

Conformational Flexibility and Size of Large *trans*-Vinylene-Bridged Thiaporphyrinoids Influence Boron Coordination Modes

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Two π -extended core-modified porphyrinoids were synthesized and structurally characterized to probe boron-induced geometry switching and modulation of electron delocalization. *trans*-Vinylene-bridged hexathiadodecaphyrin forms the largest fully characterized porphyrinoid BODIPY-type complex while retaining the parent open-form geometry, whereas octathiahexadecaphyrin does not support boron coordination. Notably, a smaller figure-of-eight tetrathiaoctaphyrin analogue exhibits unusual direct C–B bond formation, highlighting the pronounced structural sensitivity of expanded porphyrinoids and their utility in accessing unconventional bonding and coordination modes.

Słowa kluczowe

Boron, Aromatic compounds, Pyrroles, Aromaticity, Macrocycles

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