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Intrinsic Semiconducting Materials on Phthalocyanine Basis

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**Abstract:** Stacked transition metal macrocycles  $[\text{MacM}(\text{L})]_n$  with M e.g. Fe, Ru, Os, Co, Rh and Mac = phthalocyanine (Pc) 1,2- or 2,3-naphthalocyanine (1,2-, 2,3-Nc) were synthesized. The bridging ligands (L) may be e.g. pyrazine (pyz) or s-tetrazine (tz). In general, these complexes  $[\text{MacM}(\text{L})]_n$  are insoluble in organic solvents; however, soluble oligomers  $[\text{R}_4\text{PcM}(\text{L})]_n$  can be prepared using metallomacrocycles  $\text{R}_n\text{PcM}$ , R = t-bu, et, OR, M = Fe, Ru, which are substituted in the peripheric positions. A systematic investigation of the influence of the bridging ligands on the semiconducting properties in  $[\text{MacM}(\text{L})]_n$  reveals that changing L, e.g., from dabco over pyz to tz leads to a steady increase of the semiconducting properties without external oxidative doping. Powder conductivities in the order of 0.1 S/cm can be reached by using s-tetrazine, 3,6-dimethyl-s-tetrazine ( $\text{me}_2\text{tz}$ ) and others, e.g. fumarodinitrile, as the bridging ligands. The intrinsic conductivities are a result of the low oxidation potential of tz and  $\text{me}_2\text{tz}$  and due to the low lying LUMO in the corresponding bridged systems  $[\text{MacM}(\text{tz})]_n$ .

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