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MOFs of a O,P,N heterotritopic Ligand –One reaction, two networks –A topological analysis

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The field of metal-organic frameworks (MOFs) is dominated by the chemistry of oxygen and nitrogen donor based ligands.^[1] Next to no work revolves around polytopic ligands containing phosphorus donors. The usage of phosphorus widens the horizon of MOF chemistry. It may broaden the structural variety, enable new applications and stabilize metal cations in low oxidation states that were previously inaccessible to MOF chemists.

The ligand 4-(3-(4-(diphenylphosphino)phenyl)-3-oxopropanoyl)benzonitrile is a prototype for the combination of the three donor atoms O, P and N. It combines a chelating beta-diketone as the oxygen donor, a nitrile representing the nitrogen donors and a triarylphosphine as a phosphorus based ligand functionality.

Using a stepwise approach we were able to synthesize a cationic heterobimetallic Fe^{III}/Ag^I MOF with Fe^{III} bound to the oxygen donors and Ag^I bound to the P and N donors. The network can emerge in 2 different topologies while the chemical connectivity remains unchanged. Type **A** corresponds to the rtl network type,^[2] Type **B** has not been observed yet. Both have a three dimensional pore system. The pores are large enough so a sphere with a diameter of 4 Å could move through them along all low-indexed directions.

1 F. Almeida Paz, Chem. Soc. Rev. 2012, 41, 1088.

2 M. O'Keeffe et al. Acc. Chem. Res. 2008, 41, 1782.

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