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Decacyanooctatetraene Dianion: A Model System for Cyanocarbon-Based Conjugated Polymers

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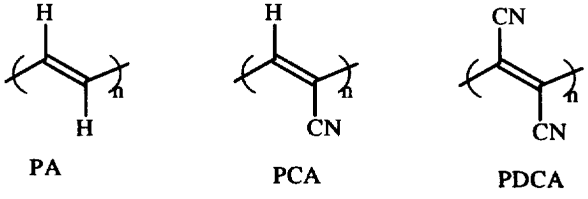
Abstract Decacyanooctatetraene (DCOT) has been prepared as its dianion and studied as a model compound for the prototypical n-dopable polymer poly(dicyanoacetylene) (PDCA).

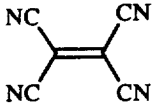
INTRODUCTION

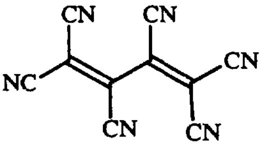
Most conjugated polymers are p-type semiconductors, i.e., they are easier to oxidize than reduce. However, there has been a demand on n-type semiconducting materials due to the recent development of organic electronic and optoelectronic devices, in which n-dopable polymers serve as conductive electrodes, transport layers and in pn junctions. One approach to make the conjugated polymers become n-dopable within a practical potential range is to incorporate electron withdrawing functional groups to lower the LUMO of the material. The cyano group is the most ideal functional group because of its strong electron withdrawing ability and its linear geometry. CN-PPV[1-5] and polydicyanothiophene (PDCNT) [6] are successful examples in this case.

Poly(cyanoacetylene) (PCA) and poly(dicyanoacetylene) (PDCA) are prototypical cyanocarbon-based conjugated polymers. PCA has a polar substituent on every alternate carbon atom which is expected to lead to very high degree of bond alternation and a high band gap. On the other hand, for PDCA, every backbone carbon atom is equivalent and the polymer is expected to have the same geometry as polyacetylene (PA). In their theoretical works, Abdelaty and Fukutome[7] considered the electronic effect of the cyano substituent on the property of PDCA and predicted that PDCA should have even smaller bond alternation and band gap than PA. Anionic polymerization of dicyanoacetylene is reported to give PDCA in a form of black powders.[8-10] Unlike most conjugated polymers, these samples are soluble in common organic solvents such as acetone. The IR spectra of these polymers exhibit intense conjugated nitrile groups which suggests that the polymer is formed through the reaction of carbon-carbon triple bonds instead of the carbon-nitrogen triple bonds. However, the transport property of the so-synthesized PDCA is much like undoped *cis*-PA, with immobile defects and low conductivity. Doping with either iodine or sodium vapor did not yield conductivity higher than 10^{-9} S/cm. These experimental facts were explained with the possibility of steric interactions and interchain interactions. However, no direct evidence supporting these arguments was reported and the poor electronic properties of the reported PDCA remained an unsolved dilemma.



In this work, we attempt to solve the long existing questions pertaining to the reported PDCA and PCA by studying the oligomers of PDCA. Percyanoalkenes, e.g., tetracyanoethylene (TCNE), hexacyanobutadiene (HCNB) and decacyanooctatetraene (DCOT) are PDCA's with 1, 2 and 4 monomer units, respectively. The molecular geometry and chemical reactivity of the larger oligomer are expected to resemble the polymer itself. But the characterization of these small molecular weight cyanocarbons is much less complex than that of a macromolecule. Since the properties of TCNE and HCNB are well documented, in this paper we will focus on the preparation and characterization of DCOT and discuss the impact of the results on the understanding of this cyanocarbon-based conjugated polymer.


TCNE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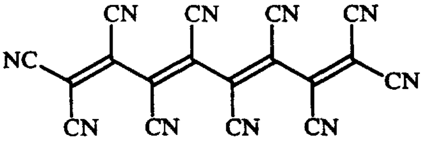
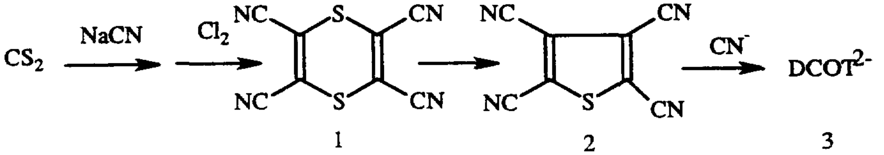

DCOT

RESULTS AND DISCUSSION

Decacyanooctatetraene was prepared as its tetraethylammonium salt or tetraphenylphosphonium salt through the reaction of tetracyanothiophene with potassium cyanide (Scheme 1).[11] The dark red solids obtained by this procedure proved to have the proposed elemental composition and the divalent nature of the anion is confirmed in the negative electrospray (ESI) mass spectrum. ^{13}C NMR of the DCOT dianion exhibits nine peaks out of a total of 18 carbons, indicating the existence of a two-fold symmetry. This fact limited the product to be one of four possible *cis-trans* isomers: *trans-trans-trans*, *cis-cis-cis*, *trans-cis-trans*, *cis-trans-cis*.



Scheme 1. Synthetic route for the preparation of DCOT dianion

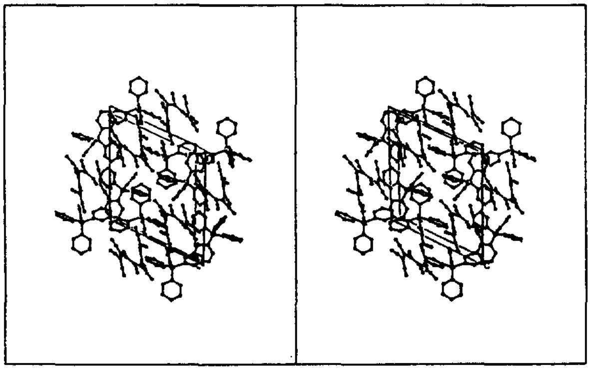


Fig. 1. Packing of the structure viewed down the a axis showing $C^+DA^{2-}C^+$ chains.

X-ray crystallography provided a more detailed look on the molecular geometry and the solid state structure of the tetraphenylphosphonium salt. The crystal structure consists of dianion species and disordered tetraphenylphosphonium cations (Figure 1). The packing of the structure is in a parallel "chain" fashion such that chains of the dianion are sandwiched between two tetraphenylphosphonium cationic chains. As shown in Figure 2, the dianion adopts an all *cis* configuration and the backbone of the molecule forms a helical structure with all the cyano groups pointing away from the center of the helix. The distortion of the molecule away from the ideal planar structure is a result of a combination of steric interaction and coulomb repulsion of the adjacent cyano groups. This effect is also seen in hexacyanobutadiene (HCBD) and its *cis* dianion. A crystallographic study has revealed[12] that HCBD is twisted about the C-C single bond by 40° from the *trans* structure. The *cis* HCBD dianion is also reported[13] to show considerable deviations from planarity and some distortion of bond angles to minimize crowding.

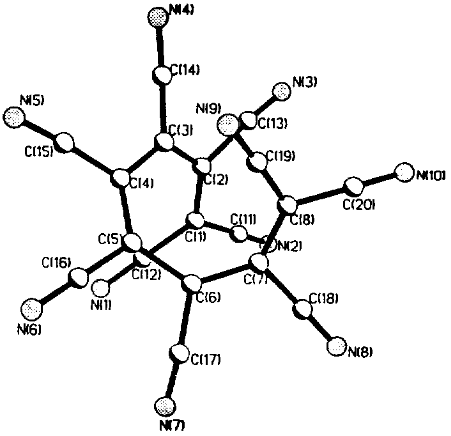


Fig. 2. Asymmetric unit with atomic labeling of DCOT dianion

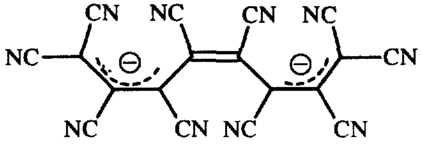
Table 1. Bond Lengths (Å) for the DCOT Dianion

Bonds	C(1)C(2)	C(2)C(3)	C(3)C(4)	C(4)C(5)	C(5)C(6)	C(6)C(7)	C(7)C(8)
Bond Length (Å)	1.35 (2)	1.39 (2)	1.51 (2)	1.39 (2)	1.45 (2)	1.39 (2)	1.36 (2)

Table 2. Selected Torsion Angles for DCOT Dianion

Atoms	Torsion Angles (°)
C(11)C(1)C(2)C(13)	8.9
C(13)C(2)C(3)C(14)	16.8
C(14)C(3)C(4)C(15)	25.5
C(15)C(4)C(5)C(16)	14.9
C(16)V(5)C(6)C(17)	34.1
C(17)C(6)C(7)C(18)	12.2
C(18)C(7)C(8)C(20)	11.8

The backbone of the molecule contains a peculiar bond alternation (Table 1). Two of the bonds, C(3)-C(4) and C(5)-C(6) are in the vicinity of typical single bonds, while the double bond character is more pronounced at the ends of the helical backbone (C(1)-C(2) and C(7)-C(8)). Separating these typical single and double bonds are three bonds (C(2)-C(3), C(4)-C(5), C(6)-C(7)) with lengths between a true single bond and a true double bond (1.39 Å). Table 2 listed selected torsion angles on the DCOT dianion. The dicyanoethylenes are planar, whereas the highest deviation from planarity is around C(3)-C(4) and C(5)-C(6) single bonds. These crystallographic data depicted a "localized delocalization" character which is also supported by our NMR results.



The "localized delocalization" of the negative charge on DCOT dianion

The *cis*-*cis*oid structure of DCOT dianion is a result of the tetracyanothiophene precursor. We attempted to obtain the *trans* isomers through thermal isomerization in both solution and solid state. However, at temperatures higher than 180 °C, deterioration of the molecule was observed, while at temperatures lower than 180 °C, there was no observable reaction. This is entirely different from the behavior of the HCBD dianion, for which the *cis*-*trans* isomers are thermally interconvertible, and the *trans* form is favored over the *cis* form[14] The stability of the *cis*-*cis*oid structure of the DCOT dianion also contradicts what was learned from polyacetylene, whose *cis*-*cis*oid structure has the highest energy and could be converted to the *trans* structure thermally or through doping.[15]

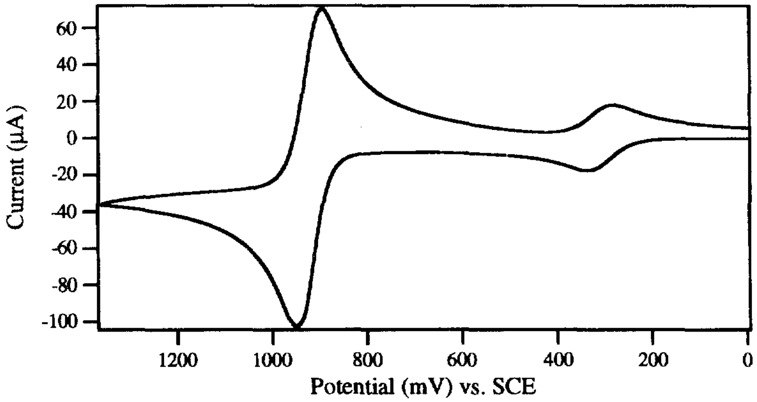


Fig. 3. Representative cyclic voltammogram of $(TPP)_2DCOT$ in acetonitrile

In cyclic voltammetry measurements, at potentials between -2 V and 2 V vs. SCE, DCOT dianion exhibits a single quasi-reversible redox couple at 0.92 V (Figure 3). Controlled potential Coulometric oxidation of the DCOT dianion at 1.0 V vs. SCE gave n_{app} of about 2.1, which means that the observed redox couple involves the transfer of two electrons, as contrasted to the HCBD dianion, which oxidizes consecutively at two different potentials.[14] This may be caused by a major conformational change involved during the oxidation of DCOT dianion to neutral DCOT. The results of cyclovoltammetry with varying scan rate are summarized in Table 3. The splitting of the single two-electron wave into two one-electron waves was not observed at the fast scan rate limit in this experiment. However, we observed large scan rate dependence of ΔE_p as well as i_{pa}/i_{pc} and $i_{pa}/v^{-1/2}$ values, suggesting some electrochemical irreversibility. Moreover, the one-electron-transfer intermediate was detected by UV-vis and EPR experiments during the oxidative electrolysis of DCOT dianion, which indicates the redox couple at 0.92 V is actually two closely spaced one-electron transfers, rather than a direct two-electron transfer.

Table 3. Typical Cyclic Voltammetry Data as a Function of Scan Rate

scan rate v (V/s)	E_{pa} (mV, vs. SCE)	E_{pc} (mV, vs. SCE)	ΔE_p (mV, vs. SCE)	i_{pa} (mA)	i_{pc} (mA)	i_{pa}/i_{pc}	$i_{pa}/v^{-1/2}$ (mA(s/V)$^{1/2}$)
0.1	941	893	48	0.092	0.096	0.96	0.29
1.0	968	870	98	0.29	0.27	1.05	0.29
2.0	969	877	92	0.39	0.36	1.08	0.28
5.1	973	866	107	0.59	0.53	1.11	0.26
10.2	983	859	124	0.78	0.69	1.13	0.24

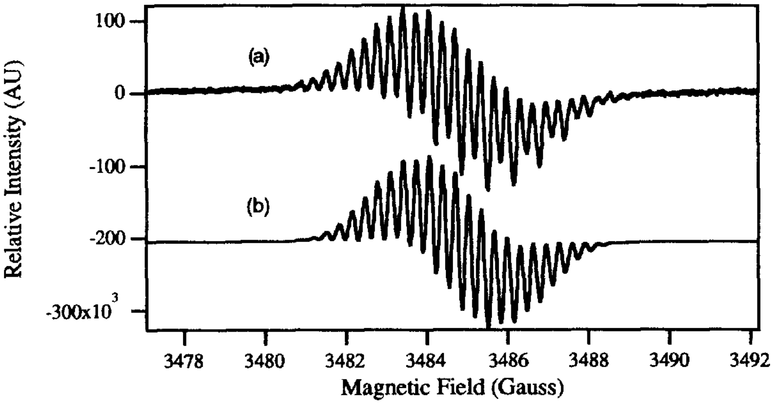


Fig. 4. ESR spectrum of DCOT radical anion in acetonitrile. (a) experimental data; (b) simulated spectrum

Table 4. Simulation results for the solution EPR spectrum of DCOT radical anion

type of nuclei	HFC	number of nuclei
^{14}N	0.69	2
^{14}N	0.59	4
^{14}N	0.32	2
^{14}N	<0.01	2

During an electrolysis experiment, a strong absorption band appeared at 692 nm and subsequently diminished. A sample of this blue-colored solution had a strong ESR signal, proving that this absorption results from the radical anion intermediate. The EPR spectrum with a hyperfine structure for the 0.75 mM solution together with the simulated spectrum is shown in Figure 4. The g-value 2.0034 is as previously reported for the purported "pristine" PDCA produced by anionic polymerization of dicyanoacetylene.[10,8] The ESR spectrum of the PDCA radical anion consisted of weak hyperfine interactions of the free radical with quadrupolar nitrogen nuclei. It is well simulated based on the "localized delocalization" structure obtained from the X-ray crystallographic data. An interesting finding from this simulation is that the hyperfine species with two equivalent nuclei has the larger hyperfine constant (HFC) than the hyperfine coupling with four equivalent nuclei (Table 4), which indicates that the resonance structure with the free radical residing on the terminal carbon is less important than the other resonance structure. The DCOT radical anion is stable under Ar atmosphere, a result of the delocalization of the spins over several atomic sites.

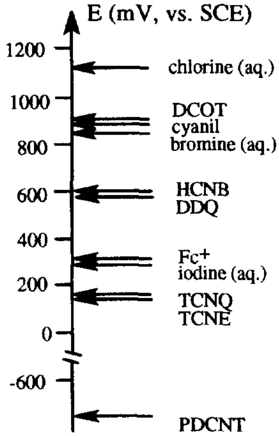


Fig. 5. Comparison of the reduction potentials of common oxidation reagents with those of DCOT and new n-dopable polymer poly(dicyanothiophene) (PDCNT).

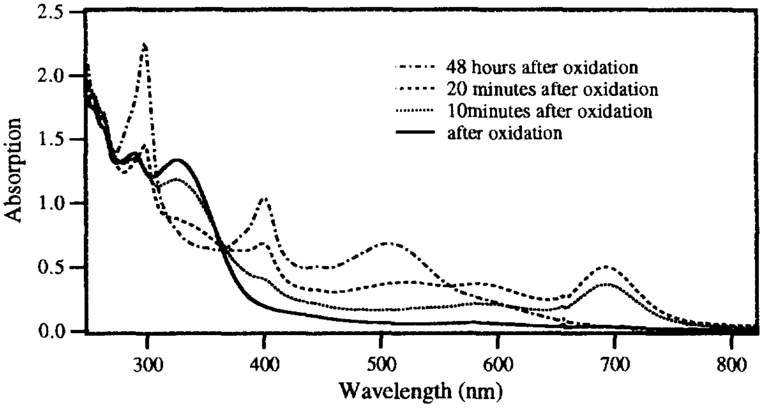


Fig. 6. UV-vis spectrum of the neutral DCOT and its reduction products

The cyclic voltammetry data demonstrated that it will take a reagent with reduction potential higher than 0.92 V to oxidize the DCOT dianion, which left very few choices among the commonly used oxidation reagents (Figure 5). The neutral DCOT is a reactive oxidant, therefore the reactions were carried out in non-reductive environment. The reaction of chlorine with the tetraethylammonium salt yielded a mixture of products with non-conjugated nitrile groups, due to possible addition of chlorine. Also, there was no reaction found between lead tetraacetate and the dianion in acetonitrile or toluene. In solid state, bromine does not react with the dianion. The reaction of bromine with the tetraethylammonium salt in acetonitrile did produce the neutral DCOT in the presence of large excess of bromine. However, a mixture of neutral DCOT and DCOT radical anion was obtained when the unreacted bromine was removed due to the existence of the following equilibrium:

$$\mathrm{Br_2 + DCOT^{2-} \rightleftharpoons Br^- + DCOT^{\cdot-}}$$
$$\mathrm{Br_2 + DCOT^{\cdot-} \rightleftharpoons Br^- + DCOT}$$
$$\mathrm{DCOT + DCOT^{2-} \rightleftharpoons 2DCOT^{\cdot-}}$$

The oxidation of DCOT dianion can be achieved electrochemically. However, once exposed to air, the product is rapidly reduced to its radical anion and eventually its dianion form (Figure 6).

CONCLUSION

The reactive nature of DCOT, together with previous studies on TCNE and HCNB as electron acceptors for charge transfer salts raises a question which has been neglected for more than 30 years: *is neutral PDCA stable in anionic polymerization environment?* Based on the result of this work, the answer is a categorical *No*. The electronegativity of PDCA oligomers increases rapidly with the increase of the number of the dicyanovinylene ("monomer") units (Figure 7). If one could base an extrapolation on a three point line, the oxidation power of PDCA would be comparable to chlorine before the chain grows to 10 "monomer" units. The professed pristine PDCA obtained from anionic polymerization of dicyanoacetylene is most likely over-reduced oligomers of PDCA, which explains its low conductivity, high solubility and the negative results of the doping experiments. It should be possible to produce neutral PDCA only in non-reductive reaction environment.

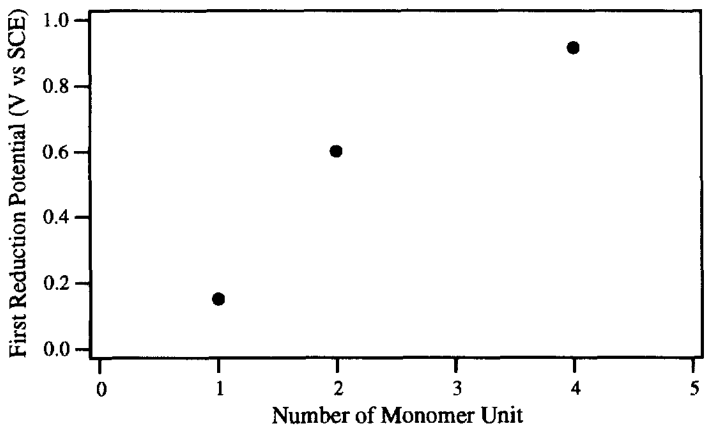


Fig. 7. First reduction potentials of PDCA oligomers: TCNE (n=1); HCNB (n=2); DCOT (n=4)

Also in account with its high reduction potential values, PDCA is prominently n-dopable. The n-doped polymer, as demonstrated by the dianion of DCOT, is environmentally stable.

The non-planar structure of DCOT and HCNB can be used to predict that PDCA will also be non-planar. As a result, PDCA is expected to have a higher band gap value which will limit achieving a high conductivity value. However, PCA and PDCA-*co*-PA should give rise to n-dopable, highly conducting polymers because of the interspersed C-H bonds between the highly repulsive C-CN.

EXPERIMENTAL

General. NMR spectra were taken at 500 MHz for ^1H and 125 MHz for ^{13}C on Varian Inova 500 spectrometer. UV-vis measurements were obtained on a Hewlett Packard 8452A Diode Array spectrometer. IR spectra were recorded on a Mattson Galaxy Series FTIR 3000 apparatus. Acetonitrile (Fisher) used in electrochemical experiments was distilled from calcium hydride and stored over 4Å molecular sieves. Immediately prior to use, it was distilled again from phosphorus pentoxide under argon. Tetrabutylammonium tetrafluoroborate (Fluka) was recrystallized from ethyl acetate and dried in a drying pistol under 1 mmHg vacuum at boiling toluene temperature for 72 hours. Ferrocene (Aldrich) was sublimed before use. Preparative column chromatography was performed at low positive pressure on deactivated alumina (contains 15% weight of water).

Crystallographic Analysis of (TPP)$_2$DCOT. Deep red prismatic crystals were obtained from acetone/ether by slow evaporation. Data were collected at 298 K on a Siemens Smart diffractometer with CCD detector, using Mo-K$_a$ radiation, $\lambda = 0.71073$ Å operating at 50 kV and 50 mA. The structure was solved and refined by using a Siemens SHELXTL program package. For the refinement, 2119 unique reflections with $I > 4s$ were used; $R(F) = 0.169$ and $S = 1.22$ for 334 parameters. All the non-hydrogen atoms from the DCOT were refined anisotropically. The phenyl groups were refined as rigid bodies with hydrogens in the riding mode. There are no unusual intra- or inter- chain interactions in the molecule except for the hydrogen-like bonding between non-terminal cyano-nitrogens N(4), N(5) and N(8) with phenyl hydrogens.

Table 5. X-ray Crystallographic Details

Formula	$C_{66}H_{40}N_{10}P_2$
Formula weight	1035.06
Crystal system	Triclinic
Space group	$P\underline{1}$
a, Å	14.1671 (15)
b, Å	14.6663 (15)
c, Å	16.1796 (17)
a, deg	109.792 (2)
b, deg	104.028 (2)
g, deg	107.361 (2)
Z	2
Density (calc), g/cm^3	1.23
Density (exp), g/cm^3	1.23
Volume, Å^3	2789.6 (5)

EPR measurement. The solution EPR analysis of the radical anion of DCOT was performed on a sample from bulk electrolysis containing partially oxidized DCOT tetraethylammonium salt in acetonitrile. EPR measurements at room temperature were carried out on a Bruker ESP-300 spectrometer. The sample (0.75 mM in acetonitrile) was placed in a flat cell inside the cavity, the microwave power level was 1 mW. Simulation of the EPR spectrum was done by calculating the energies and intensities of the lines, followed by convolution with a Lorentzian lineshape in the time domain. Variation of the parameters (linewidth and hyperfine coupling) was done by using the downhill simplex algorithm, until the residuals between the spectrum and fit reached a minimum.

Electrochemical measurements. Both cyclic voltammetry and controlled potential bulk electrolysis were carried out using a Bioanalytical Systems 100A/W electrochemical analyzer in a one-compartment cell with a platinum working electrode, a platinum counter electrode and a Ag/AgNO$_3$ reference electrode. For CV experiments, the potential was corrected against ferrocene internal standard added immediately after each measurement. The reported potentials were related to the SCE reference using a value of 0.307 V vs. SCE for the $Fc^{+/0}$ couple. The potential at which electrolysis was performed was determined by a preceding CV measurement.

Preparation of tetracyanodithiin (1). The synthesis of 1 has been reported in the literature.[16] To a 500 ml round bottom flask equipped with reflux condenser, addition funnel and mechanical stirrer, finely powdered NaCN 16.3 g (0.333 mol) and 150 ml DMF was charged. CS_2 20 ml (0.333 mol) was added dropwise to the vigorously stirred suspension during a period of 10 minutes at 0 °C. The cooling bath was removed when the addition was completed. The reaction mixture was stirred at room temperature for 20 min. and then 55-60 °C for 45 min. After the resulting brownish black solution was cooled down to room temperature, a slow stream of chorine was passed through the reaction flask until a persisted yellow color was obtained. Celite, 4 g was added and stirred with the reaction mixture for 10 minutes. The DMF solution was isolated through filtration and then poured into 1.5 L water with vigorous stirring. The precipitated solid was collected and repeatedly recrystallized from 1,2-dichloroethane to give bright yellow tetracyanodithiin 6.16 g (34% yield). IR (KBr): 2240, 2229, 2217, 1519, 1176, 1157, 1026, 1012, 976, 521 cm^{-1}; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 125.52, 112.44 ppm; UV-vis (CH_2Cl_2) λ_{max}: 246, 280, 318, 332 nm.

Preparation of tetracyanothiophene (2). The synthesis of 2 has been reported in the literature. [16] Tetracyanodithiin 3.0 g was mixed with 15 ml 1,2,4-trichlorobenzene in a flask equipped with a reflux condenser, a mechanical stirring bar and a thermometer. The mixture was then immersed in an oil bath preheated to 220 °C. After refluxing for 10 minutes, the reaction mixture was cooled down to room temperature. The crystalline solid was collected through filtration and washed with CS_2. Recrystallization from toluene afforded colorless tetracyanothiophene 2.36 g (yield 91%). IR (KBr): 2239, 2231, 1623, 1513, 1153, 486 cm^{-1}; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 124.99, 120.80, 110.04, 110.01 ppm; UV-vis (CH_2Cl_2) λ_{max}: 236, 282 nm.

Preparation of decacyanooctatetraene dianion (3) The synthesis of 3 has been reported in literature.[11] Potassium cyanide 1.0 g (15.3 mmol) was powdered and dried before being suspended in 10 ml acetonitrile. The mixture was heated to reflux. Tetracyanothiophene 1.0 g (5.43 mmol) in 20 ml of acetonitrile was added dropwise in a period of five minutes. Reflux was continued for 17 more hours. The resulting dark brownish-red solution was filtered and concentrated *in vacuo*. The reddish solid was redissolved in 30-40 ml water. To this solution was added a concentrated aqueous solution of 15 mmol tetraethylammonium bromide or tetraphenylphosphonium chloride with vigorous stirring. The precipitated solid was collected through filtration and dissolved in 300 ml methylene chloride. The CH_2Cl_2 solution was washed with water, dried over $MgSO_4$ and concentrated *in vacuo*. The solid was then dissolved in minimum amount of acetonitrile and passed through a column packed with deactivated alumina. The first band was collected to give a deep red solid. Recrystallization from 1,1,2-trichloroethane for $(TEA)_2DCOT$ or CH_2Cl_2/ether for $(TPP)_2DCOT$ gave analytically pure samples. The silver salt was obtained by treating the $(TPP)_2DCOT$ solution in CH_2Cl_2 with silver tetrafluoroborate.

decacyanooctatetraene dianion, di(tetraphenylphosphonium) salt ($(TPP)_2DCOT$) (1.02 g, 36% yield): mp 182-183 °C. IR (DRIFT): 3061, 2198, 1589, 1488, 1468, 1438, 1279, 1190, 998, 1110, 753, 726, 691, 533 cm^{-1}; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 135.21, 134.50, 134.39, 130.38, 130.26, 119.07, 118.01, 117.51, 117.12, 117.06, 115.59, 114.15, 112.37, 103.11, 90.39, 58.20 ppm; UV-vis (CH_3CN) λ_{max}: 298, 348, 400, 510 nm; Anal. Calcd. for $C_{66}H_{40}N_{10}P_2$: C, 76.59; H, 3.90; N, 13.53. Found: C, 76.66; H, 3.96; N, 13.51.

decacyanooctatetraene dianion, di(tetraethylammonium) salt ($(TEA)_2DCOT$) (950 mg, 44% yield). IR (DRIFT): 2995, 2198, 1484, 1455, 1404, 1395, 1282, 1171, 1001, 783, 547, 504, 458 cm^{-1}; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 119.21, 117.65, 117.20, 115.75, 114.29, 112.51, 103.22, 90.52, 58.35 51.41, 51.39, 51.37, 7.15, 7.11, 7.06, 7.01 ppm; UV-vis (CH_3CN) λ_{max}: 298, 348, 400, 510 nm; ESI MS m/z 178.2 ($DCOT^{2-}$).

decacyanooctatetraene dianion, disilver salt (Ag_2DCOT). IR (DRIFT): 2300, 2272, 2237, 2217, 1490, 1473, 1457, 1405, 1367, 1286, 1247, 1031, 930, 537, 493, 462 cm^{-1}; ^{13}C NMR (125 MHz, DMSO-d_6) δ: 119.24, 117.67, 117.20, 115.77, 114.29, 112.53, 103.23, 90.55, 58.40 ppm.

Preparation of decacyanooctatetraene and its radical anion by electrooxidation: DCOT dianion salt 5.0 mmol and pre-dried acetonitrile 5 ml were added into a well-dried home-made one-compartment electrolysis cell under argon atmosphere. Immersed in the solution were a magnetic stirring bar, a cylindrical working electrode made of 4 cm^2 platinum foil, a Ag/$AgNO_3$ reference electrode and a platinum counter electrode which was separated from the bulk solution by a Vycor Tip. The oxidation was done under constant current or constant potential conditions. Based on the time of the reaction or the magnitude of the residue current, the oxidation was stopped at different stages to give neutral DCOT or its radical anion. DCOT: UV-vis (CH_3CN) λ_{max}: 290, 326 nm. DCOT radical anion: UV-vis (CH_3CN) λ_{max}: 692 nm.

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