Synthesis of a Black Dye with Absorption Capabilities Across the Visible-to-Near-Infrared Region: A MO-Mixing Approach via Heterometal Coordination of Expanded Porphyrinoid

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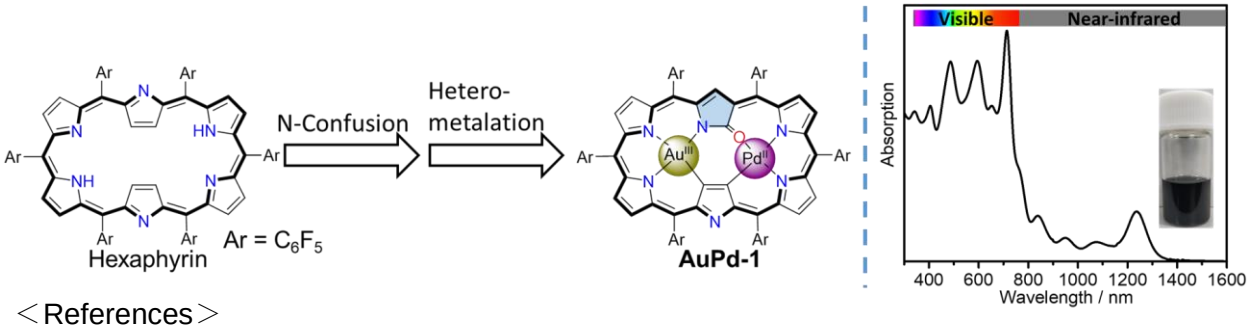
Blackened dyes with efficient light-harvesting capability at a wavelength longer than 1000 nm have been attracting attention for the development of light-driven functional materials. Porphyrins and their expanded analogs (e.g., hexaphyrin) have been utilized as potential dye-scaffolds because of the high tunability of their optical properties via skeletal modification of the chromophoric core. The concise synthesis of panchromatic porphyrinic dyes is, however, highly challenging due to the inherently strong configurational interactions in their degenerated MOs.[1]

We herein report a distinct design strategy based on the coordination chemistry of a modified expanded porphyrin, namely, N-confused oxohexaphyrin (**1**)[2] to attain the absorption capabilities across the visible-to-near-infrared (NIR) range.[3] The peculiar unsymmetrical coordination core of **1** was useful for hetero-metalation. Appropriate combination of the heavier 4d/5d metal ions (e.g., Pd(II) and Au(III)) facilitates the stronger d_π-p_π orbital interaction, in the complex (i.e., **AuPd-1**), leading to a broad visible absorption with the substantial contribution of the metal-ligand charge-transfer bands.



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