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New Rare-Earth MOFs: Through polyhedral diversity to multifunctional properties

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Much of the current efforts on polymeric metal-organic complexes are directed toward synthesis of interesting frameworks in search of potentially useful materials. Judicious choice of appropriate molecular building blocks provides the means to create a rich variety of new materials with interesting useful properties. In our ongoing studies of arene-sulfonate group as a linker in the search of multifunctional materials, we report here eight 2D and 3D Metal-Organic Framework (MOFs) rare earth naphthalenedisulfonates have been obtained, its characterization, single crystal structures, and some catalytic, magnetic and optical properties are reported. The different geometry of the naphthalenedisulfonic acids used as connectors [(1,5-NDS) and (2,6-NDS)] gives rise to the three new structure types. In $\text{Ln}(\text{OH})(1,5\text{-NDS})\text{H}_2\text{O}$, LnPF-1 ($\text{Ln} = \text{La}, \text{Nd}, \text{Pr}, \text{Sm}$ and Eu) the lanthanide ion is octacoordinated. Its 3D structure is formed by $(\text{Ln}_2\text{O}_{14}) - \text{S} - (\text{Ln}_2\text{O}_{14})$ infinite chains, connected through complete NDS connectors. LnPF-2 ($\text{Ln} = \text{Nd}$), with the same empiric formula that the former, and the lanthanide in octa- and nona-coordination, owns an arrangement of sulfonate bridges and neodymium polyhedra that gives rise to a 2D structure. $[\text{Ln}_5(2,6\text{-NDS})_5(\text{OH})_9(\text{H}_2\text{O})_4](\text{H}_2\text{O})_2$, LnPF-3 ($\text{Ln} = \text{Nd}, \text{Eu}$), evidences that getting a 3D structure with (2,6-NDS) is possible when a greater Ln/connector ratio is employed. It is worth pointing out the existence, in this latter family of compounds, of a $\mu^5\text{-OH}^-$ group, whose hydrogen atom is very close to one of the five coordinated Ln atoms (distance $\text{Ln}\cdots\text{H} = 2.09\text{\AA}$). The materials, with high thermal stability, act as active and selective bifunctional heterogeneous catalysts in oxidation of linalool yielding cyclic hydroxy ethers. Their activity depends more on the number of active centers with possibility of increasing the coordination number during the catalytic reaction, than on other structural effects, and, obviously, for the same structure type, on the rare earth size. Magnetic susceptibility measurements showed that the three NdPF-1 , NdPF-2 and NdPF-3 , follow the Curie-Weiss law with the only low temperature deviations due to the splitting of the $^4\text{I}_{9/2}$ Nd^{3+} ground state under the influence of the CF in each case. Clear room temperature PL at $\sim 1.34\ \mu\text{m}$ and $\sim 1.06\ \mu\text{m}$ has been observed for Nd^{3+} in NdPF-1 , NdPF-2 and NdPF-3 . The influence of the PF matrix results in a better PL efficiency for NdPF-1 , which moreover could be improved exploring ways to reduce the PL quenching.

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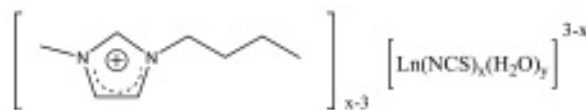
Crystal Structures of Anionic Lanthanide Complexes as Constituents of Ionic Liquids

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Ionic liquids have gained considerable attention during the past few years due to their extremely low vapor pressure, the wide liquid range, the good electrolytic properties and large electrochemical window as well as the 'green' character due to their reusability.^[1] Transition metal containing ionic liquids based on imidazolium salts are regarded as promising new materials with the properties of ionic liquids and additional intrinsic magnetic, catalytic or e.g. spectroscopic properties dependent on the included metal ion.^[2] Lanthanides have already been used dissolved in ionic liquids as spectroscopic solvents, but have probably because of their high charge so far not been used as anions or cations of ionic liquids.^[3]



Scheme 1: Structure of $\text{BMIM}_{x-3}[\text{Ln}(\text{SCN})_x(\text{H}_2\text{O})_y]^{3-x}$ ($x=6-8; y=0-2$)

We present a selection of crystal structures of lanthanide-containing ionic liquids based on an imidazolium cation and lanthanide thiocyanate anions of the general formula $[\text{Ln}(\text{SCN})_x(\text{H}_2\text{O})_y]^{3-x}$ ($x=6-8; y=0-2; \text{Ln} = \text{Y}, \text{Sc}, \text{La-Lu}$). Most of these ionic liquids are liquids at room temperature. The hydrogen bonding of the coordinated water molecules and the thiocyanate anions and the hydrogen bonds of the imidazolium cations have been studied. The lanthanide-containing compounds exhibit a good miscibility with other imidazolium based ionic liquids like $[\text{BMIM}][\text{Tf}_2\text{N}]$ ($\text{Tf}_2\text{N} = \text{bis}(\text{trifluoro-sulfonyl})\text{imide}$) and are therefore interesting candidates for applications in catalysis, spectroscopy or for the design of ionic liquid crystals.^[4]

- [1] a) T. Welton, *Chem. Rev.* 1999, 99, 2071; b) P. Wasserscheid, W. Keim, *Angew. Chem., Int. Ed. Engl.* 2000, 39, 3772; c) P. Wasserscheid, T. Welton (Eds.), *Ionic Liquids in Synthesis*, VCH-Wiley, Weinheim, 2003.
- [2] a) Y. Yoshida, J. Fujii, G. Saito, T. Hiramatsu, N. Sato, *J. Mater. Chem.* 2006, 16, 724-727; b) J. E. L. Dullius, P. A. Z. Suarez, S. Einloft, R. F. de Souza and J. Dupont, *Organomet.*, 1998, 17, 815-819; c) M. H. Valkenberg, C. deCastro and W. F. Hölderich, *Appl. Catal., A*, 2001, 215, 185-190; d) S. Hayashi, S. Saha, H. Hamaguchi, *IEEE Transact. Magnet.* 2006, 42, 12-14; e) I.J.B. Lin, C.S. Vasam, *J. Organomet. Chem.* 2005, 690, 3498-3512; f) S. Hayashi, H. Hamaguchi, *Chem. Lett.* 2004, 33, 1590-1591.
- [3] a) E. Guillet, D. Imbert, R. Scopelliti, J.-C.G. Bünzli, *Chem. Mater.* 2004, 16, 4063-4070; b) K. Driesen, P. Nockemann and K. Binnemans, *Chem. Phys. Lett.* 2004, 395, 306-310; c) P. Nockemann, E. Beurer, K. Driesen, R. Van Deun, K. Van Hecke, L. Van Meervelt, K. Binnemans, *Chem. Commun.* 2005, 4354-4356; d) S. Arenz, A. Babai, K. Binnemans, K. Driesen, R. Giernoth, A.-V. Mudring, P. Nockemann, *Chem. Phys. Lett.* 2005, 402, 75-79.
- [4] K. Binnemans, *Chem. Rev.* 105 (2005) 4148.