Pathway Control and Supramolecular Polymerization of discrete π-Conjugated Square Planar Metal Complexes

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Self-assemblies of metal complexes have gained considerable attention not only because of the inherent properties of the metal ions but also due to the versatility of non-covalent interactions when a metal fragment is part of the molecular design.[1] Our group has investigated the supramolecular polymerization of dichlo(bis)pyridyl Pd(II) and Pt(II) metal complexes featuring a π-conjugated surface derived from oligophenyleneethynylene (OPE).[1a] The introduction of polar triethylene glycol (TEG) chains induces a slipped stacking of the monomer units within the self-assembled structure.[2] In contrast, remarkably different packing modes (slipped *vs*. parallel for Pt(II)[3a] and Pd(II),[3b,c] respectively) are observed if alkyl chains are present. Very recently, we have discovered that the attachment of additional hydrogen bonding motifs to our metal complexes[4] provides access to more versatile packing modes that are in competition under certain experimental conditions. This is particularly striking for complex I (Figure 1), which self-assembles into two coexisting stable assemblies in solution with different molecular packing (slipped *vs*. pseudo-parallel) that do not interconvert over time. Interestingly, the presence of metal-polarized Cl ligands as well as hydrogen bonding synthons strongly influence the molecular rearrangement *via* various types of unconventional non-covalent forces including NH···Cl and NH···O(alkoxy) interactions.[5] These findings in supramolecular polymers bear close resemblance to the phenomenon of *concomitant packing polymorphism* that has been widely observed in crystals.

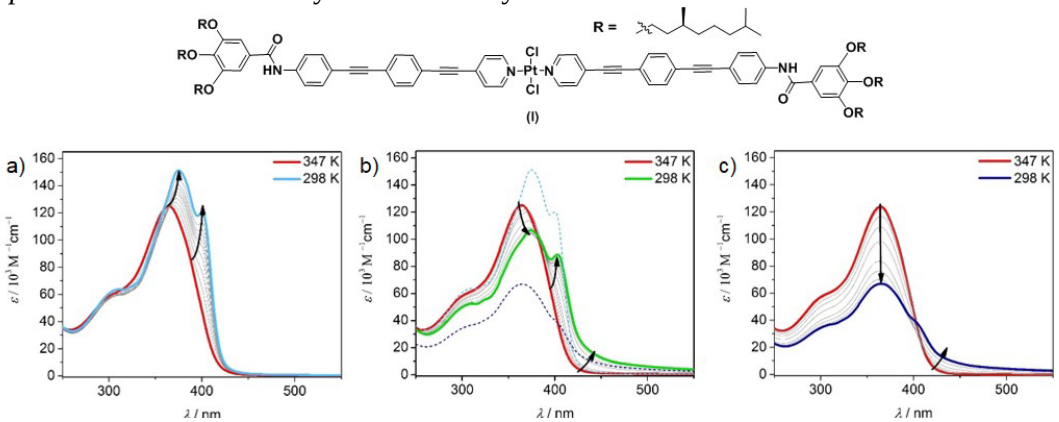

Figure 1. *Chemical structure of Pt(II) complex (I) and variable temperature UV-Vis (100 μM) in methylcyclohexane with a cooling rate of a) 2K min^{-1} , b) 0.5 K min^{-1} and c) 0.1 K min^{-1}.*

References

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