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Octacyanotetramethylene-substituted dicyclopentanaphthalene: a new anionic electron acceptor with multi-stage reversible redox behavior

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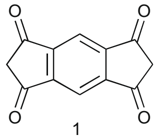
ABSTRACT

The dianion of 2,2′,2′′,2′′′-dicyclopenta[*b*,*g*]naphthalene-1,3,6,8-tetraylidenetetramalononitrile **4** exhibits relatively strong electron-accepting properties and undergoes reversible electrochemical reductions to the tetra- and hexaanionic species.

During the past decades, organic multi-stage reversible redox systems remain the focus of numerous investigations. The interest toward this group of organic compounds has initially been arisen by their potential as electrochromes[1] and components of electroconducting and superconducting materials (organic metals).[2] Currently, this field of research is supported by the rapid development of such applications as corrosion protection, organic LEDs, molecular wires, switches, and memories.[3] In spite of the variety of potential applications, the number of organic compound types that exhibit multi-stage reversible redox behavior is relatively small. Thus, the neutral electron acceptors are represented mostly by the tetracyanoquinodimethane and dicyanoquinodiimide derivatives and the neutral electron donors by the polyacenes and tetrathiafulvalene derivatives.[4] The most employed cationic electron acceptors are derived from 4,4′-bipyridylium salts[5] and the anionic electron donors and acceptors are practically unknown. Recently, moderate aromaticity has been predicted to exist in dicyclopenta-fused polyacenes.[6] The corresponding dianions, being iso-π-electronic with aromatic polyacenes, should be even more aromatic and, therefore, this class of organic derivatives can be promising for the design of new reversible redox systems.

Recently, we elaborated an efficient synthetic approach toward tetraketo derivatives **1** and **2** (*Janus diones*),[7] which enables the preparation of these derivatives in relatively large scale. The corresponding octacyanomethylene derivatives **3** and **4** should form stabilized by extended charge delocalization dianions and are of special interest. Herein we report on the first preparation, spectroscopic, and redox properties of derivative **4**.

Refluxing **2** with a large excess of malononitrile in water in the presence of sodium acetate under Ar afforded derivative **4** in 75% yield (after chromatographic purification) as shining deep blue crystals. The same procedure can be used for the synthesis of derivative **3**[8] from **1**.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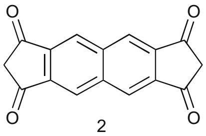
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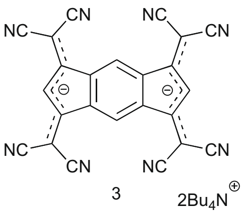

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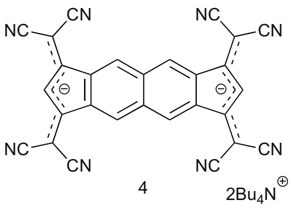

4

The X-ray structure determination[9] confirmed the anticipated structure of the dianion (Fig. 1). Derivative **4** is almost planar (the deviation from planarity of the dicyanomethylene moieties does not exceed 3°). The deviation from planarity may stem from the short contacts between the cyano groups and the methylene groups of the tetrabutylammonium cation (CN···CH$_2$N 2.55–2.75 Å). Judging by the bond lengths within the C5–C4–C9–C10 fragment both the negative charges are effectively delocalized

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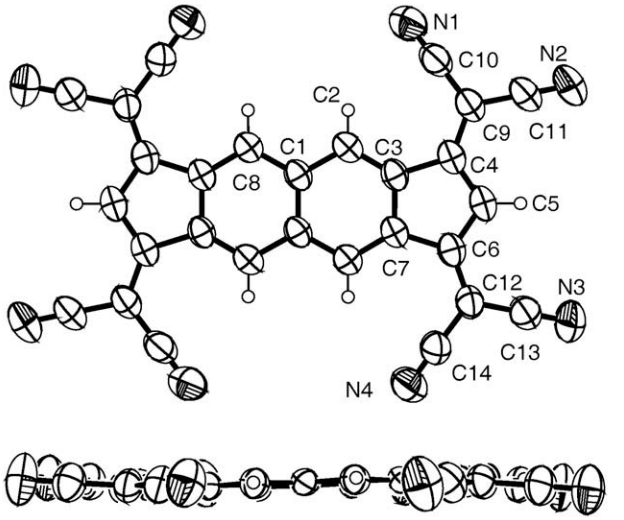


Figure 1. ORTEP plot of **4** at 50% probability level. The TBA cations are omitted for clarity. Selected distances in Å: C1–C2 1.418(5); C1–C8 1.420(5); C1–C1 1.422(7); C2–C3 1.358(5); C3–C7 1.426(5); C3–C4 1.486(5); C4–C9 1.384(5); C4–C5 1.389(5); C5–C6 1.402(5); C6–C12 1.380(5); C6–C7 1.485(5); C9–C10 1.415(7); C9–C11 1.421(6); C10–N1 1.137(6); C11–N2 1.145(5); C12–C13 1.424; C12–C14 1.425(6); C13–N3 1.144(5); C14–N4 1.135(5). Dihedral angles N1–C9–C4–C3 1.5°, N2–C9–C4–C5 3°.

between the cyano groups and the pentadiene moieties. The geometry of the naphthalene moiety is very close to that observed in 2,3,6,7-naphthalenetetracarboxylic dianhydride.[10] A strong peak at 2189 cm^{-1} (CN stretching) is observed in the IR spectra of **4**. The UV–Vis spectrum of **4** features a system of vibronically split overlapping bands (Fig. 2). The longest wave split band is centered at about 600 nm. The second absorption band is centered at about 440 nm.

Geometry optimization[11] without symmetry constraints using the B3LYP/6-31G(d,p) method yielded a planar structure of D_{2h} symmetry. The experimental bond lengths and the IR spectra are well reproduced. The electronic spectra calculations using the TD B3LYP/6-31G (d,p) method predicted 618 and 446 nm for the first two electronic transitions matching well to the observed spectrum. The first electronic transition can be safely interpreted as basically HOMO→LUMO transitions.

The electrochemical redox properties of derivative **4** are of special interest. Scanning toward the negative potentials revealed two reversible reduction peaks at $E_p^1 = -0.86$, $E_p^2 = -1.10$ V (vs SCE) (Fig. 3). Under the same conditions, the reduction peak of *p*-naphthoquinone was observed at −0.70 V. The quantitative measurements using tetrathiafulvalene as the internal standard showed that each peak corresponds to two-electron transfer. The overall reduction process involves conversion of the aromatic dianion into the formally nonaromatic tetraanion and further into the aromatic hexaanion, as shown in Scheme 1.

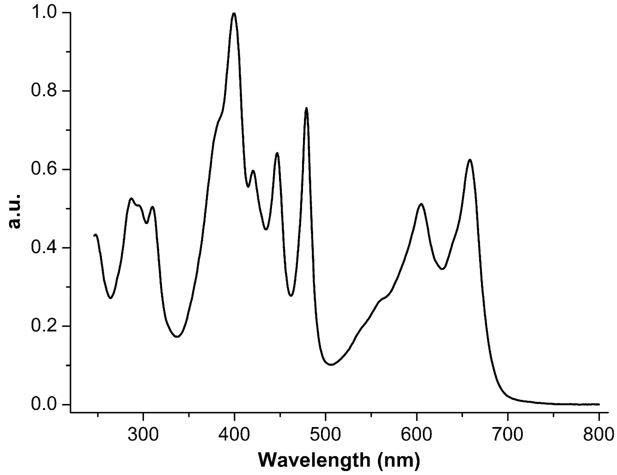


Figure 2. UV–Vis spectra of **4** in MeCN.

Scanning toward the positive potentials showed two irreversible oxidation peaks at 0.83 and 1.01 V (vs SCE). In this case, two-electron oxidation should afford a biradical, in which the two unpaired electrons cannot be coupled and may undergo polymerization. Oxidation of the 1,3-indandione anions is known to yield the corresponding dimers.[12] Indeed cycling around the oxidation potential or holding the potential just above the oxidation peak led to deposition of a black shining insoluble layer on the electrode surface. The nature of the oxidation product is currently under investigation.

We conclude that the dianion of octacyanotetramethylene-substituted dicyclopenta-fused naphthalene derivative **4** is a relatively strong electron acceptor comparable to *p*-naphthoquinone. This compound can easily be prepared from 2,3,6,7-naphthalenetetracarboxylic dianhydride and can serve as a promising component or precursor of molecular and polymeric advanced materials.

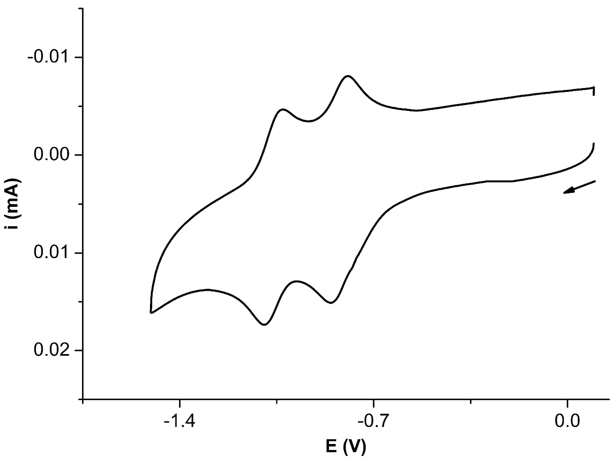
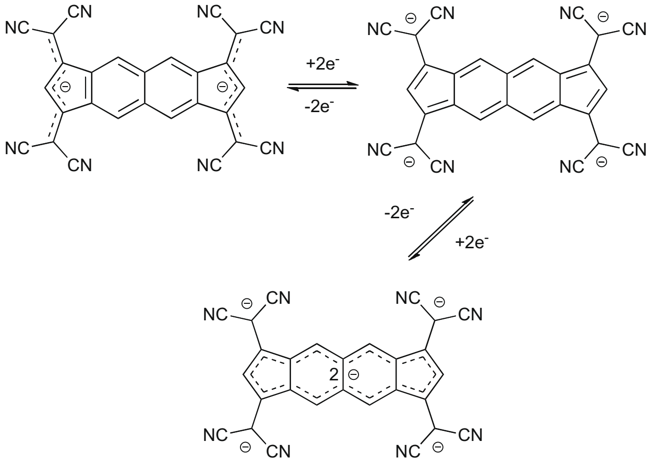


Figure 3. CV of **4** in MeCN versus SCE, Bu$_4$NBF$_4$, GC electrode, sweep rate 100 mV/s.



Scheme 1. Reversible four-electron reduction of **4**.

Acknowledgments

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