Predicted high energy density MN_8 with polynitrogen monolayers based on fused 18-rings acting as cryptand

PITIE Sylvain*;[A] **WANG Busheng**[A], **GUEGAN Frédéric**[A], **FRAPPER Gilles***[A]

A) Applied Quantum Chemistry group, E4, IC2MP, UMR 7285 Poitiers University, CNRS, 86073, France.

*sylvain.pitie@univ-poitiers.fr, *gilles.frapper@univ-poitiers.fr

The application of polynitrogen as a high-energy density material (HEDM) is hampered because of the high reactivity of most predicted allotropic phases of nitrogen. However, mixing nitrogen with other elements M can help to overcome this kinetic instability. By modulating pressure, MN_x products can be stabilized and then quenched to obtain "polymerized nitrogen" and nitrogen-rich compounds. Our theoretical exploration of different M-N binary phase diagrams under pressure[1,2] has resulted in the emergence of appealing N-based molecular motifs like chains or layers. For instance, we predicted the isolation of a layered unsaturated 18-crown-like N_8 material.[3] We explored the possibility of predicting the emergence of novel and viable nitrogen-rich MN_8 compounds by mixing an electropositive metal with the unsaturated moieties.[4] Our investigation involved a wide range of solid-state compounds MN_8 under pressure, with M supporting different oxidation numbers such as Na^+, Ag^+, Ca^{2+}, Pb^{2+}, Y^{3+}, and Hf^{4+}. By assessing dynamical (phonons), thermodynamic (enthalpies), and kinetic (AIMD) stabilities, we predicted over 14 viable compounds with different crystalline phases. To locate the different phases of the 2D 18-crown-6 MN_8, we used the evolutionary algorithm "USPEX"[5] combined with DFT calculations at various levels of theory (PBE, PBE-D3(BJ), r^2SCAN+rVV10, or HSE06) depending on the evaluated property (structure, energy, phonons, AIMD, DOS, COBI, energy gap, bands, etc.). The results of our exploration indicate that the extended crown-like N_8 net is a stable and common topological motif, which is stabilized by cations through ionic interactions. We also investigated the stoichiometric modulation of the metal intercalant M into the interlayer spaces of M_x@2D-N_8 (x = 0.5 - 1). These metal 18-crown-6 ring-based polynitrogen compounds, as expected due to their high nitrogen content (eight nitrogen atoms per metal), could potentially serve as new high-energy density materials the detonation velocity ranges from 10.1 to 17.9 km.s−1 , which is higher than the experimentally determined range of explosive (CH2)4(NNO2)4 HMX (VoD ~9.1 kms−1). Additionally, a prospective study was conducted to examine the stabilizing capability of 18-crown-6 2D-N_8 towards molecular cations such as H_3O^+ and NH_4^+.

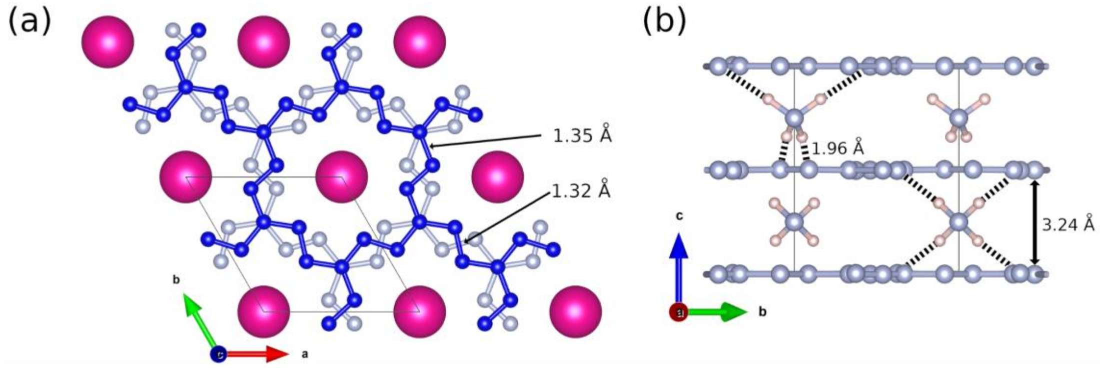

Figure 1. Crystal structures of (a) *P*6/*m* Rb@2D-N_8 and (b) *Ccc*2 (NH_4^+)@2D-N_8.

Keywords: HEDM; periodic-DFT; Evolutionary Algorithm; Material Design

1 B. Huang and G. Frapper, *Chem. Mater.*, **2018**, *30*, 7623-7636.
2 B. Wang, R. Larhlimi, H. Valencia, F. Guégan and G. Frapper, *J. Phys. Chem. C*, **2020**, *124*, 8080-8093.
3 B. Wang, F. Guégan and G. Frapper, *Journal of Materials Chemistry C*, **2022**, *10*, 10374-10381.
4 S. Pitié, B. Wang, F. Guégan and G. Frapper, *Inor. Chem.*, **2024**, *in press*.
5 USPEX: https://uspex-team.org/en.