

## Heteroleptic metal complexes as chromophores for nonlinear optical materials

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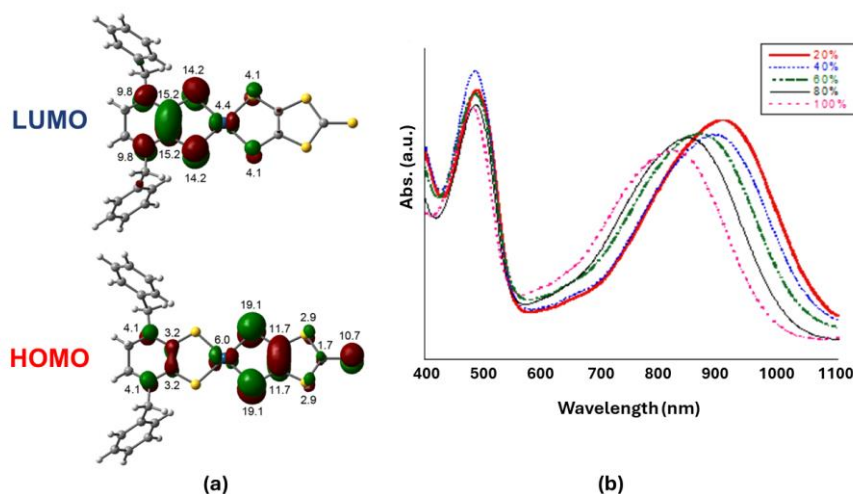
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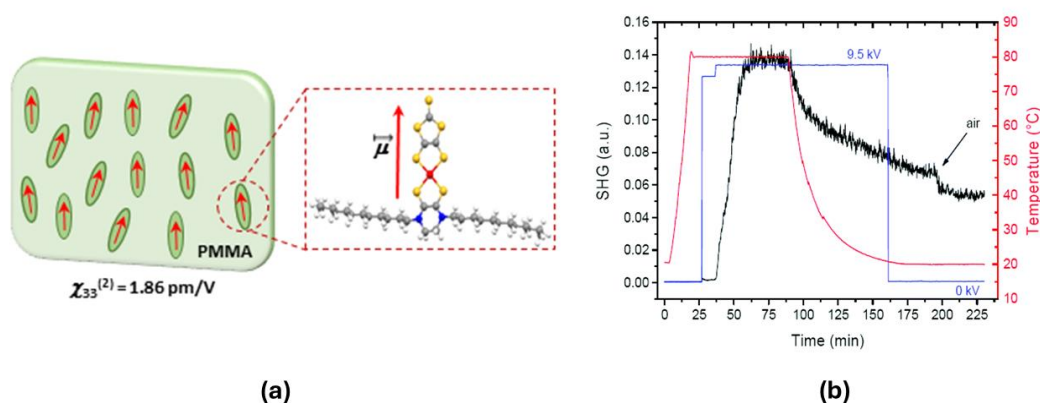
The development of laser technology allowed several nonlinear optics (NLO) effects to be discovered or experimentally demonstrated. Many materials with NLO properties have been prepared and studied for applications in optics, photonics and optoelectronics [1]. Among these, molecular-based materials with second-order NLO properties (denoted by  $\beta$  and  $\chi^{(2)}$  at the molecular and bulk level, respectively) have been the subject of studies both for the high  $\beta$  values and for the ease with which they can be processed in the preparation of devices [2]. Many square planar metal complexes of the *push-pull* type have been reported in the literature as molecular chromophores with high  $\beta$  values, in particular dithione-dithiolates [3] and diimine-dithiolates [4]. These complexes are formed by a metal ion and two ligands with different electron-withdrawing capacity: the *push* ligand, with electron-donating substituents which raise the energy of the orbitals, and the *pull* one which is instead stabilized by the presence of electron-withdrawing substituents. Therefore, the *pull* ligand contributes most to the formation of the HOMO while the LUMO is mainly formed by the *push* ligand (Figure 1a). These features give to the HOMO-LUMO electronic transition, which plays a crucial role in the generation of  $\beta$ , a charge transfer (CT) character with a solvatochromic behaviour (Figure 1b). By appropriately choosing the metal ion and the substituents at the periphery of the two ligands, it is therefore possible to modulate the electronic properties of the frontier orbitals (FOs), the dipole moment of the molecule ( $\mu$ ) and the energy of the CT transition. Moreover, one or both moieties may be conveniently functionalized to enable the switching of the NLO property. In addition, these complexes are usually redox active and show reversible bleaching of the solvatochromic peak for mono-reduction, being thus suitable candidates to be used for switching the second-order NLO response.



**Figure 1** – Frontier orbitals of the [Pt(Bz<sub>2</sub>pipdt)(dmit)] complex (a) and its solvatochromic behaviour in DMF and its mixtures with CS<sub>2</sub> ranging from DMF 100% to 20% (b). (Reprinted with permission from ref. 5. Copyright 2011, American Chemical Society).

Many *push-pull* chromophores crystallize in space groups with a center of symmetry; consequently, despite they show high  $\beta$  values at the molecular level, they present  $\chi^{(2)} = 0$  in the solid state. One approach to overcome this drawback, given the importance for application purposes of having the NLO property in the solid state, involves the embedding of the chromophores into polymeric matrices such as poly-methyl methacrylate (PMMA; see Figure 2).

This talk will present examples of heteroleptic metal complexes, focusing on their design, features and properties, with the aim to highlight the structure-properties relationship in this class of compounds.



**Figure 2** – Representation of the PMMA film of [Pd(Dod<sub>2</sub>pipdt)(dmit)] complex (a) and its poling (b). SHG (black line), temperature (red line) and electric field (blue line). (Reprinted with permission from ref. 6. Copyright 2016, Royal Chemical Society).

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