



Review

Tetrapyrizinoporphyrazines and their metal derivatives. Part II: Electronic structure, electrochemical, spectral, photophysical and other application related properties



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ABSTRACT

Tetrapyrizinoporphyrazines (TPyzPzs), the heterocyclic azaanalogs of the phthalocyanine macrocycle, known since the 1930 s, but became an object of intensive studies in the last decades. In Part I (Coord. Chem. Rev. 2016, 309, 107–179) the synthesis of variously substituted TPyzPzs and their metal complexes as well as of their precursors was presented. In the present Part II, we consider the peculiarities of their electronic structure, electrochemical, spectral, acid–base and photophysical properties. The focus is made on the related perspectives of practical applications in the fields of nonlinear optical properties, liquid crystals, catalysis, sensors, dark quenchers of fluorescence, photodynamic therapy (PDT, including the specific aspects of water-soluble and targeting TPyzPzs, *in vitro* PDT results, bi- and multimodal therapy) and light harvesting.

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1. Introduction

Tetrapyrrolic porphyrans (TPyzPz), tetrapyrrolic macrocycles (Chart 1) characterized by well distinct physicochemical behavior and potentialities of applications from those of the well-known parallel class of porphyrans (Pz) named phthalocyanines (tetrabenzoporphyrans, Pcs), have been the object of intense research work in the last two–three decades. They were first reported by Linstead et al. in 1937 [1], the systematic research of unsubstituted TPyzPz and some alkyl substituted derivatives began in 1970th [2–9] and publications until 2000 were considered in several reviews [10–14].

Due to the high level of insolubility of the unsubstituted macrocycles, in the most recent times the major efforts have been directed to the preparation of a variety of tetrapyrrolic porphyrans having external substituents able to determine solubility in non-aqueous solvents and in the water medium. Since TPyzPz are most commonly obtained by macrocyclization of appositely prepared precursors, synthetic procedures leading to these latter species have also received increasing attention. In Part I of this review [15], methods of preparation and the main structural features were reported for dinitrile precursors and related symmetrical TPyzPz. The work, which also included a large number of low-symmetry porphyrans macrocycles, was extensively illustrated with the help of Schemes, Charts, Figures, and Tables summarizing data on a variety of TPyzPz. Among the multiplicity of substituents

used to enlarge the macrocyclic framework, external fragments able to give rise to the formation of multinuclear or multicharged species were also considered. Single-crystal X-ray work allowed elucidation of the structure of many of the precursors and eventually of their metal derivatives, some of them the object of recent further attention [16]. Due to problems of appropriate solubility or because obtained as amorphous often hydrated species, rare TPyzPz have so far been isolated in a crystalline form and could be structurally elucidated.

In the present contribution, it is reported that the availability of the new prepared TPyzPz allowed in the most recent times to achieve knowledge of their solid state and solution properties with findings indicative of their occurrence in monomeric or aggregated forms depending on the type of solvent. It will be shown that quantum chemical calculations provide plenty of information on the relationship between the UV–visible spectral features of the TPyzPz and their Pc analogs. Both classes of compounds are characterized by the presence of intense absorptions in the Soret (300–450 nm) and Q-band regions (600–800 nm). Their spectral behavior will be examined in detail also in proton-acceptor and proton-donor media. Reported will also be the explored area of the electrochemical behavior of insoluble TPyzPz using appropriate systems of deposition, and for enough soluble TPyzPz macrocycles the redox properties were also examined in a comparison with the parallel series of the Pc compounds. Large attention has been devoted to the description of the photophysical properties of several classes of TPyzPz in the light of perspectives of practical applications as to their response in terms of fluorescence and singlet oxygen quantum yields (Φ_F , Φ_Δ), with implications in some cases of a competitive intramolecular charge transfer (ICT) process. A conclusive report is extensively centered on the applications of TPyzPz and deals various fields, with evidence given of the potentialities of the different topics presented in the order: (a) nonlinear optical properties, (b) liquid crystals, (c) catalytic properties, (d) sensors, (e) dark quenchers of fluorescence, (f) photodynamic therapy, (g) light harvesting.

For the purpose of this article, the particular structures named in this paper will be presented in square brackets with addition of substituents while abbreviation for general macrocycle will be

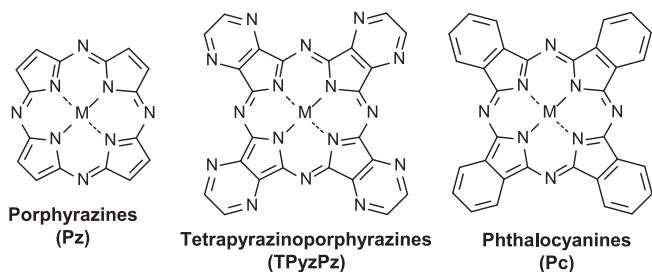


Chart 1. Structure of porphyrans and its benzo and pyrazine fused analogs.

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