Abstract

The present PhD thesis entitled "Functional hybrid materials for the optical recognition of nitroaromatic explosives involving supramolecular interactions" is based in the blending of Supramolecular Chemistry and Material Science principles for the preparation of new functional organic-inorganic hybrid materials with the ability of detecting nitroaromatic explosives in liquid environments.

As a first step a complete and exhaustive search dealing with optical sensors (chromogenic and fluorogenic) explosives described in the literature has been carried out. This search cover examples appeared from 1947 since 2011. The results of this bibliographical search are reflected in chapter 2 of this PhD thesis.

The third chapter deals with the use of the ion-channel sensor approach for the preparation of a hybrid organic-inorganic material for the chromo-fluorogenic sensing of nitroaromatic explosives. At this respect, silica nanoparticles were functionalized with thiols (reactive units) and lineal polyamines (binding units). Then, the transport of a selected dye (squaraine) from the bulky solution to the surface of the silica nanoparticles was studied in the absence and in the presence of selected explosives. In the absence of explosive molecules, squaraine dye (that presented a blue color and an intense emission band) is free to diffuse to the nanoparticle surface. Once in the surface, squaraine reacts with the thiol moieties yielding a colorless non-fluorescent derivative (with the subsequent bleaching of the initial blue solution). When nitroaromatic explosives are present, an inhibition of the squaraine-thiol reaction is produced, and the suspension of the nanoparticles remained blue. This inhibition is ascribed to the formation of charge-transfer complexes between the grafted polyamines and the nitroaromatic explosives.

Hybrid materials equipped with biomimetic cavities based in MCM-41 silica mesoporous support as scaffold have also been prepared (see chapter 4). In order to prepare these biomimetic materials, three organic fluorophores (pyrene, dansyl and fluorescein) has been grafted in the inner of the pores of the inorganic support. Then, the inner of the pores were made hydrophobic by the reaction of

the silanol moieties (located in the surface) with 1,1,1,3,3,3-hexamethyldisilazane. This two-step procedure yielded hydrophobic cavities containing selected fluorophores. Acetonitrile suspensions of these hydrophobic materials are highly fluorescent whereas addition of nitroaromatic explosives induced marked emission quenching. The observed quenching was ascribed to the inclusion of the nitroaromatic explosives into the biomimetic cavities and subsequent formation of charge transfer complexes (through π-stacking interactions) with the grafted fluorophore. One important feature of these hybrid sensory materials is their reusability after explosive extraction from the hydrophobic biomimetic cavities.

The last part of this PhD thesis deals with the synthesis and application of hybrid gated organic-inorganic materials for the optical detection of nitroaromatic explosives (see chapter 5). Again, MCM-41 mesoporous silica has been selected as inorganic scaffold. In a first step, the pores of the inorganic scaffold were loaded with a selected dye/fluorophore. Then, in a second step, the external surface of the loaded material was functionalized with selected organic molecules that presented a high electron donor character (such as pyrene and tetrathiafulvalene derivatives). These electron-rich molecules formed a highly dense monolayer (through dipole-dipole interactions) around the pore outlets that inhibit the release of the entrapped dye/fluorophore. Upon addition of nitroaromatic explosives, the monolayer of the electron-rich molecules is disrupted (due to π-stacking interactions) with the subsequent release of the entrapped dye/fluorophore to the solution. This release induced a chromo-fluorogenic response that indicated the presence of the nitroaromatic explosive.