A stable organic radical stacked by in situ coordination to Rare Earth cations. Natalia Snejko, a Felipe Gándara, b Angeles Monge, a Enrique Gutiérrez, a Alicia de Andrés, a Jesús Rodríguez, a José Gómez-Sál a Instituto de Ciencia de Materiales de Madrid, Cantoblanco, 28049, Madrid, Spain. b Universidad de Cantabria, Avda. de los Castros, 39005, Santander, Spain
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Face-to-face π-stacks of extended aromatics with the d-surfaces located within van der Waals distances have emerged as promising nanowires and are among the best performing organic conductors [1]. We have recently started to explore the strategy, involving the coordination of the aromatic containing building-blocks to metal cations and observing that aromatic molecules can be incorporated in polymeric frameworks with π-π stacking interactions at short distances [2], [3]. The in situ formation and crystal state isolation of the semiquinone species of the anthraquinone molecule has not been reported up to date. With the correct choice of the solvothermal conditions, we have achieved the unprecedented in situ formation of the free radical form of the anthraquinone-1,5-disulfonate molecule (AQDS), and its favorable organization, incorporating this radical into a new type of rare-earth polymeric frameworks, RPF8, by coordination to the lanthanide cations. The reaction of Na2AQDS with a nitrate salt of Ln3+ (Ln=La, Pr, Nd, Sm, Gd, Eu, Dy, Tb, Ho, Er) results in the formation of the new material. The obtained products are crystalline dark solids, formed by small green crystals and crystallized in the orthorhombic system, space group P21212 with a=11.526 Å, b=21.064 Å, c=7.171 Å and V=1727.65 Å3 in the case of La compound. The formula of the compounds is Ln(L(H2O)3)-AQDS3, where L = 1,5-AQDS3-. The Ln atoms are octacoordinated to three water molecules, and to five oxygen atoms from 1,5-AQDS3-, three of the SO3- groups, and two of quinonic groups producing a 2D framework. The anthraquinone ions in the RPF8 exist as AQDS3- anion radicals. In the semiquinone species, the additional charge is delocalized over the anthraquinone central ring and the quinonic oxygen atoms. In order to prove the radical semiquinone species existence, we performed magnetic susceptibility measurements for the La-RPF8 compound. The result was a paramagnetic material, with an effective magnetic moment \( b=21.064 \) μB per formula unit, which confirms the semi-reduced state of the anthraquinone anion. The obtained materials have a very high charge mobility of charge carriers and electric conductivity through the π-π interactions. The conductivity measurements were carried out in a single crystal of the La-RPF8 compound. The current intensity was measured versus the applied voltage, in the range 0-100 V along the stacking direction that corresponds to the (001) plane. The calculated r. t. conductivity for La-RPF8 crystal is 3.3 \( \times 10^{-3} \) S cm\(^{-1}\).


Keywords: rare earth materials; structure and properties; conductive polymers

Blue luminescent compounds from aromatic molecules that absorb in the UV region are in high demand in the search for stable blue emitters for EL devices and for their potential for fluorescence sensors [1]. Mixed-ligand complexes were prepared from d10 Zn(II) acetate reacted sequentially with 1,2,4,5-benzenetetracarboxylic acid as a a primary ligand (L1) and carboxylic acids (malonic acid 1, tartaric acid 2, and picolinic acid 3) as secondary ligands (L2). Compositions of the crystalline products were characterized by SEM/EDX microscopy, XRD, and TGA/DSC thermal analysis, and FT-IR spectra of the compounds indicate the nature of metal-ligand coordination environment. Presence of (O-H) shifted to lower energy indicate H-bonded carboxylic acid, while band positon changes for v(carboxylate) and v(CO) indicate monodentate carboxylate [2] coordination in 1, 2, and 3. UV-vis and fluorescence spectra at room temperature reveal that all three complexes have photoemission in the blue region.


Keywords: zinc compound; coordination polymer; luminescence

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