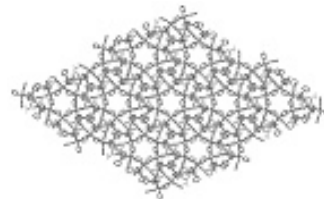
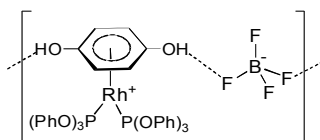


W0226

The Use of Pi-Bonded Organometallic Quinonoid Complexes in the Construction of Self-Assembled Metal-Organic Hybrid Materials. D.A. Sweigart, S.U. Son, J.A. Reingold, S.B. Kim, G.B. Carpenter, Dept. of Chemistry, Brown Univ., Providence, RI 02912 USA.

The coordination of organometallic fragments such as $[\text{Mn}(\text{CO})_3]^+$ or $[\text{Rh}(\text{P}(\text{OPh})_3)_2]^+$, to the carbocyclic ring in hydroquinone, 1,4- $\text{C}_6\text{H}_4(\text{OH})_2$, results in activation of the $-\text{OH}$ groups to deprotonation. The resulting pi-bonded quinone complexes function as ligand spacers by connecting through the oxygen atoms to metallic nodes. The 1-, 2-, or 3-D metal-organometallic coordination networks formed in this manner span an interesting range of architectural motifs that depend in a predictable manner on the nature of the node and the experimental conditions.

Crystal engineering of the salt $[(1,4\text{-hydroquinone})\text{Rh}(\text{P}(\text{OPh})_3)_2]^+\text{X}^-$ is possible because of *charge-assisted* hydrogen-bonding to the anion X^- . The structure of the solid network depends on the nature of the anion (SbF_6^- , OTf^- ,



OTs^- , PF_2O_2^- , BF_4^- , ClO_4^-), and can be monomeric, dimeric, 1-D polymeric, C_2 helical or C_3 helical. These materials exhibit three types of noncovalent interactions – hydrogen-bonding, charge pairing, and pi-pi stacking of the aromatic hydroquinone rings. The hydrogen-bonding from the $-\text{OH}$ groups to the anion, illustrated for $\text{X}^- = \text{BF}_4^-$, results in a supramolecular assembly featuring hydrophobic channels of aromatic phenyl rings from the triphenyl phosphite ligands. The nature of the channels may make this material a useful model for certain guest-host studies.

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