

Atropisomerism and Conformational Dynamics in Dioxo[6]helicene Enamine Constructs with Near-Infrared Absorption and Emission

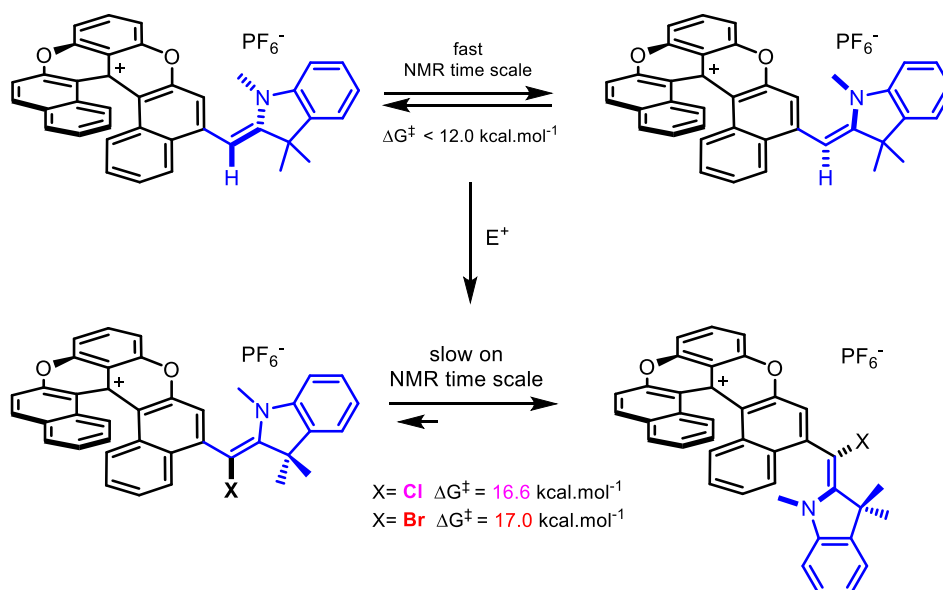
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Helicenes are an important class of chiral *ortho*-fused polyaromatic derivatives characterized by an asymmetry originating from the steric repulsion between terminal substituents or rings.^[1] In previous studies, direct oxidative cross-coupling between dioxo[6]helicene and methylindoline fragments was realized.^[2] X-ray structural analysis revealed an out-of-plane twist of the cyclic enamine moiety, giving rise to two atropisomers in rapid conversion on the NMR time scale, even at $-90\text{ }^{\circ}\text{C}$. Herein, alkene functionalization by electrophilic substitution is reported. As a consequence, barriers of epimerization increase up to 17 kcal.mol^{-1} (slow exchange NMR time scale). Detailed conformational investigations reveal unexpected geometrical changes.^[3] In addition to the strong donor-acceptor character of hemicyanine core, halogens (F, Cl, Br) promote strong bathochromic shifts, extending absorption and emission further into the near infrared region (NIR), a domain of light particularly advantageous for biological applications.^[4]



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[2] J. Bosson, G. M. Labrador, C. Besnard, D. Jacquemin, and J. Lacour *Angew. Chem. Int. Ed.* **2021**, 60, 8733-8738.

[3] M. Fragkiadakis, M. Thomaidi, T. Stergiannakos, E. Chatziorfanou, M. Gaidatzi, A. Michailidis Barakat, C. Stoumpos, C. Neochoritis, *Chem. Eur. J.* **2024**, 30, e202401461.

[4] S. Wang, B. Li, F. Zhang, *ACS Cent. Sci.* **2020**, *6*, 1302-1316.