A novel stable [7] helicene with partial biradical character

Helicenes, a class of polycyclic aromatic compounds consisting of nonplanar ortho-fused aromatic rings, have attracted significant research attention owing to their unique structural and physical properties and their significance in fundamental science, as revealed in recent studies. A helicene with an open-shell biradical ground state would be able to participate in a variety of kinds of chemistry. In this state, one of the π bonds is taken to the limit of dissociation, and two weakly coupled unpaired electrons are generated in the molecule. This endows the helicene with interesting chemical bonding activities and local aromaticity that ensure remarkable optoelectronic and magnetic properties. Collaborating with Professor Yao-Ting Wu from the Department of Chemistry at National Cheng Kung University and Professor Pi-Tai Chou from the Department of Chemistry at National Taiwan University (NTU), the research team led by Prof. Chu-Chen Chueh from the Department of Chemical Engineering at NTU recently focused on exploring the semiconducting property of [7] helicene (5,14-diarylindeno[2,1-f:1′,2′-j]picenes, 1) derivatives 1ab, 1bb, and 1ac (Figure 1), which have open-shell biradical features that enable outstanding field-effect transistor (FET) performances on par with those of existing organic biradical devices.

The helicenes synthesized by Professor Wu’s group show not only high thermal and chemical stability but also stable biradical character due to the inherent o-quinodimethane (o-QDM) moiety in the backbone. The charge-transporting abilities of the helicenes were evaluated in FETs prepared at NTU by spin coating, and different annealing temperatures were evaluated to clarify the influence of heat on the molecular packing. The FETs fabricated based on the as-cast films of these compounds displayed clear p-type characters without obvious hysteresis. The optimized devices (annealed at 100 °C) of 1ab yielded a hole mobility (μh) of ~1.9 × 10⁻³, which is comparable to the values reported for existing organic biradical FETs prepared by vapor deposition of the film. Furthermore, for 1ab and 1bb, annealing at 200 °C lead to ambipolar characteristics (Figure 1), which are rarely reported for solution-processed biradical films.

The morphologies of the films of 1ab, 1bb, and 1ac after annealing were further examined by GIWAXS analysis to clarify the discrepancies in the performances of these devices. After annealing, the films of 1ab and 1bb both presented desirable crystallinities, while the film of 1ac showed a similar isotropic orientation, which indicated that the ambipolar characteristics...

*Figure 1. Molecular structures of the synthesized helicenes and the transfer characteristics of the solution-processed (a) 1ab and (b) 1bb FETs annealed at 200 °C. Vgs is fixed at ±80 V.*
were manifested in the improved interchain arrangement. Compared with the compounds, the bulky pendant group of 1ac was the main factor interfering in the molecular packing. Moreover, the superior performance of the 1bb FET can be attributed to the geometric difference in 1ab; the interior Mes moiety of 1bb results in a more twisted backbone. The results thus demonstrated that the absence of a bulky pendant moiety and increased twisting of the helical structure of the studied helicenes enhance molecular packing and the resulting charge-transport properties.

The study not only presents a successful synthetic method for preparing helicenes but also highlights the effectiveness of helical structures for charge transportation. On the basis of our findings, additional extended helicene derivatives can be designed, and they are expected to show better performances in certain applications.

References

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Long-term observations reveal variability of the Kuroshio east of Taiwan

Currents act as rivers in the sea. Like a giant river in the western Pacific Ocean, Kuroshio is the western boundary current of the North Pacific subtropical gyre, and it originates from the northern branch of the North Equatorial Current (NEC) bifurcation off the east coast of the Philippines. The Kuroshio links the Asian marginal seas by flowing northward to the east of Luzon Island, by the Luzon Strait, east of Taiwan, along the continental slope of the East China Sea, and along the south coast of Japan. The current discharges approximately ~20 million tonnes (or Sv) of warm water every second, which is ~20 times the discharge value of all the world’s rivers, from the tropics to the cold zone. Therefore, the Kuroshio plays a critical role in regulating the Earth’s climate. The research team at the Institute of Oceanography at National Taiwan University investigated the variability of the Kuroshio east of Taiwan at a cross-stream transect using an array of three moored acoustic Doppler current profilers (ADCPs) that collected measurements for ~23 months (Figure 1). The dataset was collected through the Observations of the Kuroshio Transport Variability (OKTV) and Observations of the Kuroshio and Mindanao Currents (OKMC) collaborative programs that are sponsored by Taiwan and the United States, respectively.

Figure 1. The technicians onboard R/V Ocean Researcher I are deploying ADCP moorings within the Kuroshio off the coast of Hualien.