

Laboratoire Hydrazines et Composés Energétiques Polyazotés
UMR 5278 UCBL/CNRS/CNES/ArianeGroup

Tetrazenes and polytetrazenes : synthesis and metal-complex properties

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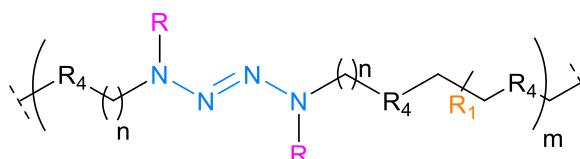
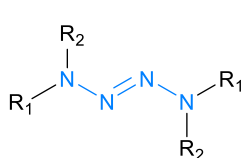
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The tetrazene moiety is composed of four successively bonded nitrogen atoms, providing three consecutive nitrogen-nitrogen bonds. The tetravalent electron-rich nature of the tetrazene function offers a structural versatility and thus, modular properties and reactivity.

As part of a previous PhD thesis carried out at LHCEP, a family of functionalized tetrazenes has been synthesized [1] and then involved, as monomers, in polycondensation or polyaddition reactions. This approach was a successful proof of concept for tetrazenic polymers development as it showed the possibility to insert tetrazene functions as repeat units in the main polymeric chain and consequently, accessing energetic binding polymers for solid propulsion applications [2]. Moreover, our work has demonstrated the possibility to depolymerize the synthesized polytetrazenic chains, which can be an asset for obsolete binders recycling.

Recently, as part of an ongoing ANR project (PRC « polytetra-aza »), we are working, in collaboration with CP2M lab, on (poly)alkyltetrazenes, with a special focus on their role in the initiation of free radical polymerization of polar and unpolar vinyl monomers [3]. Indeed, introducing tetrazene function into the ends of polymer chains can give the opportunity to depolymerize the polymer by decomposing the tetrazenic chain ends (de-zipping). The decomposition of the tetrazene function in the chain end allows for the formation of macroradicals, which can lead to diblock polymers or cross-linking upon re-initiation.





The complexing properties of alkyltetrazenes were reported in a handful of publications [4-6] in the 60s and 70s, for Hg(II), Cd(II), Zn(II) and Al(III). Tetraalkyl-2-tetrazenes are described as proton acceptors and therefore exhibit variations in the absorbance maxima of salts and coordination complexes. Coordination complexes of tetramethyltetrazene (TMTZ) with mercury or cadmium halides have been isolated and characterized, revealing that Cd(II)-TMTZ salts are stable crystalline materials, insoluble in water and slightly soluble in organic solvents, while Hg(II)-TMTZ compounds are much less stable, without giving a stability constant for these complexes. The authors [5] have also described a 1:1 adduct resulting from the reaction between TMTZ and trimethylaluminium (AlMe₃). Zn(II)-TMTZ complexes have been used for the generation of aminyl radicals following their thermal decomposition and engaged in an addition reaction on styrene-type olefins leading to the corresponding diamine derivatives [6].

This thesis project aims at exploring the ability of the tetrazene function to selectively chelate metal ions and to form metal-polymer assemblies. These properties could be harnessed for a wide range of applications, from depolluting, traces detection to catalysis or energetic materials. It will be possible to design tetrazene poly(complexes) whose degradation by strong acids or UV irradiation will lead to the release of incorporated metals. The structure of metallo-polymers will also be studied, as these are new hybrid objects featuring supramolecular architectures that could lead to interesting catalytic properties.

This thesis will provide skills in synthetic chemistry, with a particular focus on N-N bonds, and also knowledge in polymers and organometallic chemistry. LHCEP has the specific expertise and equipments required to study nitrogen-rich derivatives, and benefits on the campus of analytic/spectroscopic platforms and all resources needed to characterize organometallic complexes or polymers.

- [1] Joucla L., Dhenain A., Darwich C., Eymann J., Jacob G. *PCT Int. Appl.* **2020**, W2020043997 A1 20200305.
 [2] a) Eymann J. *PhD dissertation*, Université Claude Bernard Lyon 1, **2020**; b) Eymann J., Joucla L., Jacob G., Raynaud J., Darwich C., Lacôte E. *Angew. Chem. Int. Ed.* **2021**, 60(3), 1578-1582.
 [3] Bourgeois L., Hammoud A., Lesage De La Haye J., Renault A., Lacôte E., Raynaud J., Darwich C. Study of the tetrazene function and its role in free radical polymerization, publication en cours.
 [4] Bull W. E., Seaton J. A., Audrieth L. F. *J. Am. Chem. Soc.*, **1958**, 80, 2516-2518.
 [5] Fetter N. R., Brinckman F. E., Moore D. W. *Can. J. Chem.*, **1962**, 40, 2184-2188.
 [6] a) Michejda C. J., Campbell, D. H. *J. Am. Chem. Soc.* **1974**, 96, 929-930; b) Michejda C. J., Campbell, D. H. *J. Am. Chem. Soc.* **1979**, 101, 7687-7693.