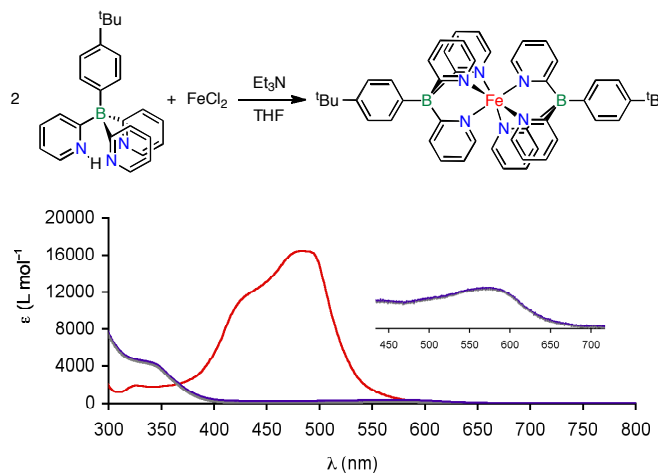


## Project E: Pyridylborates For Metal-Containing Supramolecular Materials

The overarching goal of this project is to take advantage of controlled/living polymerization methods such as atom transfer radical polymerization (ATRP), nitroxide-mediated polymerization (NMP), reversible addition-fragmentation chain transfer (RAFT), and ring-opening metathesis polymerization (ROMP) for the preparation of functional metal-containing polymers. The successful preparation of metallopolymers under controlled conditions and with well-defined architectures is expected to allow us to take advantage of the unique electronic, magnetic, and optical characteristics and catalytic behavior of transition metal complexes. Polymers with multiple phosphine or polypyridyl binding sites have been studied extensively in this respect. However, their synthetic preparation is often less than straightforward and fine-tuning of the ligand properties on a polymer scaffold can be challenging, which has limited the variety of suitable polymeric ligands introduced so far.

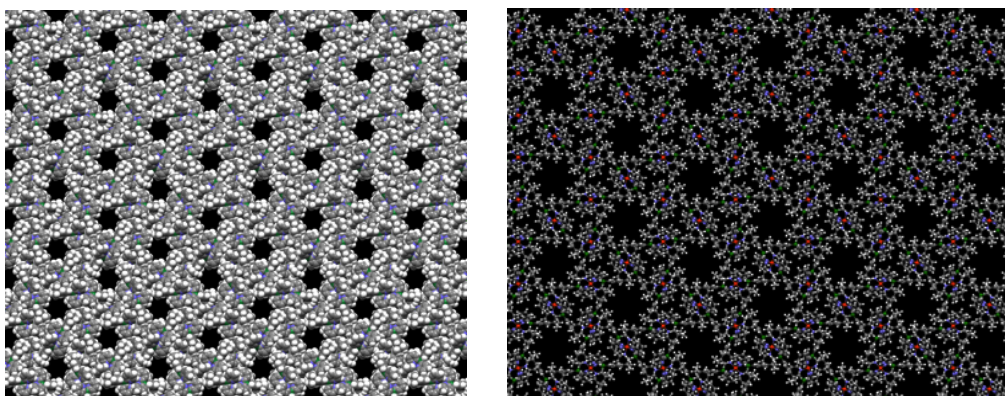
**1) From Tris(pyrazolyl)borate to Tris(2-pyridyl)borate Ligands [E1-E3].** Our initial work focused on polymer modification routes to prepare tris(pyrazolyl)borate-functionalized polymers. However, we found that the susceptibility of the B-N bond to (acid-promoted) cleavage posed some significant challenges, especially when incorporating these functional groups into polymeric materials. Guided by our earlier work on weakly coordinating organoborate polymers which feature electron withdrawing pentafluorophenyl pendant groups, we surmised that attachment of pyridyl groups to boron could circumvent some of these issues. Hence, we developed a new class of scorpionate-type ligands that only features relatively non-polar B-C bonds, the tris(2-pyridylborate) (Tpyb) ligands. These ligands are obtained in modest yields by reaction of an aryldibromoborane ( $\text{ArBBr}_2$ ) with the isolated and purified pyridyl Grignard reagent  $(\text{PyMgCl})_2(\text{THF})_{3,5}$  in non-polar solvents. The products are remarkably stable and the pyridylborate moiety is even amenable to reversible protonated in 6N HCl without decomposition.

**2) Complexation of Pyridylborate Ligand to Metal Ions [E4-E5].** Initial studies on the ligand properties of tris(pyridyl)borates have focused on the ability of the tris(pyridyl)borate to form complexes with  $\text{M}^{2+}$  metal ions ( $\text{M} = \text{Mg}, \text{Fe}, \text{Mn}, \text{Cu}$ ). These studies were performed with a non-polymerizable model compound, *t*-BuPh-Tpyb, that features a *t*-butylphenyl as the fourth substituent on boron. As an example, treatment of *t*-BuPh-Tpyb with  $\text{FeCl}_2$  in THF/MeOH in the presence of  $\text{NEt}_3$  resulted in a red solid that was purified by column chromatography and recrystallized from toluene. Based on  $^1\text{H}$  NMR data, the iron complex is diamagnetic in solution at RT, suggesting a low spin configuration, which is consistent with solid-state data derived from a single crystal X-ray diffraction analysis. UV-vis measurements were performed in  $\text{CH}_2\text{Cl}_2$  to further explore this aspect. The absorption maxima at ca. 480 and 430 nm can be assigned to  $\text{M} \rightarrow \text{L}$  charge transfer (CT). The corresponding cationic Fe(II) complexes  $[\text{Fe}\{(\text{py})_3\text{CH}\}_2][\text{NO}_3]_2$  (439, 370 nm) and  $[\text{Fe}\{(\text{py})_3\text{PO}\}_2][\text{NO}_3]_2$  (465, 385 nm) show similar absorption bands, but at slightly higher energy. Cyclic voltammetry studies revealed that the complex can be reversible oxidized at very moderate potentials. The preparative oxidation of the Fe complex was accomplished by layering a solution in  $\text{CH}_2\text{Cl}_2$  with an aqueous solution of  $\text{FeCl}_3$  followed by vigorous mixing. As expected for the formation of a paramagnetic product, the  $^1\text{H}$  NMR exhibited large chemical shifts as compared with the corresponding neutral Fe(II) complex. Related complexes with other M(II) metal ions (e.g. Mg(II), Cu(II), Ru(II)) are readily prepared using similar procedures.

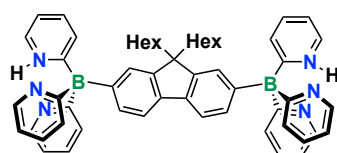


**Figure E1.** Synthesis of  $(\text{BuPh-Tpy})\text{Fe}$  and comparison of the UV-vis spectra of the neutral complex (red) and the respective oxidized species (purple).

**3) Supramolecular Assembly into Porous Materials [E5-E6].** During the course of our studies we made a surprising discovery that these metal complexes form unusual porous supramolecular structures. Depending on the crystallization procedure, supramolecular structures could be generated with relatively smaller (ca. 4-5 Å) or larger (ca. 8 Å) diameter pores that propagate throughout the crystal lattice. Although the supramolecular structures are held together only by weak intermolecular C-H... $\pi$  interactions, the solvent in the larger channels could be completely removed without any loss of crystallinity or degradation of the framework. Surface area and gas uptake measurements on the Mg(II) complex further confirmed the permanent porosity, while the calculated NL-DFT pore diameter of 8.6 Å proved to be in excellent agreement with that obtained from single crystal X-ray crystallography. Our new materials are remarkably thermally stable as degradation did not occur up to ca. 400 °C based on TGA analyses, and a sample of the Mg(II) complex showed no loss of crystallinity even after heating to 140 °C under high vacuum for 72 h according to single crystal X-ray diffraction data.

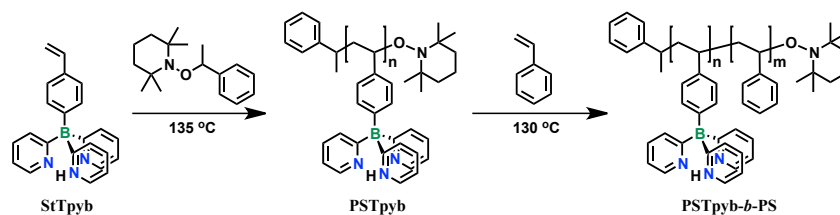


**Figure E2.** Space filling and ball-and-stick views of the extended structures of  $(Tpyb)_2Mg$  (left) and  $(Tpyb)_2Fe$  (right) along the crystallographic  $c$ -axis; diffuse solvent molecules were removed using the SQUEEZE routine in Platon.



A series of 3<sup>rd</sup> generation Tpyb ligands that containing functional groups (I, B(OR)<sub>2</sub>, alkynyl) has recently been prepared and studies on their incorporation into polymeric materials are under way. Along the same lines, we are also exploring ditopic tris(2-pyridylborate) species for potential use as building blocks of novel coordination polymers. An example is the synthesis of a fluorene derivative that contains solubilizing alkyl group.

**4) Pyridylborate-Functionalized Polymers [E7-E8].** We are also developing new polymeric materials that feature tris(2-pyridyl)borate chelate ligands for the attachment of metal complexes. This work constitutes a collaboration with the Sheridan group at Rutgers University-Newark. First, we prepared a styryl derivative and explored its polymerization via controlled radical polymerization methods. We succeeded when using nitroxide-mediated polymerization (NMP) techniques and obtained the homopolymer and a corresponding block copolymer with polystyrene. The latter undergoes self-assembly in polar organic solvents, resulting in nanoparticles that can be cross-linked by addition of M(II) metal ions.



One of the drawbacks of NMP method described above is that the synthesis required very high temperatures and the scope of the second block was limited to non-polar polystyrene. The challenges encountered in the free radical polymerization process likely arise due to the highly electron-rich nature of the pyridylborate

moieties. More versatile and controlled/living polymerization techniques are therefore required to fully develop this class of Tpyb-functionalized block copolymers. Toward this end, we prepared norbornene derivatives as new ligand-functionalized monomers, to study the controlled polymerization via ROMP, and to investigate the stimulus-responsive self-assembly of the polymeric products.

The synthesis of a tris(2-pyridyl)borate (Tpyb) functionalized block copolymer was accomplished via sequential ring-opening metathesis polymerization of the norbornyl-substituted Tpyb monomer and a carboxylate-functionalized oxanorbornene using Grubbs 3<sup>rd</sup> generation catalyst. The block copolymer was characterized by multinuclear NMR and GPC analysis, which confirmed chain extension as the molecular weight increased with increasing amounts of added monomer. The self-assembly of a thin film of the block copolymer was imaged by AFM, suggesting lamellar ordering. The ester groups of the copolymer were then hydrolyzed with NaOH and the pH dependent self-assembly in aqueous medium was studied by DLS and SEM. Hydrolysis of the ester functionalities resulted in a “schizophrenic” block copolymer that self-assembles in water and is



responsive to changes in pH. Thus, aggregates with the Tpyb block in the core or shell can be reversibly produced by variation of the pH. Crosslinking of the polymer aggregates by metal complexation was explored and the possibility of metal exchange was demonstrated. Based on these findings, we envision potential applications of these types of functional block copolymers in areas ranging from pH-controlled drug release to polymer-based metal ion remediation systems.

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