Organic electronic materials, Organic magnetic materials

Synthesis and elucidation of physical properties of a hydrocarbon molecule with a triplet ground state

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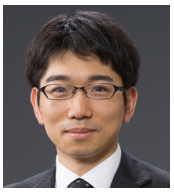
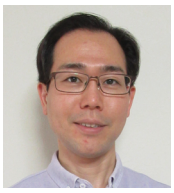




Abstract

Since the first reported production in 2004, researchers have been hard at work using graphene and similar carbon-based materials to revolutionize electronics, sports, and many other disciplines. Now, we have made a discovery that will advance the long-elusive field of nanographene magnets.

In a study recently published in Journal of the American Chemical Society, we have synthesized a crystalline nanographene, a triangulene, with magnetic properties that have been predicted theoretically since the 1950s, but until now have been unconfirmed experimentally except at extremely low temperatures.

Background & Results

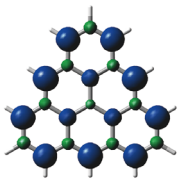
Graphene is a single layer, two-dimensional sheet of carbon rings arranged in a honeycomb lattice. Why does graphene excite researchers? Graphene has impressive properties—it exhibits efficient, long-distance charge transport and has a much higher strength than similarly thick steel. Nanostructures of graphene have edges that exhibit magnetic and electronic properties that researchers would like to exploit. However, graphene nanosheets are difficult to prepare and it's difficult to study their zigzag edge properties. Overcoming these challenges by using a simpler, yet advanced, model system known as triangulene is something we aimed to address.

Triangulene has long eluded synthesis in a crystalline form because of its uncontrolled polymerization. In this study, this polymerization was prevented by introducing bulky substituent groups that didn't affect triangulene's underlying properties. The triangulene derivative is stable at room temperature but must be kept in an inert atmosphere because it slowly degrades when exposed to oxygen. Nevertheless, crystallization was possible, which enabled confirmation of its theoretically predicted highly symmetric structure and aromaticity of all six-membered rings. Localization of unpaired electrons on the zigzag edges of the molecule was confirmed by ESR measurements. This is an electronic state that can serve as an experimentally tractable model for zigzag-edged nanographene. By measuring its magnetic properties, we confirmed that the triangulene derivative is in the triplet ground state with large ferromagnetic interaction of unpaired electrons. Its fundamental optical and electrochemical properties were also elucidated.

Significance of the research and Future perspective

This is the first study to elucidate the crystal structure of a hydrocarbon molecule with a triplet ground state. We can extend the long-sought synthetic procedure reported here to increase the number of carbon rings in the molecule and perform chemical syntheses of advanced forms of nanographene. In so doing, we may be able to synthesize materials that are foundational for future advanced electronics and magnets, and supplement the silicon that's ubiquitous in modern electronics.

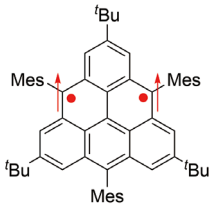
Spin Density



Two electron spins ferromagnetically interact.

Carbon atoms with a large spin density are reactive.

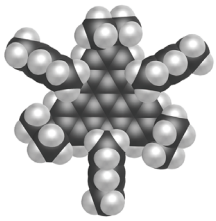
Molecular Structure



Mes = 2,4,6-$Me_3C_6H_2$

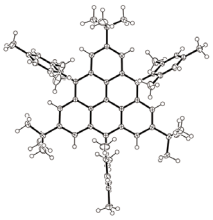
Bulky substituent groups are introduced.

Space-Filling Model



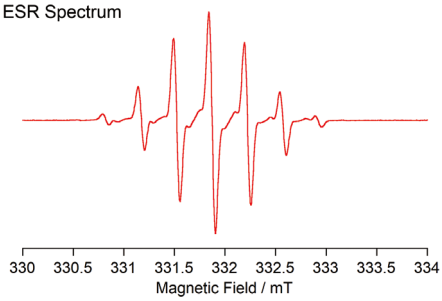
Reactive carbon atoms are sterically protected.

Crystal Structure

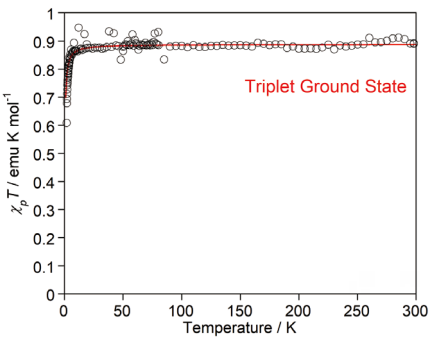


Purification and isolation become possible.

ESR Spectrum



Magnetic Susceptibility



Patent
Treatise Arikawa, Shinobu; Shimizu, Akihiro; Shintani, Ryo et al. Synthesis and Isolation of a Kinetically Stabilized Crystalline Triangulene. J. Am. Chem. Soc. 2021; 143(46): 19599-19605. doi: 10.1021/jacs.1c10151
URL http://www.chem.es.osaka-u.ac.jp/poc/
Keyword magnets, spins, radicals, hydrocarbons, organic molecules