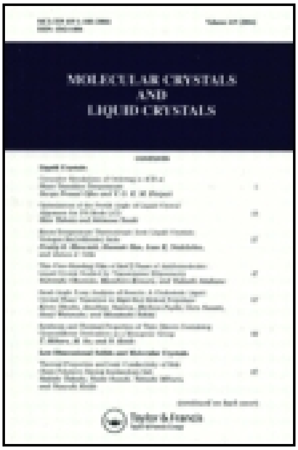

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Tetrazine-Bridged Phthalocyaninatometal Complexes: A New Class of Intrinsic Semiconductors

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TETRAZINE-BRIDGED PHTHALOCYANINATOMETAL COMPLEXES: A NEW CLASS OF INTRINSIC SEMI-CONDUCTORS

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Stacked metallomacrocycles $[MacM(L)]_n$ can be obtained by the so-called "shish kebab" approach[1] in which transition metallomacrocycles (MacM) are linked together by bidentate bridging ligands (L). Such bridged macrocyclic metal compounds $[MacM(L)]_n$ with transition metals e.g. Fe, Ru, Os, Co, Rh in various oxidation states have been synthesized by us.[1] Mostly as macrocycles (Mac), not only phthalocyanine (Pc), tetrabenzoporphyrine (TBP), but also macrocycles containing more extended p-systems like 1,2- or 2,3-naphthalocyanine (1,2-, 2,3-Nc) or phenanthrenocyanine (Phc) are used.[1,2,3] The bridging ligands (L) are bifunctional organic donor molecules, e.g. pyrazine (pyz), *s*-tetrazine (tz), *p*-diisocyanobenzene (dib), 1,4-diazabicyclo[2.2.2]octane (dabco) for metals in the oxidation state +2, or e.g. cyanide (CN^-), thiocyanate (SCN^-) or azide (N_3^-) for transition metals in the oxidation state +3.[1a] In general, these complexes $[MacM(L)]_n$ are insoluble in organic solvents, however, soluble oligomers $[R_4PcM(L)]_n$ can be prepared using metallomacrocycles R_4PcM, R = *t*-bu, et, M = Fe, Ru, which are substituted in the peripheric positions.[4]

The coordination polymers [MacM(L)]n can be either chemically or electrochemically doped leading to stoichiometric compounds $[MacM(L)Y_x]_n$, $Y = I_3^-$, BF_4^-, which show comparatively high thermal stability and good long time semiconducting properties in the order of 0.1 S/cm.[5]

In this paper we report about a systematic investigation of the influence of the bridging ligand on the conductivity of the bridged phthalocyaninato and 2,3-naphthalocyaninatotransition metal complexes. As bridging ligand mostly tetrazine (tz) and its derivatives e.g. 3,6-dimethyl-*s*-tetrazine (me_2tz) is used. Due to the low oxidation potential of tz and me_2tz and due to its low lying LUMO it was expected that the corresponding bridged systems $[MacM(tz)]_n$ could exhibit intrinsic conductivities.

The synthesis and characterization of $[PcM(tz)]_n$, with M = Fe, Ru, Os and $[2,3\text{-}NcFe(tz)]_n$ is described. In case of the phthalocyaninatoiron systems detailed Mößbauer studies are reported.

A systematic investigation of the influence of the bridging ligands on the semi-conducting properties in $[MacM(L)]_n$ reveal, that changing L, e.g from dabco over pyz to tz leads to a steady increase of the semi-conducting properties without external oxidative doping. Powder conductivities in the order of 0.1 S/cm can be reached by using *s*-tetrazine, but also substituted tetrazine e.g. 3,6-dimethyl-*s*-tetrazine (me_2tz) are used as the bridging ligands in such complexes.

The influence of the central transition metal in the metallomacrocycles MacM on the conductivity of the bridged systems is investigated and it will be shown that an increase in conductivity without additional external doping can only be obtained, if group 8 metals (Fe, Ru, Os) are used.

The influence of peripheric substituents on the conductivity of the tetrazine-bridged phthalocyaninatometal complexes is also investigated, e.g. $[(CN)_4PcFe(tz)]_n$ only exhibits a very low conductivity.

The electrical and physical properties, especially the Mößbauer spectra of the tetrazine-bridged macrocyclic iron complexes are discussed in respect to intrinsic semi-conducting properties of these compounds.

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