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Radical Cation of Helical, Cross-Conjugated *β*-Oligothiophene

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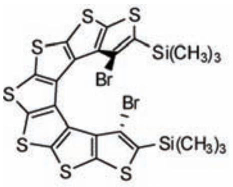
Charged oligothiophenes have attracted great interest in the pursuit of better understanding transport properties of π-conjugated organic materials.[1] Among the most thoroughly studied are the radical cations of α-oligothiophenes.[2−6]

[*n*]Helicenes, helical molecules of rigid, *n ortho*-fused aromatic rings, have recently attracted renewed attention.[7] Nevertheless, radical ions of such helical π-systems have been scarcely studied, even though their near-infrared (NIR) chirooptical properties are of great interest for many important applications.[7a] Among a few examples are radical anions of [6]helicene, thia[7]helicene, and bisquinone-helicenes,[8] as well as radical cations of "helicene-like" molecules derived from diquat.[9] To our knowledge, chirooptical properties of these radical ions were not investigated experimentally.

We have prepared thiophene-based [*n*]helicenes in which *β*-oligothiophene are annelated into a helical structure.[10−12] Such [*n*]helicenes with a cross-conjugated π-system possess strong chirooptical properties and a relatively large optical band gap, $E_g \approx 3.5$ eV.[11,13,14] Here we report an unprecedented radical cation of helical *β*-oligothiophene with a cross-conjugated π-system, [7]helicene **1**. To our knowledge, $\mathbf{1}^{\bullet+}\mathrm{PF}_6^-$ is the first radical cation with a chiral π-system that is configurationally stable at room temperature.



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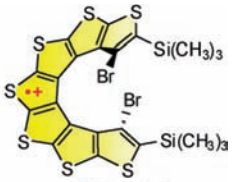

$\mathbf{1}^{\bullet+}\,\mathbf{PF_6}^-$
radical cation

Electrochemical oxidation of **1** is carried out in a homemade spectroelectrochemical cell designed to maintain an inert atmosphere. Cyclic voltammetry of *rac*-**1** in a solvent electrolyte system, consisting of dichloromethane (DCM) and n-Bu$_4$NPF$_6$, shows two reversible waves at $E_1^\circ = +1.34$ and $E_2^\circ = +1.82$ V.[10] These oxidation potentials are much more positive than those for typical alkyl-substituted oligothiophenes, e.g., α-sexithiophene with $E_1^\circ = +0.80$ and $E_2^\circ = +1.00$ V.[3] In analogy with the oxidation of α-oligothiophene at E_1°, the observed wave at $E_1^\circ = +1.34$ is expected to be the one-electron oxidation of *rac*-**1** to its radical cation $\mathbf{1}^{\bullet+}\mathrm{PF}_6^-$. The UV−vis−NIR spectra of **1** are consecutively recorded at stepwise increasing potentials of the working gold-minigrid electrode from 1.10 to 1.30 V (Figure 1 and Figure S1, Supporting Information (SI)).

The first recorded spectrum at 1.10 V shows a prominent band at 255 nm that is identical to that of the neutral [7]helicene **1**.[10] Upon stepwise increase of electrode potentials, the band at 255 nm decreases while new UV−vis bands at 235, 360 (sh), and 500 nm are observed with increasing intensity. The spectrum recorded at 1.30 V is further corrected in the NIR spectral region by subtraction from that of the neutral [7]helicene recorded at 1.10 V, to reveal a weak and broad NIR band at ~950 nm (Figure 1). A potential cycling experiment, in which the UV−vis and EPR spectra of **1** are recorded at 1.3 and 0 V cycles, indicates that formation of the oxidized species that gives rise to those new UV−vis bands is reversible (Figure S2, SI). Most importantly, a strong EPR signal in the $|\Delta m_s| = 1$ region is detected after the 1.3 V cycle. We assign the species formed at 1.30 V to the [7]helicene radical cation $\mathbf{1}^{\bullet+}\mathrm{PF}_6^-$.

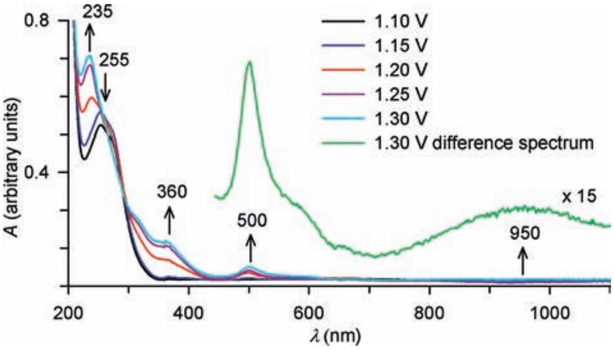

Figure 1. Spectroelectrochemistry of [7]helicene *rac*-**1** in DCM/n-Bu$_4$NPF$_6$: UV−vis−NIR spectra at 1.10−1.30 V.

For chemical oxidation of *rac*-**1** to its radical cation ($E_1^\circ = +1.34$ V), nitrosonium hexafluorophosphate [NO][PF$_6$] ($E^\circ = +1.40$ V in DCM) is selected as an oxidant. All experiments are carried out in homemade Schlenk vessels designed for in situ UV−vis−NIR and EPR or CD spectroscopic measurements to monitor the oxidation of **1**.

A brief exposure of *rac*-**1** in DCM to solid [NO][PF$_6$] provides a yellow colored reaction mixture, which is immediately decanted into the corresponding cell compartments for consecutive UV−vis−NIR and EPR measurements. The reaction mixture shows an intense band at $\lambda_{\max} = 405$ nm in the UV−vis−NIR spectrum, but it is EPR-silent (Figure 2). This result suggests formation of $[\mathbf{1}\text{---NO}]^+\mathrm{PF}_6^-$, a diamagnetic charge transfer complex between [7]helicene **1** and [NO][PF$_6$].[15,16]

Vigorous stirring of the yellow reaction mixture under static vacuum (i.e., vapor pressure of DCM ca. 400−500 Torr) leads to a gradual color change to red-purple.[16] This change coincides with the decrease of the $\lambda_{\max} = 405$ nm band and increase of the new band at $\lambda_{\max} = 510$ nm in the UV−vis−NIR spectra, with approximate isosbestic points at $\lambda = 380$ and 430 nm (Figure 2). In the NIR region, a broad band at $\lambda_{\max} \approx 900$ nm emerges. Most importantly, these spectral changes are associated with a strong

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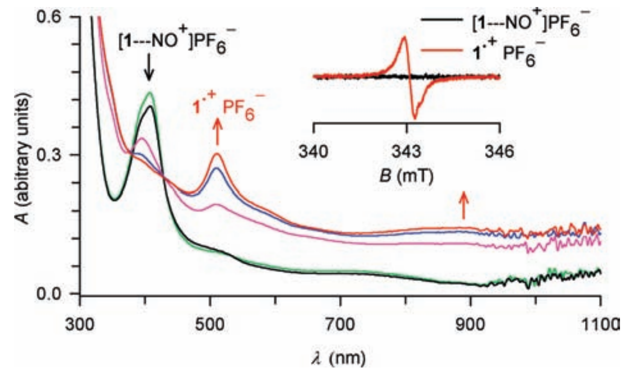

Figure 2. UV−vis−NIR/EPR spectroscopic monitoring of chemical oxidation of [7]helicene *rac*-**1** with [NO][PF$_6$]. EPR spectra are obtained after the UV−vis−NIR spectra corresponding to [**1**---NO]$^+$PF$_6^-$ and **1**$^{\bullet+}$PF$_6^-$.

EPR signal in the $|\Delta m_s| = 1$ region (Figure 2, inset). These spectral features are assigned to radical cation **1**$^{\bullet+}$PF$_6^-$, in agreement with the spectroelectrochemical results.

The absorption bands in the visible and NIR region for cross-conjugated **1**$^{\bullet+}$PF$_6^-$ with seven annelated thiophene rings are found at comparable wavelengths to those reported for radical cations of conjugated α-oligothiothiophenes with only three thiophene rings.[3a] In the EPR spectra, the observed *g*-value, $g \approx 2.006$, for **1**$^{\bullet+}$PF$_6^-$ is relatively large, compared to that reported for the radical cation of alkyl-substituted α-sexithiophene, $g = 2.0023$,[3b] which is very close to the free electron *g*-value. The large *g*-value implies significant spin density at heavy atoms, such as sulfur atoms in helical **1**$^{\bullet+}$PF$_6^-$, similar to that observed for sulfur-rich radical cations.[17] Also, EPR spectra of **1**$^{\bullet+}$PF$_6^-$ remain intense at low temperatures (Figure S3, SI). This is in contrast to the radical cations of α-oligothiophenes, in which their EPR signal mostly disappears at low temperature, due to formation of diamagnetic π-dimers.[1,2] The low propensity for formation of diamagnetic π-dimers may be associated with the helical shape and large terminal substitution in **1**$^{\bullet+}$PF$_6^-$.[5,6]

The procedure for chemical oxidation of [7]helicene (−)-(*M*)-**1** ($[\alpha]_D = -912$) with solid [NO][PF$_6$] is identical to that of the [7]helicene *rac*-**1**. The formation of the radical cation is monitored by the increasing intensity of the UV−vis band at $\lambda_{max} \approx 510$ nm. Once the band at $\lambda_{max} \approx 510$ nm appears very intense, the CD spectrum of the reaction mixture is recorded. The CD spectrum of the radical cation, (*M*)-**1**$^{\bullet+}$PF$_6^-$, shows a negative band at $\lambda_{max} = 287$ nm, which overlaps the intense negative band observed in neutral [7]helicene (−)-(*M*)-**1**.[10] Notably, the new negative bands at $\lambda_{max} \approx 510$ and 360 nm are observed (Figures S6 and S7, SI).

The observed CD spectrum of (*M*)-**1**$^{\bullet+}$PF$_6^-$ provides evidence that the radical cation of (*M*)-**1** retains its helicene structure, as opposed to a plausible planar structure of quasi-[8]circulene.[18] Most importantly, the radical cation **1**$^{\bullet+}$PF$_6^-$ is configurationally stable at room temperature.[19] However, **1**$^{\bullet+}$PF$_6^-$ has limited persistence with a half-life of ∼15−20 min at room temperature (Figure S4, SI).

Electronic CD and UV−vis absorption spectra of radical cation structures derived from **1**$^{\bullet+}$PF$_6^-$ are computed using the TD-UB3LYP/6-31G(d) method and IEF-PCM-UA0 solvent model for dichloromethane (Tables S1 and S2, SI).[20,21] The calculated spectra for the lowest energy structure of **1**$^{\bullet+}$PF$_6^-$ (and nearly so for counterion-free structure **1**$^{\bullet+}$) qualitatively reproduce the UV−vis and CD band positions in the experimental spectra (Figure S9, SI). The exception is the mismatch of the broad NIR band at 900−950 nm, which may reflect the well-known deficiency of the TD-DFT method in the calculations of absorption bands with a large degree of charge transfer.[22] The calculated structures of the radical cation, **1**$^{\bullet+}$PF$_6^-$ and counterion-free **1**$^{\bullet+}$, have a significant fraction of spin density, ∼0.4 unpaired electrons, localized on sulfur atoms (Table S2, SI), in agreement with a relatively large *g*-value found in the EPR spectra.

Configurationally stable radical cations, such as that of helical β-oligothiophenes, as well as other chiral π-conjugated systems, may have an impact in the emerging field of chiral conductors,[23,24] similar to the role of α-oligothiophene radical cations and their π-dimers in organic conductors.[1,2]

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Supporting Information Available: Complete ref 20, experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) Prior to the TD-DFT calculations of spectra, the ground state geometries for considered monomer and dimer structures of radical cation of **1** were fully optimized within the respective point group of symmetry at the UB3LYP/6-31G(d)/IEF-PCM-UA0 level and determined to be minima by the vibrational analyses (SI).
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(24) When solutions of **1**$^{\bullet+}$PF$_6^-$ are allowed to stand at room temperature, the UV−vis and CD bands at $\lambda_{max} \approx 510$ nm diminish and Dyson-like EPR line appears (Figure S8, SI), suggesting formation of conducting solids.

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