The directed non-bonding interactions play an important role in modern supramolecular chemistry. Concerning phosphorus, so-called pnictogen bonding is usually mentioned in this context [1]. However, cyclic polyphosphorus ligands open new perspectives for the supramolecular chemistry. Since many years we have been using pentaphosphaferrocenes [Cp RFe(\pi\pi\pi-P_5)] (Cp R=\pi\pi\pi-C_5R_5, R=Me, CH_2Ph, etc.) as building blocks to obtain coordination polymers and giant supramolecules [2-5]. The X-ray diffraction studies proved that cyclo-P_5 planar aromatic ligand of the pentaphosphaferrocene is capable of the \pi-\pi stacking interactions with the other aromatic \pi-systems. The interplanar spacing of 3.5-3.8 Å, parallel arrangement of the aromatic fragments as well as \textsuperscript{31}P MAS-NMR data show the presence of intermolecular interaction. These interactions influence the orientation of the guest molecules in the central cavities of the supramolecules [2-4] and the crystal packing in the coordination polymers [5].

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