Coronene Diimide Containing Redox Active Electrochromic Polymer Film via Electropolymerization of Diphenylamine End Groups

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A new monomer containing coronene diimide with diphenylamine end groups (DCTD) has been synthesized and polymer thin films were electropolymerized onto gold, glassy carbon and ITO electrode surfaces. The resulting polymers show a reversible 2e− oxidation of the diphenylbenzidine unit and reversible reductions of the aromatic diimide. AFM was used to characterize the polymer film morphology. The electronic and electrochromic properties of these films were evaluated for use in organic electronic applications.

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Research in the field of organic semiconducting polymers and their uses in electronics has grown rapidly in recent decades. Considerable effort has been given to developing new monomers and investigating their properties. Our research group has focused on synthesizing new monomers containing a central redox active moiety flanked by two electropolymerizable functional groups and subsequently, studying the mechanism of this process as well as their optical and electronic properties.

Perylene diimides have been reported as electron-transport materials with high electron mobility as well as having good chemical, thermal and photochemical stability. Coronene derivatives have shown columnar discotic liquid-crystalline (LC) mesophases making them important candidates for organic electronic transport materials due to extensive molecular ordering. Coronene with an extended core size over perylene appears to have stronger intermolecular interactions leading to better charge-carrier mobility. Polymers based on perylene and naphthalene diimides have been synthesized and used as n-type semiconductors for organic field effect transistors. Thiophene, thienophene, thienopyrrole, and phenothiazine have all been incorporated in the bay position of perylene diimide and copolymers of these have been chemically synthesized.

Usta et al. prepared the first reported coronene diimide polymer, a donor–acceptor pi conjugated polymer of dithiencorone diimide with electron and hole mobilities of up to 0.30 cm2/Vs and 0.04 cm2/Vs respectively. Recent theoretical studies of coronene imides showed that functionalization in the imide position also controls the electronic properties. Electropolymerization allows precise control for producing new functional materials. Conducting polymers have been prepared via electropolymerization of a wide variety of organic molecules, pyrrole, aniline, thiophene, furan, indole, thianaphthene and carbazole. P‐phenylenediamine and diphenylamine also can be electropolymerized at moderate oxidation potentials and make excellent end groups for electroactive monomers. In our lab, diphenylamine functionalized at the imide position of perylene and naphthalene moieties have been synthesized and polymer films synthesized via electropolymerization. Spectroelectrochemistry of naphthalene diimide polymers show a solvent-dependent absorption energy band. We have also used electrochemical quartz crystal nanogravimetry to explore the mechanism of film formation and kinetics of ion incorporation into polymer films in case of perylene and naphthalene diimide polymer. Also these polymers exhibit robust, stable colors in different redox states making them promising candidates for electrochromic materials. Spin coating is the most used method to make thin films for fabricating optoelectronic devices. However, in the spin coating process, a polymer has to be well soluble in a solvent. Due to this low solubility semiconducting polymers are difficult to fabricate into organic field effect transistor (OFET). Processes that result in highly self-organized thin films are desirable for better interchain pi‐pi stacking. It has been reported that electropolymerized 3-hexylthiophene thin films show a broader optical absorbance range than spin-coated samples but also comparable pi‐pi stacking. Manipulation of film thickness is easy using electropolymerization techniques by controlling the time of reaction and the number of scans. Repeated scanning effectively results in low temperature annealing of the films.

Here we synthesized a new coronene diimide monomer containing a diphenylamine end group, N,N′-di-(phenylaminophenyl)-5,11-dihexyl coronene tetracarboxylic diimide (DCTD). DCTD was electropolymerized onto different conducting surfaces, such as Au, GC, and ITO glass slides. To our knowledge, this is the first example of an electrosynthesized polymer containing coronene diimide. Electrochemistry, potential dependent UV-Vis-near IR characterization as well as electrochromic properties and polymer microstructures are discussed.

**Experimental**

Reagents and materials.—CH3Cl2, hexane, and CHCl3 were purchased from BDH Chemicals. Dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and methanol were obtained from EMD Millipore Corporation. Trifluoroacetic acid (TFA) (Aldrich) and tert-butyl hydroperoxide (DMSO) and methanol were obtained from EMD Millipore Corporation, Trifluoroacetic acid (TFA) (Aldrich) and tert-butyl hydroperoxide (Alfa Aesar) were used as received. CH2Cl2, CH3CN and dichloromethane were freshly distilled from calcium hydride (Alfa Inorganics Inc.). DMSO, DMF and quinoline (Aldrich) were distilled under vacuum before use. Anhydrous toluene and THF were obtained from a solvent purification system (Pure Process Technology). Perylene tetracarboxylic dianhydride, bromine, cyclohexylamine, copper iodide, Pd(PPh3)4, triethylamine (anhydrous), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were obtained from Sigma-Aldrich. 4-amino-diphenylamine was purchased from Acros Organics and used after recrystallization from ethanol. The ionic liquid, 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (BMIM TFSI) was purchased from Ionic Liquid Technologies, USA. H and 13C NMR spectra were obtained from either Bruker 600 or 400 MHz NMR instruments. Mass spectrometry data were collected from Waters Quadrupole Time of Flight (Q-TOF) mass spectrometer with electron spray ionization (ESI) or a Bruker MALDI-Q-TOF instrument where sinapic acid (Sigma-Aldrich) was used as a matrix. An Agilent 8453 UV-Visible spectrophotometer, a Shimadzu IR Prestige-21 FTIR spectrometer and a Shimadzu RF-6000 Spectrofluorometer were used to characterize the product of the monomer synthesis.

**Synthesis of N,N-Di-(p-phenylenediphenyl)-5,11-dihexyl coronene tetracarboxylic diimide (DCTD)**—80 mg of 5,11-dihexyl coronene-2,3,8,9-tetracarboxylic dianhydride was dissolved in...
6.20 mL of quinoline containing 96.9 mg N-phenyl-p-phenylenediamine (4 equiv.) and 8.8 mg of zinc acetate. The temperature of the reaction mixture was held at 180°C for 24 h under Ar. After cooling to room temperature, 20 mL diethyl ether was added to the reaction flask; the precipitate filtered and washed with water and then diethyl ether. The product was dried under vacuum (30 mm Hg) overnight and 102 mg pure product were isolated (yield 82%).

1H NMR (600 MHz, CDCl3 + d-TFA): \( \delta = 10.08(\text{s, 2H}), 9.91(\text{s, 2H}), 8.88(\text{s, 2H}), 7.88-7.61(\text{m,18H}), 3.71-0.90(\text{m, 26H}); \) UV-Vis(CHCl3 + TFA): \( \lambda_{\text{max}} (\varepsilon, M^{-1} cm^{-1}) = 521(24000), 486(16000), 434(101400), 409(52000), 386(18200), 333(132800); \) Fluorescence (CHCl3, \( \lambda_{\text{ex}} = 478 \text{nm})): \( \lambda_{\text{em}} = 523 \text{nm}; \) FT-IR(KBr): \( \text{cm}^{-1} = 3384, 2956, 2927, 2856, 1710, 1665, 1604, 1595, 1518, 1495, 1467, 1401, 1343, 1320, 1305, 1244, 926, 810, 796, 754, 584; \) MS(MALDI): m/z = 942.04(M+H+). (Calculated 941.12).

The synthesis of 5,11-dihexyl coronene-2,3,8,9-tetracarboxylic dianhydride was performed using perylene-3,4,9,10-tetracarboxylic diimide as starting material by modifying similar literature procedures.21,39–41 (see Supplemental Materials)

Electrochemistry.—Cyclic voltammetry was performed on a modified AFRDE4 Bi-Potentiostat (Pine Instrument Co.) electrochemistry workstation.7 The measurements were done using a three electrode electrochemical cell equipped with spiral Pt wire counter electrode and Ag/AgCl reference electrode saturated with KCl. The working electrodes were glassy carbon disks (3 mm diameter), Au disk (1.5mm diameter) and Indium Tin Oxide (ITO) coated glass (variable dimension) electrodes. The Au and GC disk electrodes were polished using alumina powder sonicated for one minute in water, cleaned with hydrogen peroxide and finally rinsed with CH2Cl2. The ITO electrodes were cleaned using aqueous detergent (Alconox liquid) in an ultrasonic bath followed by cleansing with acetone and ethanol for 20 minutes each and finally rinsed with CH2Cl2. The solutions were purged with argon gas before all measurements which were done at room temperature.

Visible-NIR spectroelectrochemistry.—The electropolymerization was performed in the long pathlength Teflon homemade spectroelectrochemical cell that employed ITO glass slides (75 × 25 × 1.1 mm, 70–100 Ω, Delta Technology Ltd) as working electrodes.7 The electrode potential was controlled by a modified AFRDE4 Bi-Potentiostat (Pine Instrument Co.), electrochemistry workstation while UV-Vis measurements were performed with an Agilent 8453 UV-Visible spectrophotometer. Solutions in the electrochemical cell were bubbled with Ar for at least 10 mins. The electrochemical potential was stepped to the appropriate value and each spectrum was taken when the cell current decayed to zero.

Atomic force microscopy (AFM).—The morphological analysis of polymer films deposited on ITO were performed using a Bruker AFM system (multimode 8). The Scan-Asyst-Air mode was used for imaging the samples. AFM imaging in the Scan-Asyst-Air mode is very similar to the peak force tapping mode in where the operation is a non-rosonant procedure. However, in the Scan-Asyst-Air mode, all the imaging parameters are automatically adjusted. All images were generated by the Bruker NanoScope Analysis 1.5 software.

Results and Discussion

Synthesis and properties of DCTD.—The DCTD monomer (Scheme 1) was synthesized from 5,11-dihexyl coronene-2,3,8,9-tetracarboxylic dianhydride. Synthesis of 5,11-dihexyl coronene-2,3,8,9-tetracarboxylic dianhydride has been reported previously.21,39–41 The electropolymerizable group, diphenylamine, was introduced in imide position by refluxing coronene dianhydride in quinoline for 24 hrs with 4-aminodiphenylamine. The structure of DCTD was confirmed by NMR, FT-IR and Mass spectrum analysis. The solubility of DCTD in organic solvents is less than N,N'-dialkyl derivatives, however the optical properties is identical to previously reported N,N-dialkyl coronene diimide derivatives.21

Electropolymerization of monomers.—DCTD has a low solubility in common organic solvents such as CH2Cl2, CH3CN, THF, dichloroethane, and dichlorobenzene. The addition of TFA greatly increases the solubility as found in perylene diimides.44 Given that CH2Cl2 is a convenient solvent due to high dielectric constant, easy purification, we chose this solvent for the electropolymerization. The cyclic voltammogram of the electropolymerization of the DCTD
monomer is shown in Figure 1. The ionic liquid, BMIM TFSI (0.1 M) and TFA (~0.008 v/v) were used as supporting electrolytes. In this electrosynthesis process, the first scan shows a large oxidation peak current at 1.05 V and the corresponding reduction shows two peaks at 0.87 and 0.62 V. During the second and subsequent scans, two oxidation peaks occurred at 0.92 and 0.74 V and the corresponding reduction peaks were observed upon reversing the scan direction (Figure 1). The oxidation and reduction peak currents gradually increases as the number of scan increased in the same potential window but the intensity of the first peak at 1.05 V decreased. This peak represents the irreversible oxidation of the diphenylamine group. Similar results have been reported in case of electropolymerization of monomers containing naphthalene diimide, ferrocene, and perylene diimides.7–13 As the first reverse scan (negative direction) of DCTD exhibits no reduction peak corresponding to 1.05 V oxidation peaks, the two new reduction peaks were assigned for the reduction of newly formed diphenylbenzidine (DPB) cations (one for DPB and the other for DPB). The proposed polymer structure is shown in Scheme 2, based on previous work on numerous perylene, naphthalene and benzene diimide diphenylamine polymers.7–13,44,45 DPB is formed by the intermolecular carbon-carbon ring coupling of either two diphenylamine radicals of two monomers (the EECC mechanism), or one diphenylamine radical from one monomer and one neutral diphenylamine from other monomer (ECEC mechanism).42 However, Hao showed that the DPB formed by oxidation of the naphthalene diimide monomer (DNTD) took place via ECEC mechanism.36

Scheme 2. Poly(DCTD).

Table I. Effect of solvent on the electrochemistry of DCTD polymer in oxidation potential (positive scan) (0.1 M BMIM TBSI).

| Solvent  | DN   | AN   | Ep1/Epa1 (V) | ΔEp1 (mV) | Ep2/Epa2 (V) | ΔEp2 (V) |
|----------|------|------|--------------|-----------|--------------|-----------|
| CH₂Cl₂   | 0    | 20.4 | 0.75/0.65    | 100       | 0.98/0.87    | 110       |
| C₂H₅Cl₂  | 0    | 16.7 | 0.50/0.53    | 30        | 0.84/0.73    | 110       |
| THF      | 20.0 | 8.0  | -            | -         | 0.92/0.82    | 100       |
| CH₃CN    | 14.1 | 18.9 | -            | -         | 1.04/0.87    | 170       |
| DMF      | 26.6 | 16.0 | -            | -         | -            | -         |
| DMSO     | 29.8 | 19.3 | -            | -         | -            | -         |

DN = Gutmann donor number, AN = Gutmann acceptor number.43

Electrochemistry of polymer film under different conditions.— We have studied the electrochemistry of these polymer films on different surfaces and in different solvents. Figure 2 shows the cyclic voltammogram of a 4 × 10⁻³ mol/cm² thick DCTD polymer on a GC electrode surface. The oxidative redox couples correspond to the presence of electroactive DPB in the polymer chain producing two radical cations, DPB and DPB⁺⁻ consistent with previous work done in our group.7–13 Also linear dependence the peak current dependence on the scan rate confirmed that the polymer film was surface confined (Figure 3). The electrochemical behavior of DPB group in non-halogenated solvents is different. In DMSO and DMF, the redox behavior of DPB is ill defined. In the negative scan range, reversible reduction peaks occur at ~0.97 and ~1.22 V vs Ag/AgCl in CH₂Cl₂. The reduction peaks are consistent with the presence of a redox active coronene tetraoxycarbonyl diimide group.22 It is worth noting that when comparing benzene diimides to naphthalene diimides to perylene diimides, a general trend toward more positive reduction potentials is found. The trend is reversed when comparing the coronene diimide polymers. While the aromatic rings of perylene diimides can twist out of plane, reducing the orbital overlap of the two radical anions, in the case of the coronene diimide the rigidity of the structure prevents that relaxation. The peak potentials in different solvents are summarized in

Table II. Effect of solvent on the electrochemistry of polymer in reduction potential (negative scan) (0.1M BMIM TBSI).

| Solvent  | DN   | AN   | Ep1/Epa1 (V) | ΔEp1 (V) | Ep2/Epa2 (V) | ΔEp2 (V) |
|----------|------|------|--------------|----------|--------------|----------|
| CH₂Cl₂   | 0    | 20.4 | -0.97/-0.90  | 70       | -1.22/-1.03  | 190      |
| C₂H₅Cl₂  | 0    | 16.7 | -1.06/-1.02  | 40       | -1.38/-1.14  | 240      |
| THF      | 20.0 | 8.0  | -0.89/-0.88  | 10       | -1.29/-1.07  | 220      |
| CH₃CN    | 14.1 | 18.9 | -0.86/0.93   | 70       | -1.28/-1.12  | 160      |
| DMF      | 26.6 | 16.0 | -0.87/-0.83  | 40       | -1.19/-1.11  | 80       |
| DMSO     | 29.8 | 19.3 | -0.80/-0.76  | 40       | -1.17/-1.07  | 100      |

DN = Gutmann donor number, AN = Gutmann acceptor number.13

Figure 1. Polymerization of 0.1mM DCTD in CH₂Cl₂ containing 0.1 M BMIM TFSI and TFA (0.008%) at a GC disk electrode (area 0.071 cm²). Scan rate 200 mV/s.
Tables I and II. For solvents with low donor number, i.e. with high Lewis acidity, the DPB group shows good electrochemical reversibility upon oxidation.\(^7,12\) In the cathodic region, the solvents THF, CH\(_3\)CN, DMF and DMSO with high donor number, the first reduction potentials are more positive than those for solvents with low donor number due to the tetracarboxylic diimide anions being stabilized by solvent donation.

Since the electrochemistry of poly(DCTD) was solvent dependent, we also investigated the electrolyte dependence. For films grown from a solution of 0.1mM DCTD in CH\(_2\)CH\(_2\) containing 0.1 M BMIM TFSI and placed in a solution of acetonitrile, the voltammetric peaks were ill-defined for the 2e\(^{-}\) oxidation of DPB in solutions containing BMIM TFSI, TEABF\(_4\), LiClO\(_4\) (Figure 4). However, the electrochemistry was reversible when the electrolyte contained TBABF\(_4\) and TBAClO\(_4\) (Figure 4). While in CH\(_2\)Cl\(_2\) containing BMIM TFSI (Figure 3), well-separated 2e\(^{-}\) oxidation and reduction signals of DPB were obtained. Therefore, in the positive potential range, the electrochemistry of poly(DCTD) was affected by both the cation and anion of the supporting electrolyte. On the other hand, upon reduction of the coronene diimide, all the voltammograms show at least two pairs of redox peaks except for LiClO\(_4\). In the LiClO\(_4\) case, the electrochemistry was not reversible indicating that the interaction of a smaller inorganic cation and the diimide anion was unfavorable. Similar behavior for the diimide anion in naphthalene and perylene diimide were reported previously.\(^13,36,43–45\)

**Spectroelectrochemistry of DCTD polymer.**—The poly(DCTD) polymer was electropolymerized onto ITO with a thickness of \(1 \times 10^{-9}\) mol/cm\(^2\) and then studied by UV-Visible-near IR spectroscopy at the different potentials. Figure 5 depicts the spectrum of the neutral state of poly(DCTD) showing absorption maxima at 513, 480, 430, 408 and 333 nm. At the oxidation potential of +0.8 V vs Ag/AgCl, a broad absorption band centered at 900 nm

![Figure 2. Cyclic voltammograms of poly(DCTD) film on GC electrode surfaces in different solvent containing 0.1 M BMIM TFSI electrolyte. GC electrode area = 0.071 cm\(^2\). Scan rate 200 mV/s. A. CH\(_2\)Cl\(_2\); B. DMF; C. CH\(_3\)CN; D. THF; E. DMSO; F. Dichloroethane.](image-url)

![Figure 3. Scan rate dependence on DPB oxidation peak of DCTD film on GC electrode surface in the 0.1 M BMIM TFSI solution of CH\(_2\)Cl\(_2\) (GC electrode area = 0.071 cm\(^2\)). The inset shows CV’s of this poly(DCTD) film, scan rate 25(smallest current) and 500(largest current) mV/s.](image-url)
Figure 4. Cyclic voltammograms of poly(DCTD) film on GC electrode surfaces in CH$_3$CN solvent containing 0.1 M electrolyte. GC electrode area = 0.071 cm$^2$.
Scan rate 200 mV/s. A. TBABF$_4$; B. BMIM TFSI; C. TBACIO$_4$; D. TEABF$_4$; E. TBAPF$_6$; F. LiClO$_4$.

was observed. Due to the low energy and broadness of the peak, we attribute this to the formation of $\pi$-stacking of the DPB$^+$ unit of poly(DCTD). The absorption for $\pi$-stacking in the polymers containing perylene, naphthalene and ferrocene exhibits a peak between 1000–1100 nm. The absorption band shift to shorter wavelengths in the case of poly(DCTD) might be due to increased steric hindrance between chains as compared to the other polymers. The absorption bands between 400 to 513 nm dramatically increased in intensity, at the same time that the intensity of the band at 333 nm decreased. Upon further oxidation, an intense absorption band appeared at 602 nm indicating oxidation to DPB$^{2+}$ with concommitant decrease in the intensity of the 900 nm band, indicating that the dication formation in the polymer chain reduces the $\pi$-stacking interaction. Upon reduction of the polymer films at $-1.0$ V vs Ag/AgCl, a radical anion is formed with new absorption bands at 620 and 982 nm. Also the absorption bands between 400 to 513 nm dramatically decrease in intensity. When applying a very negative potential of $-1.3$ V, the tetracarboxylic diimide reduces to a dianion, and the spectrum showed
Figure 5. Visible-near IR spectroelectrochemistry poly(DCTD) film on the surfaces of ITO electrode at different potentials (vs Ag/AgCl) in 0.1 M BMIM TFSI solution of CH₂Cl₂.

additional peaks at 562, 676 and 824 nm together with a diminution of the peak at 982 nm.

Electrochromic behavior.—Poly(DCTD) displays reversible color changes upon oxidation and reduction. Figure 6 shows photographs of the polymer film in a 0.1 M BMIM TFSI solution of CH₂Cl₂ at different potentials. In the neutral state, the color of the polymer film was similar to that of the monomer in solution. Upon oxidation DPB⁺ forms and the polymer film changes to green. The intense yellow color of neutral state of the polymer is similar to the color of the first oxidation state so a color change is not pronounced. The steric hindrance due to the coronene group could impede π-stacking overlap of the DPB groups in the radical cation state. Upon further oxidation, the color changes to blue which is consistent with the previous results. A cathodic change in potential results in a color change from yellow to violet to green, i.e. the two reduced states of polymer showed two different colors.

Morphology of the polymer film.—To investigate the microstructure and morphology of the poly(DCTD) film on ITO surfaces, AFM analysis was performed. Figure 7 shows both phase and height images of a polymer film, where we found very small grain sizes indicating that the large continuous domain has not been grown the polymer bed. This might be due to the side chain at the 5 and 11 positions of the coronene core structure or because the film is too thin to be grown for the large domain. However, the grain growths were very uniform and smooth reflecting a self-organizing behavior that enabled better π–π stacking formation.

Conclusions

A novel coronene diimide containing diphenylamine end group monomer has been successfully synthesized and electropolymerized on different conductive surfaces for the first time. The synthesized polymer is electroactive and in 0.1 M BMIM TFSI solution of CH₂Cl₂, the film shows multistep reversible redox reactions in both anodic and cathodic directions. Solvents with high Lewis acidity show more reversible DPB oxidations. In contrast solvents with high Lewis basicity, the imide reduction appeared at more positive potential values. The
larger electrolyte cations, BMIM or TBA were more efficient for both oxidation and reduction of DPB and tetracarboxylic diimide groups, respectively. Spectroelectrochemistry experiments show a strong absorption at near IR region the first oxidation step of DPB due to π-stacking on the polymer film. Reversible electrochemical behavior has been observed in both anodic and cathodic potential changes which is a rare in phenomenon organic polymers. On the basis of this electronic and electrochromic properties, this polymer material could be useful to design organic optoelectronic devices.

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Figure 7. AFM images of a 6.22 × 10^{-9} mol/cm² thick poly(DCTD) on ITO electrode surface: Phase image (top) and height image (bottom).