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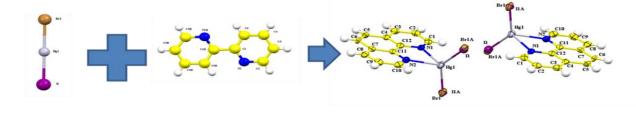
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Inorganic noncentrosymmetric building block for the construction of new NLO materials: a new perspective

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The recent success in the design and synthesis of novel materials based on metal-organic coordination networks has prompted the scientific attention to the supramolecular engineering of non-centrosymmetric solids by exploiting the strong and highly directional metal-ligand coordination bonds. The organometallic approach in this field however consists usually in the use of versatile organic molecules associated with stable and inorganic part with electronic peculiarities. The asymmetric center that generates the noncentrosymmetric structure usually is the organic ligand. We tried to reverse this perspective, using an inorganic noncentrosymmetric building block to control the space group symmetry of the crystalline compounds, and the organic part to modulate the electronic properties. This different approach has been applied in the synthesis of a series molecular materials based on organic ligands with different symmetries 2.2'-bipyridine. 2,2';6',2"-terpyridine, 1,10-phenanthroline and 2-pyridilnaphtiridine) with the asymmetric HgBrl unit. This inorganic salts is well known to be a good material for SHG in the solid state [1]. The obtained materials have been analyzed through SHG microscopy [2] in powder and single crystal form, in order to obtain the different tensor components of the emission, and the results show that the use of different ligand and a rational control of substitutional disorder allow a new way of modulating NLO properties.



Molecular point group: Cwe Space Group: Cm c21 Molecular point group: C_i

Figure 1: Molecular complex obtained with HgBrI (noncentrosymmetric) and 2,2'-bipy (centrosymmetric)

[1] Q. Wu, Y. Li, H. Chen, K. Jiang, H. Li, C. Zhong, X. Chen, J. Qin, *Inorg. Chem. Commun.*, **2013**, *34*, 1
[2] D. Marabello, P. Antoniotti, P. Benzi, C. Canepa, E. Diana, L. Operti, L. Mortati, M.P.Sassi, *J. Mat. Sci.*, **2015**, *50*(*12*), 4330