10,15-di(4-pyridyl)-5,20-di(4-tolyl)-21-thiaporphyrin as a building block for porphyrin coordination arrays.

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Streszczenie

10,15-di(4-pyridyl)-5,20-di(4-tolyl)-21-thiaporphyrin, (SDPyDTP)H, was prepared by condensation of 2,5-bis(4-tolylhydroxymethyl)thiophene, pyrrole and 4-pyridinecarboxaldehyde in boiling propionic acid. The synthesis introduced two pyridyl substituents at two defined (opposite to thiophene) *meso* positions of the porphyrin periphery. The self-assembly of the angular 10,15-dipyridyl-21-thiaporphyrin modules with *cis* square-planar diphosphineplatinum(II) complex leads to a cyclic rhomboid dimer [Pt(DPPP)(SDPyDTP)H]$_2$(OTf)$_4$. The molecule acquires butterfly geometry. The ^{1}H NMR studies confirmed the π-π stacking of the pyridyl ring with the equatorial phenyl rings of the phosphine fragment. The conformational equilibrium, interchanging the phenyl ring positions and affording the mixture of seven conformers in solution, has been considered. ^{1}H NMR> spectroscopy was applied to identify oligomeric species, constructed by coordination of (SDPyDTP)H to the paramagnetic nickel(II) complex 5,10,15,20-tetra(4-tolyl)-21-thiaporphyrin, (STTP)Ni^{II}Cl. (SDPyDTP)H acts as a mono- or bidentate ligand coordinating by *meso*-pyridyl substituents. Using the paramagnetically shifted resonances as an unambiguous spectroscopic probe, ^{1}H NMR spectroscopy readily discriminated between five- {[(STTP)Ni^{II}]((SDPyDTP)H)} and six-coordinate {[(STTP)Ni^{II}]((SDPyDTP)H)$_2$} oligomeric subunits. The applicability of 10,15-di(4-pyridyl)-5,20-di(4-tolyl)-21-thiaporphyrin as a suitable building block in construction of larger molecules was confirmed. The new route to modify the porphyrin coordination arrays, which preserves the overall architecture but modifies intrinsic chemical properties, using heteroporphyrin was demonstrated.

Słowa kluczowe

porphyrin coordination dimers, thiaporphyrin

Adres publiczny

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