(solv)}$. In detail: $\Delta G^{\circ}(I) = IP + \Delta G^{\circ}_{evr,gas}$. IP is the ionization potential and the $\Delta G^{\circ}_{evr,gas}$ term reflects the difference in thermal contributions to the Gibbs energy of the redox system due to changes in the electronic, vibrational, and rotational partition functions, upon the oxidation process (where reference is made to the reaction $C_{(g)} \rightarrow C^{+}_{(g)} + e$). In the present work the contribution of the $\Delta G^{\circ}_{evr,gas}$ has been neglected because its value is often found negligible, despite the time and resource costs needed for its calculation; a procedure already adopted and justified in the literature.^{32,33} $\Delta G^{0}(II)_{(solv)}$ and $\Delta G^{0}(III)_{(solv)}$ are the solvation Gibbs energies of the reduced and oxidized species respectively, the two lateral branches of Supporting Information Scheme S1. Note that, the solvation terms in Scheme S1 actually refer to a bulk solvation process; in the present case the situation can be somehow different as in some instances the redox couple can be adsorbed on the electrode surface. We calculated the solvation energy of the species as they are sketched in Figure 2 of the main text, i.e. the whole cluster is considered solvated.

Scheme S1						
Thermodynamic cycle for the calculation of the oxidation potential.						
	$\mathbf{C}_{(g)}$	\rightarrow	$C^{+}_{(g)} + e^{-}$			
		$\Delta G^{0}(I)$				
$\Delta G^{0}(II)_{(solv)}$	\downarrow		\checkmark	$\Delta G^{0}(III)_{(solv)}$		
	C (solv)	\rightarrow	$\mathbf{C}^+_{(\mathrm{solv})} + e$			
		$\Delta G^{0}(IV)$				
	$\mathbf{H}^{+}_{(aq)} + e^{-}$	\rightarrow	$1/2 \ H_{2(aq)}$			
		$\Delta G^{0}(H)$				

Note that $\Delta G^{0}(H) = 4.44 \text{ eV}^{34}$

The solvation energy contribution of the carbon cluster is assumed both negligible in absolute value and almost constant (thus cancelling out in the calculation of the whole variation, $\Delta G^{\circ}_{red}(IV)$ +

 ΔG°_{ox} , where the difference between the solvation energies of the reduced and oxidized species, $\Delta G^{\circ}_{s}(III) - \Delta G^{\circ}_{s}(II)$, are reckoned). Gas phase optimized geometries were used for all the calculations.

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