

Twisting a C=C Double Bond in Crowded Alkenes: The Synthesis and Characterization of Small-Molecule Electron Acceptors

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Abstract:

There is currently a need for novel, non-fullerene-based electron acceptors in organic photovoltaic devices (OPVs). The synthesis and characterization of various 9,9'-bifluorenylidene (9,9'-BF) derivatives are described. The dihedral angles of the derivatives were determined using DFT calculations and were determined to increase upon introduction of methyl substituents on the inner C1 and C8 atoms. The red shifted UV-vis absorption spectra and negative shift in oxidation potential, determined by cyclic voltammetry, were observed with increasing the C=C dihedral angles of the derivatives. This is, to our knowledge, the first experimental evidence that the degree of C=C bond twisting has profound effects on the bandgap and redox properties of small molecules.

Introduction:

One of the major objectives for materials science is the optimization of the performance of organic photovoltaic devices (OPVs). In such devices, an appropriate combination of donor and acceptor materials is necessary for efficient charge separation and migration. While several research groups have recently reported a wide range of new polymeric donor molecules, there have been fewer reports on new structures of acceptor molecules [1]. Most current acceptor molecules contain fullerene derivatives — however, due to their difficulty in synthesis and purification, along with their weak absorption in the visible region, the synthesis of new and versatile acceptor molecules is urgently required [2].

There is an inherent potential in acceptor molecules based on 9,9'-bifluorenylidene (9,9'-BF), because the one-electron reduction of 9,9'-BF affords a stable radical anion due to steric strain relief and gain in aromaticity to a 14π electron system [3]. The purpose of this study was to synthesize and characterize a series of novel 9,9'-BF derivatives that differ in the twisting angle of the central C=C double bond, but are similar in other electronic properties. The twisting angle of each 9,9'-BF derivative was correlated to its bandgap and redox properties, which were determined by UV-vis spectroscopy and cyclic voltammetry, respectively.

Experimental Section:

Chemicals were purchased from Sigma-Aldrich and used as received without further purification. All dry solvents

were freshly distilled under argon prior to use. ^1H and ^{13}C NMR measurements were performed in CDCl_3 using a JEOL ECS-400 spectrometer. Chemical shifts are expressed in ppm relative to CHCl_3 (7.26 ppm for ^1H NMR and 77.36 ppm for ^{13}C NMR). Mass spectrometry was performed by a Shimadzu AXIMA-CFR Plus. Computational analysis and graphical representation were carried out with Spartan '14 software. Optimized equilibrium geometries were obtained with DFT (B3LYP/6-31G** level basis set) calculation. UV-vis spectra were recorded on a JASCO V-670 using CH_2Cl_2 solutions of the 9,9'-BF derivatives in 1 cm quartz cuvettes at 298K. The spectrum of each derivative was then normalized to its maximum absorption (typically 450-500 nm). The electrochemical measurements were carried out with an Eco Chemie AUTOLAB PGSTAT12 potentiostat in a deaerated solvent containing TBAPF6 (0.10 M) as a supporting electrolyte at 298K. A conventional three-electrode cell was used with a glassy carbon working electrode and a platinum wire as a counter electrode. The redox potentials were measured with respect to a reference electrode: Ag/AgNO_3 (1.0×10^{-2} M) with TBAPF6 (0.10 M) in acetonitrile. Ferrocene was employed as an external standard.

Results and Discussion:

Compounds **1**, **2**, and **3**, shown in Figure 1, were synthesized via a coupling reaction according to a previous work [1]. The formation of these compounds was confirmed using ^1H and ^{13}C NMR, along with mass spectrometry.

Although the introduction of methyl groups was shown to increase the twisting angle, they should not significantly alter the electronics of the 9,9'-BF derivatives because they are very weak electron donors. This is proven by the comparison of the reduction potentials between non-substituted fluorenone (-1.80 V vs. Fc/Fc^+) and 1,4-dimethylfluorenone (-1.89 V vs. Fc/Fc^+). Methyl groups are therefore an ideal substituent to investigate the effect of C=C twisting on bandgap and redox properties.

The UV-vis absorption spectra for compounds 1, 2, and 3 are shown in Figure 2. It was observed that as the twisting angle increased, there was a red-shift in the absorption spectra, indicating a decrease in the bandgap energy. Additionally, the degree of red shift was observed to be directly related to the increase in twisting angle. These results suggest that the bandgap of 9,9'-BF derivatives can be selectively tuned by modifying the twisting angle.

To investigate the redox properties of the derivatives, cyclic voltammetry was performed, shown in Figure 3. Each HOMO-LUMO bandgap of the derivatives was determined from the oxidation and the reduction potentials, $E_{\text{ox}} - E_{\text{red}}$. There was a significant decrease in the HOMO-LUMO bandgaps of the derivatives upon an increase in twist angle (from 2.50 eV for compound 1 to 2.27 eV for compound 3). This result clearly indicates that the C=C twisting angle of the 9,9'-BF derivatives affects the redox potentials, which is fairly consistent with the UV-vis absorption change.

Conclusions and Future Directions:

We showed the synthesis and characterization of a series of new 9,9'-bifluorenylidene derivatives. The central C=C twist angle was correlated to the bandgap and redox properties of the 9,9'-BF derivatives. Future work will involve performing x-ray crystallography on the 9,9'-BF derivatives to accurately determine C=C twisting angles. Additionally, the versatile synthetic scheme established in this work will be applied to the synthesis of other 9,9'-BF derivatives that have even greater C=C twisting angles, such as derivatives with $-\text{Si}(\text{CH}_3)_3$ substituents.

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References:

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- [2] Eakins, et al. *Can. J. Chem.*, 2013, 91, 1059-1071.
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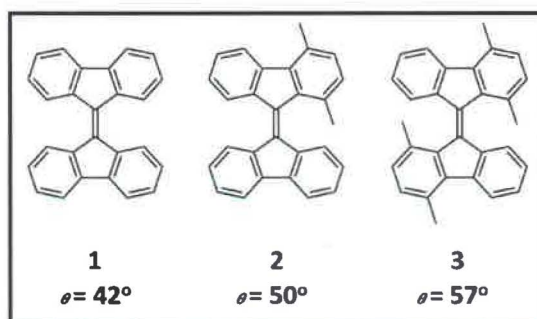


Figure 1: Structures and C=C double bond twisting angles of compounds 1, 2, and 3.

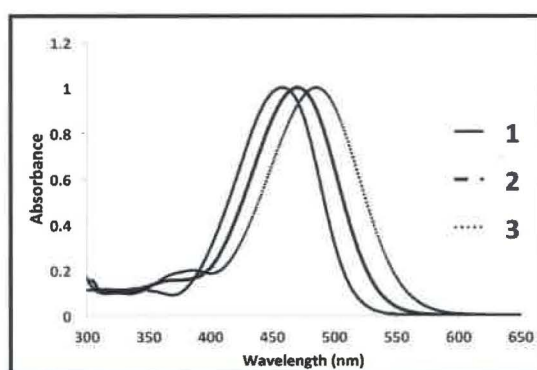


Figure 2: UV-vis absorption spectra of compounds 1, 2, and 3.

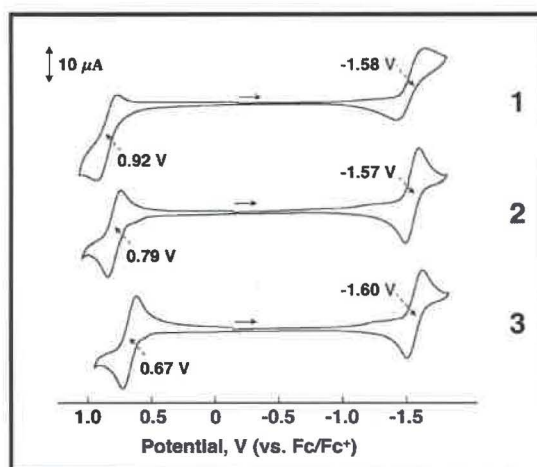


Figure 3: Cyclic voltammograms of compounds 1, 2, and 3.