Porphyrin-Integrated Crystalline Molecular Rotors: Engineering Spinning-Top Dynamics of in NHC Moieties

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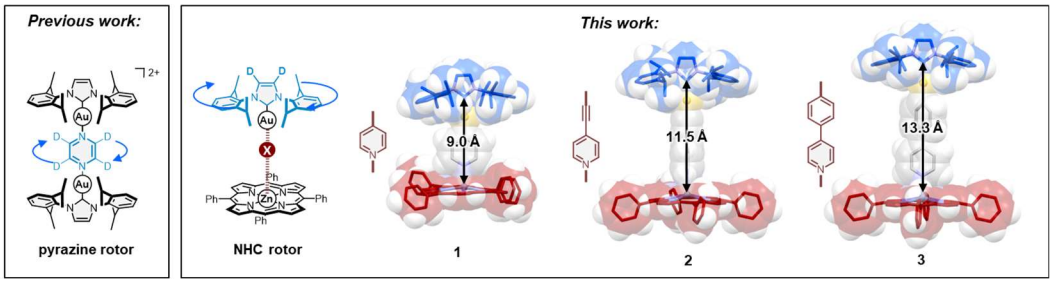
Porphyrins, prominent macroheterocyclic ligands in coordination chemistry, are celebrated for their distinct molecular structures, which endow them with unique spectral, optical, magnetic, and photoelectric properties. Upon complexation, these compounds serve various functions as luminescent materials, photosensitizers, single-molecule magnets, and catalysts or photocatalysts across a range of reactions.[1]

In our ongoing exploration of *N*-heterocyclic carbene (NHC)-based crystalline molecular rotors,[2] we have, for the first time, integrated a porphyrin unit as a stator within a crystalline molecular rotor system. This stator is paired with an NHC gold(I) moiety and linked via pyridinyl (**1**), ethynylpyridine (**2**), and phenylpyridine (**3**) ligands, which serve as rotational axes. The larger porphyrin stator provides the NHC moiety with sufficient local free space to exhibit molecular dynamics in the crystalline solid state, resulting in observable disorder in the single-crystal X-ray structures. To confirm this dynamic behavior, we employed solid-state ^{2}H spin-echo and ^{13}C cross-polarization/magic-angle spinning (CP MAS) NMR techniques. We found that the length of the rotational axis can influence rotational motion of NHC moiety. While NHC rotor **1**, with a short pyridinyl linker, the NHC moiety remains static, the longer ethynyl-pyridine and 4-phenylpyridine ligand linkers in rotors **2** and **3**, the NHC moieties exhibit rapid 4-fold rotational motion. This study highlights the effective application of a porphyrin complex, offering new insights for future solid-state molecular rotor design.



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