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Radical Cations of Twisted Acenes: Chiroptical Properties and Spin Delocalization

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We introduce the first series of enantiopure twistacene radical cations, which form reversibly upon chemical or electrochemical oxidation. Their vis-NIR chiroptical properties (Cotton effect and anisotropy factor) increase systematically with backbone twist. The hyperfine constants observed by EPR demonstrate significant spin delocalization even for large backbone twist angles.

Chiral molecules capable of forming stable organic radicals are attracting growing interest for their charge transfer properties,¹ as building blocks for enantioselective synthesis, and for their electro magneto chiral properties.^{2, 3} Largely in consequence of their strong chiroptical properties, considerable research effort is focused on exploring the potential of helicene and its derivatives to function as chiroptical redox switches.⁴⁻⁶ While parent helicenes usually do not form stable cation radicals, they can be functionalized with redox centers to form chiroptical switches (e.g., transition metals, quinone moieties),^{7, 8} phenalenyl to form stable biradicals,⁹ and heteroatoms or nanographenes for stable cations.^{10, 11} By contrast, the chiroptical properties of the enantiopure radical cations of the *para*-fused analogs of helicenes, namely twisted acenes, are unexplored.

Acenes and their derivatives are perhaps the most commonly studied *p*-type organic semiconductors, as long acenes are stable in their oxidized state.^{12, 13} While parent acenes are planar, they are readily twisted out of planarity upon substitution. Twisted acenes (twistacenes), first introduced by Pascal,^{14, 15} are more stable and soluble compared with their parent acenes,^{16, 17} to the extent that even their radical cations are twisted out of planarity. For example, the rubrene radical cation is twisted by ~27°.¹⁸ However, most twistacenes undergo rapid racemization, as they twist back and forth between the *M*

and *P* helicities.¹⁹ This fluxional behavior greatly complicates efforts to investigate them in enantiopure form. Indeed, Rathore's group investigated the properties of the chiral anthracene radical cation, but its fast racemization prevented study of the enantiopure form.²⁰ To the best of our knowledge, the chiroptical properties of twistacene radical cations remain unexplored.

We recently introduced a new twistacene family, Ant-Cn, whose conjugated backbones are helically locked by a diagonal tether that prevents back and forth flipping around the backbone and, consequently, racemization (Fig. 1).²¹ By adjusting the length of the tether, we synthesized a series of stable M and P Ant-Cn enantiomers. The enantiomerically pure series members exhibit different twist angles while bearing identical numbers of backbone substituents, which minimizes substituent effects. We found the optical and electronic properties of the π conjugated backbone to be strongly and systematically affected by twist angle, such that increased twisting decreases both the fluorescence quantum efficiency and optical band gap of Ant-Cn.²¹ Furthermore, tethering acenes increases their stability and solubility, both of which are important for the future synthesis of long acenes.²² The Cotton effect and absorption anisotropy factors (q_{abs}) of **Ant-C***n* increase systematically with twist angle, apparently because (unlike the case of helicenes) their magnetic and electric transition dipole moments lie in parallel.



Fig. 1 Chemical (FeCl₃) and electrochemical oxidation of **Ant-C***n* (yellow) to the cation radical, **Ant-C***n*⁺⁺ (green) in acetonitrile. The colouring of the molecules is as per their appearance as neutral (left) and cation radical (right) species in acetonitrile solution. The red arches represent the tether, **C***n*. TBAPC, tetrabutylammonium perchlorate, $R = CF_3$.

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While charge and spin delocalization are important factors governing the performance of conjugated systems, the question of how twisting an aromatic system out of planarity affects charge delocalization remains open. Having a measure of spin delocalization vs. twist angle in polyaromatic systems could serve to indicate the degree of twist that an aromatic ring can endure before losing delocalization, and so assist in the design of novel nonplanar aromatic compounds.

Here we introduce the first enantiopure series of radical cation twistacenes. In the vis-NIR spectral region, the series exhibits strong chiroptical properties (Cotton effect and g_{abs}), which increase significantly with increasing acene twist. An EPR study reveals the presence of the cation radical, which shows increasing charge localization with increasing twist.

The structures of **Ant-Cn**⁺⁺ were optimized at the DFT/UB3LYP/6-31G(d) level of theory (Table S2, see ESI). In the neutral state, twisting in **Ant-Cn** ranges from 22° to 43°, which is in line with the range observed in their single crystal structures $(22^{\circ}-38^{\circ})$.²¹ The radical cations, **Ant-Cn**⁺⁺, show a similar, albeit more narrow, range of twisting angles, from 31° for **Ant-C6**⁺⁺ to 44° for **Ant-C3**⁺⁺. Thus, tether length induces a systematic twist in the acene core in both the neutral molecule and its radical cation.

Upon addition of FeCl₃ to an acetonitrile solution of **Ant-***Cn* to produce **Ant-***Cn*⁺⁺, the pale yellow solution turns bright green (Fig. 2a). UV-vis-NIR absorption spectra showed that the π - π * transition of **Ant-***Cn* at ~400 nm gradually decreases, giving rise to three new transitions for **Ant-***Cn*⁺⁺ at ~ 500 nm, 600–750 nm, and a broad transition at 1000–1800 nm (Fig. 2).

The peak around 500 nm does not show a vibronic pattern, and assigned to the $^{2}B_{2g} \rightarrow ^{2}B_{1u}$ might be transition $(SOMO \rightarrow LUMO+1)$ ²³ In contrast, the transition at 600–750 nm, which displays a clear vibronic pattern, can be assigned to the $^{2}B_{2g} \rightarrow ^{2}A_{u}$ transition (HOMO-1 \rightarrow SOMO).²⁴⁻²⁶ This transition is expected to be centered around the acene core, and is observed in parent anthracene at ~720 nm.²⁷ We note that, in a manner similar to that observed for neutral twistacenes,²² the extinction coefficient increases with increased twist from 2500 cm⁻¹M⁻¹ for Ant-C6*+ to 3600 cm⁻¹M⁻¹ for Ant-C3*+. This is probably related to the vibronically allowed transition, whose likelihood increases as anthracene increasingly deviates from D_{2h} symmetry towards C_2 symmetry.²⁸ This transition is also bathochromically shifted with increasing twist, as observed for the neutral twistacenes.²¹

The low energy transition that Ant-Cn⁺⁺ exhibits at 1000–1800 nm might be attributed to the ${}^{2}B_{2g} \rightarrow {}^{2}B_{3g}$ transition, not observed in parent anthracene (forbidden).²⁴ We found that, although this transition is similarly not observed for 9,10-diphenyl anthracene, which has D_{2h} symmetry, it can be observed for 1,5-diphenyl anthracene, which exhibits C_{2h} symmetry, as also supported by TD-DFT calculations (see sections S4 and S5 in the ESI).²⁹ This transition increases in intensity with increasing twist. However, we note that this increase is likely to be related not only to the anthracene twist, but also to the orientation of the substituents. Addition of hydrazine results in the full recovery of the neutral Ant-Cn

spectra (Fig. S9, see ESI), rendering these materials potential chiroptical switches.⁴⁻⁶ DOI: 10.1039/C9CC02735A



Fig. 2 (a) Circular dichroism (CD) spectra showing the formation of Ant-C4⁺⁺ by stepwise addition of FeCl₃ solution and (b) vis-NIR spectra of the formed radicals at a 1:1 ratio of Ant-Cn:FeCl₃ in acetonitrile.

Since enantiopure **Ant-Cn** series members are excellent chiroptical materials, displaying an increase in their Cotton effect with increasing twist,²² we were interested to examine whether their radical cations follow a similar trend. The ECD spectra for **Ant-Cn**⁺⁺ display positive transitions for the *M* enantiomer, similar to the π - π * transition in their neutral states (Fig. 3), with the lower energy transitions at 500 nm and 600–750 nm clearly observed. The vibronic shoulders for the HOMO-1 \rightarrow SOMO transitions, with spacing of around 0.17 eV (~1400 cm⁻¹, corresponding to C=C stretch), indicate that the structure of the acene remains rigid also in the radical cation state.



Fig. 3 Circular dichroism (CD) spectra of *M* and *P* enantiomers (solid and dashed lines, respectively) of **Ant-Cn** (red) and **Ant-Cn**⁺⁺ (blue) in acetonitrile.

Upon increasing the twist angle, there is a significant increase in the Cotton effect (Fig. 4). The molar circular dichroism ($\Delta\epsilon$) for the ${}^{2}B_{2g} \rightarrow {}^{2}B_{1u}$ transition increases three fold from 6.1 M⁻¹cm⁻¹ for **Ant-C6**⁺⁺ (characterized by a 31° twist angle) to 19 M⁻¹cm⁻¹ for **Ant-C3**⁺⁺ (characterized by a 44° twist angle) (Fig. 4, green trace). The $\Delta\epsilon$ for the ${}^{2}B_{2g} \rightarrow {}^{2}A_{u}$ transition also increases from 5 M⁻¹cm⁻¹ for somewhat twisted **Ant-C6**⁺⁺ to 8 M⁻¹cm⁻¹ for strongly twisted **Ant-C3**⁺⁺ (Fig. 4, red trace). The Cotton effect at ~750 nm is relatively strong compared with other all-organic chiral redox chromophores. The value of g_{abs} (Fig. 4, blue trace)

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increases from 2.2 × 10⁻³ for a 31° twist to 3.2 × 10⁻³ for a 44° twist (Fig. S12, see ESI), which is comparable with other cyclophane cation derivatives.³⁰ Overall, the increase in chiroptical properties does not moderate even for twisting of >40°. It is therefore reasonable to assume that applying a larger twist to acene radical cations will result in an even stronger Cotton effect.



Fig. 4 Change in the absolute molar circular dichroism ($\Delta \epsilon$) for **Ant-Cn⁺⁺** (green and red) and absorption anisotropic factor (g_{abs} ; blue) with twist angle.

Charge delocalization in polyaromatic systems is directly related to their morphology.³¹ The deviation from planarity of aromatic systems affects aromaticity,^{32, 33} energy levels,³⁴ and π -orbital overlap.^{35, 36} The effect of twisting on charge localization is important for the design of non-planar polyaromatic compounds, yet this effect was not studied experimentally in a systematic manner for lack of a suitable experimental system. We were therefore interested to observe how charge localization varies as a function of twist angle in the **Ant-Cn⁺⁺** series, using electron paramagnetic resonance (EPR) spectroscopy.^{37, 38}

In-situ EPR electrochemistry measurements in acetonitrile using tetrabutylammonium perchlorate as the electrolyte revealed a signal for all Ant-Cn⁺⁺ (Fig 5a).³⁹ Simulation of the data revealed three pairs of weak hyperfine coupling constants assigned to the three pairs of hydrogens on each terminal rings (Fig. 5a, black line).⁴⁰ Data analysis suggests that the electron is localized mostly on the central ring, as is commonly observed for acene cation radicals. While the changes in the hyperfine values are subtle, it can be observed clearly that the values decrease with increasing twist (Fig. 5b). This indicates that delocalization decreases with increasing twist, most likely because of the reduced overlap of the π -conjugated system upon twisting. The most affected hydrogens are H₂ and H₃, which are more distant from the central ring, while H₄, located nearer the central ring, is the least affected (Fig. 5b, for calculated spin density see Fig S1 in the ESI).

It is interesting to note that the hyperfine coupling constants change significantly only for a twisting angle larger than 40° (13° per benzene ring), whereas the changes are small for smaller twists. This may indicate that each benzene ring can bear a twist of up to 13° without significant loss of delocalization. We believe that this finding may serve as a design principle for future nonplanar aromatic systems.

Although a trend is evident in the hyperfine values from Ant-C3⁺⁺ to Ant-C6⁺⁺, the hyperfine coupling Constants for Open anthracene radical cation do not follow that trend (Fig. S13, see ESI). Due to the lack of molecular constraint the hyperfine coupling constants for open-anthracene radical cation represent averaged molecular motions and therefore it do not follow the trend laid out by Ant-C3⁺⁺ to Ant-C6⁺⁺. We postulate that the lack of structural constraints on open-anthracene and its consequently greater flexibility underlie it not following the trend of decreasing hyperfine coupling values with increasing twist angle.



Fig. 5 (a) EPR signals from Ant-Cn⁺⁺ obtained by electrochemical oxidation of the neutral parent molecule in acetonitrile solution (coloured lines) compared with the simulated spectrum (black lines). (b) The change in hyperfine coupling vs. anthracene twist for H_2-H_4 .

Conclusions

In summary, we have investigated the first series of twisted acene radical cations in their enantiopure form. To the best of our knowledge, this is the first enantiopure radical cation twistacene system that is configurationally stable at room temperature. We find a systematic increase in their optical and chiroptical properties, such that they display a significant Cotton effect in the NIR spectral region, with increasing twist. Overall, the findings indicate that twistacenes are potential components for chiroptical redox switches. The radical cations display an EPR signal that exhibits only a slight decrease in hyperfine coupling with increasing twist angle up to a 13° twist per benzene ring. This may serve as a design principle for future twisted aromatic systems.

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Conflicts of interest

There are no conflicts to declare

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 At X-band EPR. Ant-Cn⁺⁺ exhibited g-factor of 2.0026 which
 - At X-band EPR, **Ant-Cn**⁺⁺ exhibited g-factor of 2.0026 which is very close to that of a free electron (2.0023). This indicates the origin of an EPR signal from spin-½ anthracene with only small contribution form the phenyls substitutents as can be also observed from the spin density calculation (Fig. S1, See ESI). We note, however, that the contribution of the variation in dehedral angles between the phenyl subtituents and the anthracene core cannot be ruled-out at this stage.
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A series of enantiopure twistacene radical cations display dependency of the chiroptical properties and the EPR signal on backbone twist.

