Hexaphyrin-Cyclodextrin Hybrids: Switching between Hückel and Möbius Aromatic Systems in Chiral Environment

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Hexaphyrins offer a versatile platform for aromaticity switching through multiple stimuli (redox, coordination, protonation, temperature, polarity and conformational constraints).[1-3] Remarkably, we recently showed that the association of an hexaphyrin to a doubly linked chiral cyclodextrin unit (HCD) provides us with two 28π diastereomeric Möbius systems with opposite bridging pattern. Focusing on a dynamic strategy, metalation of these Möbius hexaphyrin with Zn(II) shows chirality transfers between the cyclodextrin, the bridging pattern and the hexaphyrin, tuning the *P/M* twist stereoselectivity up to 60% *de*.[4] Following a different approach, Osuka group achieved metalation with Pd(II) binap salt, resulting in 23% *ee* and further enabling chiral separation.[5] In order to obtain potentially resolvable diastereomers, metal coordination with Pd(II) was done on HCD systems which gave us two *pseudo* enantiomeric monometallic complexes (PdHCD) F1 and F2 with induced chiral communication from the cyclodextrin to the Möbius twist. These conformationally stable isomers allow to easily switch between Hückel and Möbius aromatic systems to develop new applications using planar chirality for chiral guest recognition and chiral sensing material.

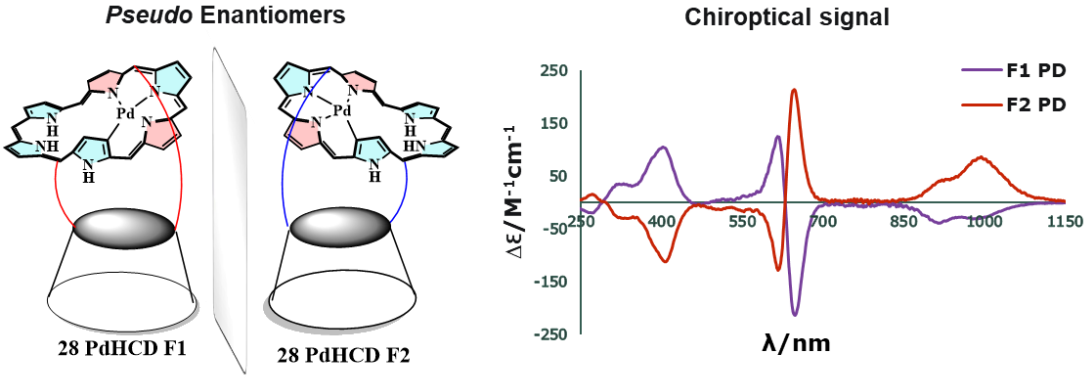

Figure: *Circular dichroism of PdHCD F1 and F2.*

28π Möbius aromatic PdHCD conjugates showed intense ECD spectra. The 28π PdHCD F1 and F2 pseudo enantiomers which show the same CD spectra with opposite Cotton effects and large ΔΕ attributed to the strong aromaticity, is interesting in view of their potential application as chiral sensors. Redox tuning of chiroptical properties was achieved both with chemical and electrochemical oxidation, to form 26π Hückel aromatic PdHCD conjugates. The 26PdHCD shows weaker CD spectra for both F1 and F2. The stability of the chiroptical switch between Möbius and Hückel aromatic systems allowed us to switch between these states up to 25 cycles. These promising results suggest to further investigate these systems with the redox process, chiral properties, host guest chemistry within confined space and further.

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