Supramolecular $M_4L_2L'_2$ Complexes with Perylene Bisimide Bispyridine as Redox-Active ligand:

*Synthesis, Characterization and Host-Guest Chemistry*

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Substituted Perylene Bisimides are widely used due to their fluorescent properties, but can also be used for their redox-properties. In literature, the synthesis of $M_4L_4$ squares containing perylene bisimides and either platinum or palladium are known. Due to the large dimensions of the perylene bisimides these squares are unattractive for host-guest chemistry, but this could be changed by using two different ligands. This research studied the synthesis and characterization of smaller molecular squares and its potential host-guest chemistry. This resulted in the synthesis of $M_4L_2L'_2$ squares containing perylene bisimide bispyridine (1) and di-carboxylate ligands in moderate to good yields. These squares were characterized using multinuclear and 2D NMR techniques, mass spectroscopy and UV-Vis and electrochemistry because ligand 1 showed to be fluorescent and redox-active. This showed that the heteroleptic square is redox-active with quasi-reversibility and the same UV-Vis absorbance. In addition, the encapsulation of pyrene, perylene and various substituted pyrenes in the heterogeneous square was studied by $^1$H and DOSY NMR. This showed that these planar aromatic guests can encapsulate but there is an equilibrium between bound and free guest. To gain a better insight in the influence of ligand 1 and the corresponding reduction or oxidation on the guest, electrochemical studies and chemical reduction should be performed. Lastly, a pyrene substituted with a rhenium-center (10) was synthesized and encapsulation was tested which showed that substituted pyrene 10 can be encapsulated in a heteroleptic square. This is promising for potential activation/deactivation of metal centers present in substituted pyrenes which should be further studied. It can be concluded that $M_4L_2L'_2$ squares can be synthesized and characterized and that they show promising results for host-guest chemistry.