Poster Presentation

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9,9'-Spirobifluorene Based MOFs: Synthesis, Structure, Catalytic Properties

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The 9,9'-spirobi[fluorene]-3,3',6,6'-tetracarboxylic acid (H4SBF), a ligand based on the spirobifluorene (SBF) core, was used as a ligand for the synthesis of the MOFs [Co(H2SBF)Phen(H2O)]n (1), and [M(H2SBF)(4,4´-Bipy)]n (M = Co, Ni, Cu) (2). The ligand H4SBF is based on the spirobifluorene (SBF) core: the interest in the SBF platform is due to its application as chiral ligand in organic electronics, as solid state laser or in third-order nonlinear optics. The MOFs with H4SBF have been obtained by hydrothermal reaction of H4SBF, the corresponding MCl2 and the base (Phen or 4,4´-Bipy) in a molar ratio H4SBF : M2+ : base = 1:1:1. The obtained MOFs are stable in air and thermally stable up to ~400ºC. The MOFs 2 (M = Co, Ni, Cu) are isostructural (proved by DRXP data). Only for 1 and 2 (M=Ni) the crystals were obtained apt for crystallographic study. The Ni compound crystallizes in monoclinic system, Cc space group with cell parameters: 40.8251 Å, 12.0031 Å, 11.8383 Å and β = 104.398°, vol. 5618.89 Å3. Ni metal center is hexacoordinated in an octahedral environment with five O atoms of two ligands and one N atom from 4,4- Bipy, which means that there is another N atom not coordinated to metal center. The structure of 2 is 2D with interlayer H bonds, which built up a supramolecular 3D net. The Co compound is triclinic, P-1 space group with cell parameters: 10.9775 Å, 12.7231 Å, 14.2381 Å, α = 65.203°, β = 87.528°, γ = 72.947°, vol. 1718.6 Å3. Like Ni compound, Co metal center is hexacoordinated in an octahedral environment with three O atoms of one ligand, two N atoms from Phen and one water coordinated molecule, which builds up a 2D structure. To test the catalytic ability, the obtained MOFs were used to oxidize styrene molecules with tert-butyl hydroperoxide oxidant. Styrene was fully oxidized into its epoxidized product by 1 in CH2Cl2 in 6 h. Under the same conditions, 1 can oxidize the most inert cyclohexane substrate at 60ºC with 80.6% substrate conversion.

Figure 1. View along [100] (left) and the covalent net (right) formed by $Co(H_2SBF)(Phen)(H_2O)$ chains running along the [100] direction in an A B C sequence.

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