Synthesis of N-doped polycyclic aromatic hydrocarbons built on 1,4-dihydropyrrolo[3,2-*b*]pyrroles via alkyne activation

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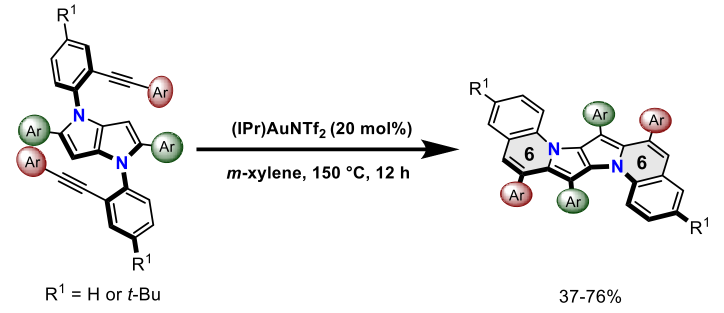
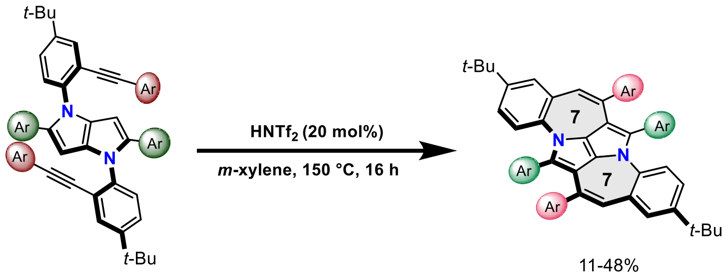
In the quest for innovative materials, non-planar polycyclic aromatic hydrocarbons (PAHs) and their heterocyclic analogues with new molecular topologies are emerging as an important candidate. Particularly, introduction of non-hexagonal rings such as pentagons and heptagons into completely planar hexagonal backbone leads to the formation of uniquely curved architectures, acquiring distinct electronic, magnetic and mechanical properties that are significantly different from their planar counterparts. Moreover, doping of heteroatom to this framework is a direct approach to tune their inherent physical and chemical properties to enable novel applications. Considering the purely benzenoid structure, intramolecular alkyne benzannulation is one among the key reactions for C-C bond formation.

The main goal of my PhD dissertation is to design pathways to synthesize aza-doped non-planar polycyclic aromatic systems featuring unique curvature and to study their photophysical properties. I started my research with synthesizing tetraaryl-1,4-dihydropyrrolo[3,2-*b*]pyrroles (TAPPs) bearing alkynyl moieties as precursors by using optimized reaction conditions reported in our lab. In the first part of the thesis, several conditions to perform alkyne annulation reaction on the precursors were explored. It turned out that only cationic gold(I) complexes catalyze this reaction, albeit accompanied by 1,2-aryl shift leading to the formation of S-shaped polycyclic π-system (**Scheme 1**). The scope of this *6-endo-dig* type annulation was further explored on electronically different substituents for tunability with respect to the photophysical properties, as well as creating additional sites for functionalization. Additional optimization experiments to determine the factors affecting the reaction were also carried out. Steady state UV/Vis spectroscopy shows that the synthesized aza-doped PAHs primarily undergoes radiative relaxation upon photoexcitation resulting in high fluorescence quantum yields. The optical properties of both precursors and products were rationalized by density functional theory (Prof. Denis Jacquemin, France).



Scheme 1. Gold-catalyzed double *6-endo-dig* alkyne annulation accompanied by 1,2-aryl shift.

In the second part of my thesis, I worked on the same TAPP precursors to induce *7-endo-dig* type alkyne annulation to synthesize unique 7-5-5-7 type cyclized system. Exceptionally strong Brønsted acid HNTf$_2$ facilitated the 7-membered ring formation (**Scheme 2**). The scope studies revealed that this reaction is highly selective towards certain substrates where electron-donating and electron-withdrawing substituents are arranged in a specific manner. Additionally, I found that subsequent intramolecular direct arylation led to the formation of N-doped nanographene possessing four seven-membered rings with 7-7-5-5-7-7 type cyclic system. Newly synthesized dyes showed weak red emission. The presence of conjugated ring systems 7-5-5-7 and 7-7-5-5-7-7 causes the bathochromic shift of absorption and emission.



Scheme 2. HNTf$_2$-mediated double *7-endo-dig* alkyne annulation.