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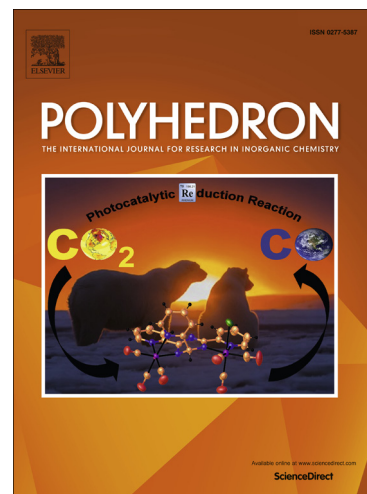
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The Suzuki cross-coupling reaction for the synthesis of porphyrazine possessing bulky 2,5-(biphenyl-4-yl)pyrrol-1-yl substituents in the periphery

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ABSTRACT:

The macrocyclization reactions led to higher-symmetry and lower-symmetry porphyrazines bearing peripheral 2,5-di(4'-chlorophenyl)pyrrol-1-yl and dimethylamino substituents, which were characterized using NMR and X-ray crystallography. The reactions were performed in the conditions of Lindsey macrocyclization with magnesium *n*-butanolate in *n*-butanol, catalytic amount of iodine in *n*-butanol with an addition of a malonitrile derivative in solid form or after dissolving it in DMF. It is interesting to note that the addition of DMF increases the total yield of the reaction from low to moderate, and forces the synthesis of the higher-symmetry over the lower-symmetry porphyrazine. The non-alternate order of peripheral substituents in lower-symmetry porphyrazine resulted in the non-equivalence of dimethylamino groups in ¹H and ¹³C NMR spectra. The X-ray crystal structures of both porphyrazines revealed an almost perpendicular orientation of the bulky, 2,5-di(4'-chlorophenyl)pyrrol-1-yl substituents to the cores. Higher-symmetry

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