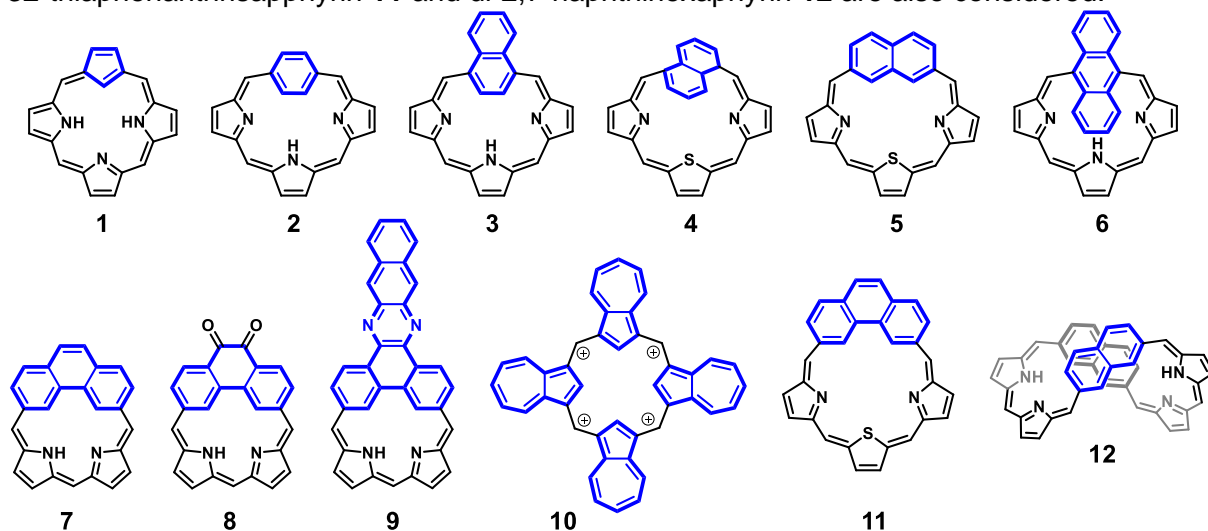


Aceneporphyrinoids: Synthesis, Organometallic Chemistry and Transformations

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Redesign of archetypical porphyrin frame to create aceneporphyrinoids, realized through replacements of pyrrolic rings with other heterocycles or carbocycles, creates innovative routes for exploration of coordination and organometallic chemistry confined in macrocyclic environments. Thus aceneporphyrinoids combine structural features of polycyclic aromatic hydrocarbons (PAH) and polypyrrolic macrocycles.^[1] The hybrid compounds are exemplified by 21-carbaporphyrin **1**, *p*-benziporphyrin **2**, 1,4-naphthiporphyrin, **3**, 22-thia-1,5-naphthiporphyrin **4**, 28-thia-1,7-naphthiporphyrin **5**, *meso*-anthriporphyrin **6**, phenanthriporphyrin **7**, 5,6-dioxophenanthriporphyrin **8** and azaaceneporphyrinoid **9**. Polycarbocations confined in thiatriazuliporphyrin or tetrazuliporphyrin frames **10**, treated as peculiar examples of tri- or tetracabaporphyrinoids, are included.^[2] Eventually examples of expanded aceneporphyrinoids: 32-thiaphenanthrisapphyrin **11** and di-2,7-naphthihexaphyrin **12** are also considered.^[3]



In general, such carbaporphyrinoids can reveal peculiar electronic and molecular features forcing atypical coordination modes and unique intramolecular reactivity.^[4] For instance a detected contraction of *m*-phenylene or *p*-phenylene to cyclopentadiene to afford **1**, triggered by insertion of rhodium(III) into *m*-benzi or *p*-benziporphyrin **2** belongs to an exclusive group of reactions where the cleavage of aromatic structure is of fundamental importance.^[5]

Significantly, the incorporation of phenanthrene moiety into porphyrin framework results in a hybrid macrocycle – antiaromatic phenanthriporphyrin **1** – merging the structural features of polycyclic aromatic hydrocarbon. The unique inner core of phenanthriporphyrin **1** consists of two carbon donors prearranged for simultaneous coordination of phenanthrene and two pyrrolic nitrogen atoms arranged toward coordination as unambiguously demonstrated by incorporation of a small cations to form hypervalent organophosphorous **1-P** or copper(III) **1-Cu** derivatives.^[1;6]

In more general terms, aceneporphyrinoids are expected to provide an insight into a broad spectrum of fundamentally important molecular properties among which are nontrivial optical effects, electron transfer and redox chemistry or three-dimensional aromaticity.

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