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Synthesis, Reactivity, and Electronic Properties of 6,6-Dicyanofulvenes

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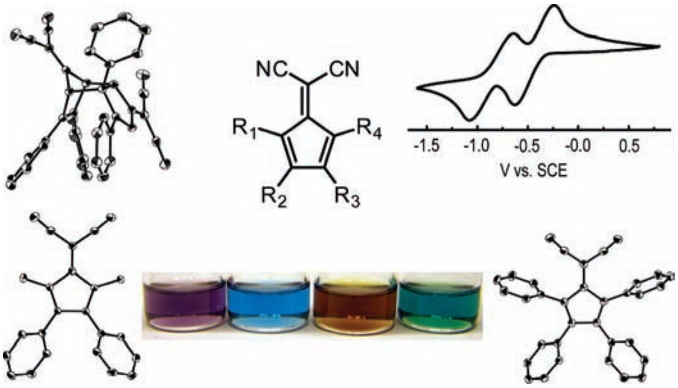
ABSTRACT



A series of 6,6-dicyanofulvene derivatives are synthesized starting from masked, dimeric, or monomeric cyclopentadienones. The reactivities of 6,6-dicyanofulvenes relative to their parent cyclopentadienones are discussed. 6,6-Dicyanofulvenes are capable of undergoing two consecutive, reversible, one-electron reductions and are presented as potential *n*-type small molecules.

During the past decade, intense research efforts have yielded numerous optimized, air-stable, *p*-type (hole-transporting) organic semiconductors with conductivities and hole mobilities that are competitive with inorganic analogues.[1] Recently, several examples of *n*-type (electron-conducting) organic materials have been utilized in thin-film organic field-effect transistors (OFETs) and photovoltaic cells,[2] but the electronic and solid-state packing properties, air stability, and processability of *n*-type semiconductors are far from being as optimized as their *p*-type counterparts.[3]

The discovery of new molecular building blocks for *n*-type materials remains germane, as the diversity in the chemical structures of proven electron conductors does not match the large population of known organic hole conductors. To date, polymeric/oligomeric/small molecule oxadiazoles,[4] benzothiadiazoles,[5] arylene imides,[6] perfluorinated[7] or perfluoroalkyl-containing arenes,[8] fullerenes,[9] pyridiniums,[10] and dicyanovinylene-[11] or tricyanovinylene-substituted arenes[12] have been demonstrated as suitable *n*-type materials. Notably, nitrile incorporation is an interesting design strategy, as it both results in desirable electronic properties (low LUMO

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energies)[13] and is capable of transforming a *p*-type organic system into an electron-accepting material.[14]

Cyclopentadienones (CPDs) and fulvenes have received little attention as *n*-type building blocks and have only been considered indirectly, as structural subunits in indenofluorenone and indenofluorene bis(dicyanovinylene) chromophores.[11a,b] Wudl et al. reported a donor−acceptor polymer containing a dithienylcyclopentadienone moiety in its repeat unit, where the CPD served as the "acceptor" component;[15] however, this polymer displayed complex electrochemistry and did not demonstrate *n*-type behavior in an OFET. The paucity of CPD- or fulvene-based building blocks could also be attributed to the reactivity and instability of these classes of molecules: many CPDs are unisolable in their monomeric form[16] (see Figure 1A), and the electrochemical stability of fulvenes is suspect.[17]

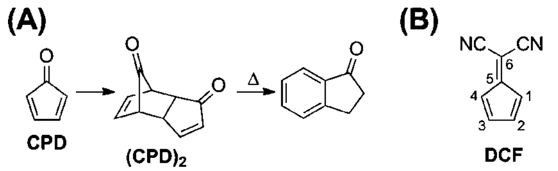
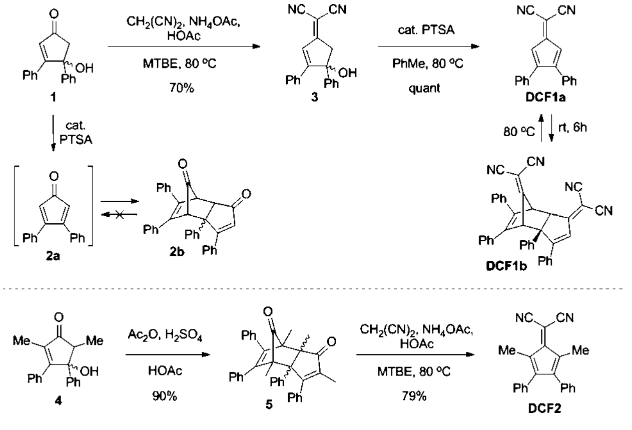


Figure 1. (A) Structures of the unisolable cyclopentadienone, CPD, and its isolable dimer, (CPD)$_2$. (B) Structure of 6,6-dicyanofulvene (DCF), depicting the numbering convention for a fulvene skeleton.

We propose, instead, the use of 6,6-dicyanofulvenes (DCFs, Figure 1B) as building blocks for electron-transport materials. In this contribution, we explore the synthesis of DCFs, their chemical stabilities, and their optical and electrochemical properties.

Informed by the instability of monomeric cyclopentadienone, we first synthesized a diphenyl derivative of 6,6-dicyanofulvene based on the hypothesis that two phenyl substituents would provide enough steric protection from dimerization. 2,3-Diphenyl-6,6-dicyanofulvene (**DCF1a**) was synthesized in two steps from the 4-hydroxy-2-cyclopenten-1-one derivative **1** (Scheme 1), which was prepared by an aldol condendation between acetone and benzil.[18] Acid-catalyzed dehydration of **1** generates the corresponding cyclopentadienone **2a**, which either irreversibly undergoes a [4 + 2] homodimerization[16] or can be trapped by suitable dienophiles to generate 1,2-diphenylbenzene derivatives after decarbonylation.[18] To avoid such undesirable side reactions, only transformations of the masked cyclopentadienone **1** were pursued. The 1,2-addition of malononitrile to compound **1** proceeded smoothly to yield **3**. We initially aniticipated the occurrence of a number of detrimental rearrangement reactions competing with the 1,2-addition of malononitrile; however, as supported by the crystal structure of **3** (Figure 2A), the desired product was the sole isolated compound. Dehydration of **3** by a catalytic amount of PTSA at elevated temperatures quantitatively generated a dark brown solution of **DCF1a**; however, this dicyanofulvene was found to dimerize at room temperature to **DCF1b**. As seen in the crystal structure of dimer **DCF1b** (Figure 2B), the endo adduct was the major isolated product.

Scheme 1. Synthesis of Select 6,6-Dicyanofulvene Derivatives



Dimerization was reversible and was accompanied by disappearance of the dark brown color of the starting **DCF1a**

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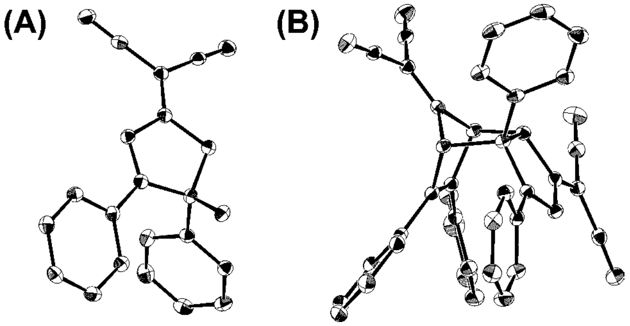


Figure 2. Crystal structures of (A) **3** and (B) **DCF1b**.

solution. The monomeric fulvene could be recovered by heating **DCF1b** to 80 °C, and we were able to cycle between monomeric and dimeric forms multiple times with little to no decomposition noticeable by ^{1}H NMR spectroscopy. This observation is in contrast to the behavior of **2a**, for which dimerization is an irreversible phenomenon (heating results in decarbonylation).[16] Moreover, the tendency of **DCF1a** to undergo [4 + 2] dimerization is not shared by other 6,6-disubstituted fulvenes, such as a 6,6-dimethylfulvene.[17]

In an attempt to isolate a monomeric 6,6-dicyanofulvene, two methyl substituents were introduced at the 2- and 5-positions of the starting hydroxy-2-cyclopenten-1-one. Compound **4** was obtained from the aldol condensation of 3-pentanone with benzil and was subsequently dehydrated to yield the cyclopentadienone dimer **5**. Compound **5** is a member of a subclass of cyclopentadienones that can be reversibly cracked to their monomeric forms at elevated temperatures, unlike the parent CPD.[16] Therefore, **DCF2** was directly accessed from **5** by conducting the 1,2-addition of malononitrile at 80 °C. Notably, dark purple, crystalline **DCF2** was isolated in its monomeric form (see Figure 3A), while the corresponding cyclopentadienone dimerizes at room temperature.

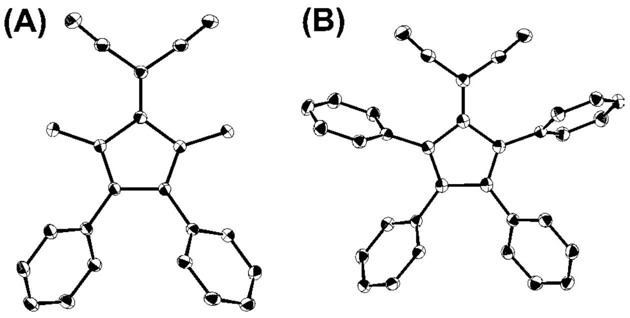
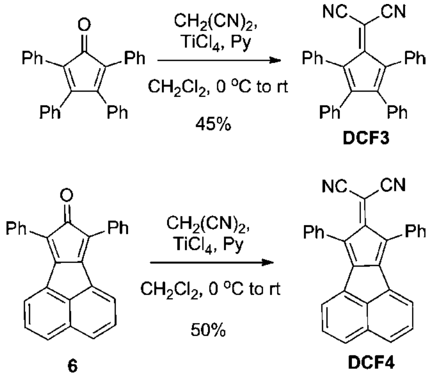


Figure 3. Crystal structures of (A) **DCF2** and (B) **DCF3**.

It was found that introduction of phenyl substituents at the 1,4-positions of the fulvene skeleton hindered the 1,2-addition of malononitrile, and therefore, the reaction conditions used in the synthesis of **DCF1-2** failed to generate the dicyanofulvene analogues of tetracyclone and **6**. Nevertheless, the use of a strong Lewis acid, such as $BF_3{\cdot}OEt_2$ or $TiCl_4$, in combination with pyridine afforded the desired cyanofulvenes **DCF3** and **DCF4** (Scheme 2). In these instances, the progress of the reaction can be witnessed optically: deep purple tetracyclone forms pea green **DCF3**, while navy blue **6** forms emerald green **DCF4**.

Scheme 2. Synthesis of 1,4-Diphenyl-6,6-dicyanofulvenes



The crystal structure of **DCF3** is shown in Figure 3B. Both **DCF2** and **DCF3** do not display edge-to-face packing in the solid state, preferring instead weak $\pi-\pi$ interactions between fulvene cores (see Supporting Information, Figures S1 and S2).

Cyclic voltammograms (Figure 4) of all monomeric dicyanofulvenes were recorded to judge their suitability as electron-transport materials in electronic devices. The electrochemical properties of **DCF2-4** are summarized in Table 1. In general, the dicyanofulvenes displayed two distinct, reversible one-electron reduction peaks. The first one-electron reduction for **DCF3** and **DCF4**, which contain two phenyl substituents in the 1,4-positions, occurred at slightly less negative potentials than in DCFs with alkyl substituents in the 1,4-positions.

Table 1. Optical and Electrochemical Properties of **DCF2-4**

compd	λ_{max}/nm (log ε)	E_{red}/V vs SCE	EA^a/eV
DCF2	275 (4.2), 370 (4.1), 555 (2.5)	−0.57, −1.24	3.83
DCF3	270 (4.2), 387 (4.1), 543 (2.6)	−0.45, −1.04	3.95
tetracyclone	265 (4.3), 338 (3.8), 509 (3.1)	−1.06	–
DCF4	333 (4.7), 638 (2.6)	−0.43, −0.85	3.97
6	334 (4.2), 381 (3.9), 580 (3.1)	−0.95	–

[a] EA = E_{red} (V vs SCE) + 4.4 eV.

For cases where the parent CPDs are monomeric, such as with **DCF3-4**, it was possible to evaluate the effects of the dicyanovinylene moiety on the electronic properties of select cyclopentadiene systems. As previously reported, cyclic

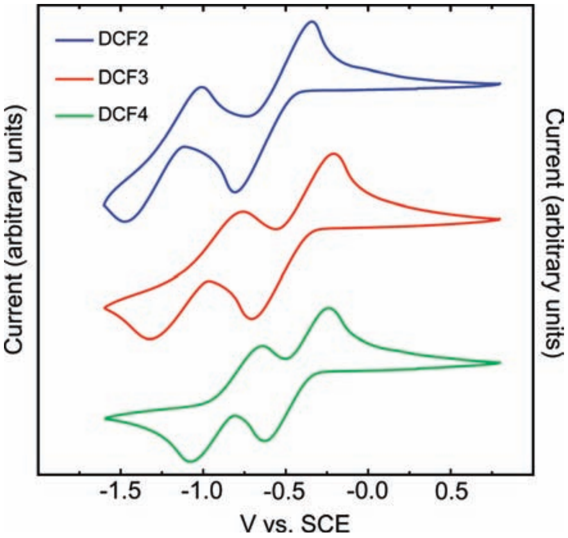


Figure 4. Cyclic voltammograms of **DCF2-4** recorded in 0.1 M $TBAPF_6$ in CH_2Cl_2 using a Pt button electrode at a scan rate of 100 mV/s. Voltage values are reported vs standard calomel electrode (SCE).

voltammograms of CPDs generally display a single two-electron reduction peak[19] (see Supporting Information, Figure S3), and the intermediate radical anion product of one-electron reduction is observed only in select cases.[15] In contrast, the intermediate radical anions of DCFs are stable, and therefore, cyclic voltammograms of DCFs display two distinct, one-electron reduction peaks. Additionally, the formal reduction potentials of DCFs are globally lower than those of the corresponding CPDs.

The electron affinities (EA) of **DCF2-4** were calculated from their formal reduction potentials using the formula EA $= E_{\mathrm{red}} + 4.4$ eV[10] and are listed in Table 1. With average electron affinities of 3.9 eV, DCFs are comparable to PCBM (EA 4.0 eV) as electron acceptors.

In conclusion, a series of substituted 6,6-dicyanofulvenes were synthesized starting from masked, dimeric, or monomeric cyclopentadienones. DCFs lacking sufficient steric bulk around the fulvene core tend to reversibly undergo a [4 + 2] dimerization. In addition to being highly crystalline, DCFs are darkly colored compounds due to the presence of electronic transitions in the visible region of the electromagnetic spectrum. DCFs display two distinct, reversible one-electron reductions by cyclic voltammetry. Based on their high crystallinity and suitable electron affinities, and buoyed by their relatively cheap and straightforward synthesis, DCFs are interesting candidates for organic electron-transport materials.

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Supporting Information Available: Experimental procedures, spectral characterization data, and crystallographic information. This material is available free of charge via the Internet at http://pubs.acs.org.

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