

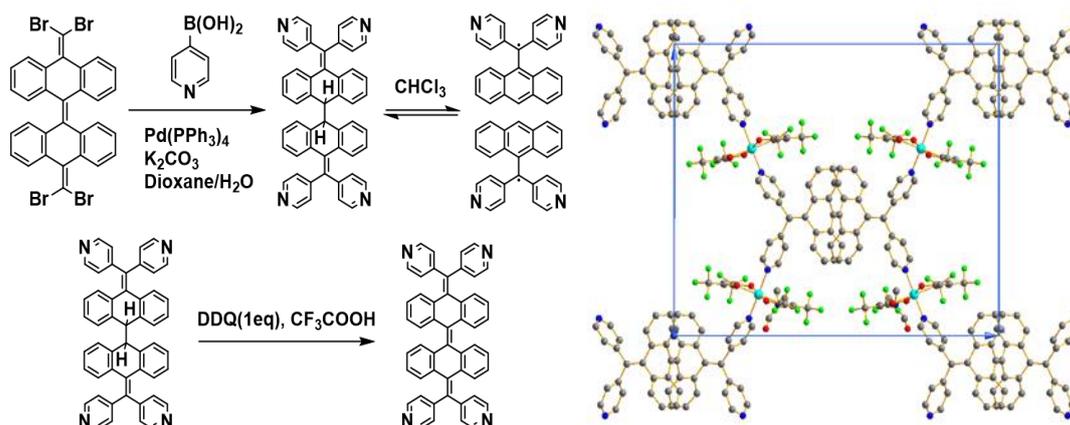
New Ligand for Metal-Organic Frameworks based on Tetrabenzo Chichibabin Hydrocarbons with Potential Close Shell-Diradical Transition

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The transition between the close-shell ground state and diradical state of organic compounds has been of interest in the past decade, especially when the spin-state transition is accompanied with a structural configuration alternation. To date, most such transitions are reported to occur in a solution state, which allows a rapid relaxation of the excited diradical state to the diamagnetic ground state. As a result, it is intriguing to explore the behavior of such diradicals in solid-state by incorporating such diradical unit into metal-organic frameworks (MOFs).

To achieve this target, a well-known diradical precursor, namely tetrabenzo Chichibabin hydrocarbon is selected and synthetically modified with four pyridine antennas. (4py-tbCH). Using the literature method to prepare the 4py-tbCH molecule, however, unprecedently yielded 2H-4py-tbCH, which exhibits a monomer-dimer equilibrium in solution. Oxidation to the 4py-tbCH could be achieved by Scholl reaction, and the MOF containing this ligand were obtained by diffusive mixing the solution of 4py-tbCH and Cu(hfac)₂. Solid-state cyclic voltammetry and electrochemistry, as well as the *ex situ* magnetometry and EPR measurements will be carried on the obtained MOF to evaluate the spin-state transition of the ligand upon the electrochemical oxidation or reduction.



References:

- 1) Zebing Zeng, *et al*, *J. Am. Chem. Soc.* **2012**, *134*, 14513–14525.