

Push-Pull Mixed-Ligand d⁸-Metal Dithiolene Complexes

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Recently an experimental and theoretical study on neutral, square-planar mixed-ligands nickel-bisdithiolenes has been performed [1]. These complexes have a common (C₂S₂)Ni(C₂S₂) core and two different terminal groups (R₂pipdt=1,4-dialkyl-piperazine-3,2-dithione; R₂timdt=1,3-dialkyl-imidazolidine-2,4,5-trithione as push ligands and dmit=1,3-dithiolo-2-thione-4,5-dithiolato; mnt= maleonitriledithiolato as pull ligands). Measurements of the first molecular hyperpolarizability (β) indicated that some of the species are NLO chromophores, due the π -delocalized character of two frontier levels which is asymmetrically perturbed by the combination of one *push* with one *pull* ligand. Experimental results indicate rather different responses between the pairs of complexes containing R₂pipdt and R₂timdt ligands. DFT calculations have been carried out to correlate geometries and electronic structures. β values have been calculated and their components have been analyzed with the simplest two-level approximation. The derived picture highlights the different roles of the two *push* and *pull* ligands, but also the peculiar perturbation of the π -electron density induced by dmit. The novel complex [Pd(Me₂pipdt)(dmit)] has been obtained and shows negative solvatochromism. Its structural and electronic properties will be compared with those of the nickel analogue.

[1] Curreli S., Deplano P., Faulmann C., Ienco A., Mealli C., Mercuri M.L., Pilia L., Pintus G., Serpe A., Trogu E.F., *Inorg. Chem.*, 2004, **43**(16), 5069-5079.

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