



Bioinspired molecular design of functional dendrimers

Dong-Lin Jiang^a, Takuzo Aida^{a,b,*}

^aERATO AIDA Nanospace Project, Japan Science and Technology Agency (JST), 2-41 Aomi, Koto-ku, Tokyo 135-0064, Japan

^bDepartment of Chemistry and Biotechnology, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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Abstract

The present article focus on a series of our recent work on bioinspired molecular design of functional dendrimers, in particular, dendrimer cobalt porphyrins as novel coenzyme B12 mimics, dendrimers for light harvesting and photoinduced electron transfer, and dendrimers for controlled self-assembly and their functions. Special emphasis is placed on size and morphology dependent properties of these dendritic macromolecules.

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Keywords: Dendrimer; Porphyrin; Conjugated polymer; Metal-coordination polymer; Fullerene; Hydrogen evolution; Light harvesting; Organic transformation; Energy transfer; Photoinduced electron transfer; Photosynthesis; Spin transition

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* Corresponding author. Address: ERATO AIDA Nanospace Project, Japan Science and Technology Agency (JST), 2-41 Aomi, Koto-ku, Tokyo 135-0064, Japan. Tel.: +81 3 5841 7251; fax: +81 3 5841 7310.

E-mail addresses: jiang@nanospace.miraikan.jst.go.jp (D.-L. Jiang), aida@macro.t.u-tokyo.ac.jp (T. Aida).

1. Introduction

Dendrimers are three-dimensional hyperbranched macromolecules that provide well-defined nanoscopic objects at the single molecular level. Unlike ordinary linear polymers, star-shaped polymers, and traditional branched polymers, dendrimers are characterized by their elaborate structure, which allows us to precisely control their molecular size, shape, and the numbers and positions of functional groups. Recent studies on dendritic macromolecules have extended the scope of research from synthesis to applications for catalysts, photoactive and electronic materials, medicinal and biomedical materials, and other functional materials [1,2].

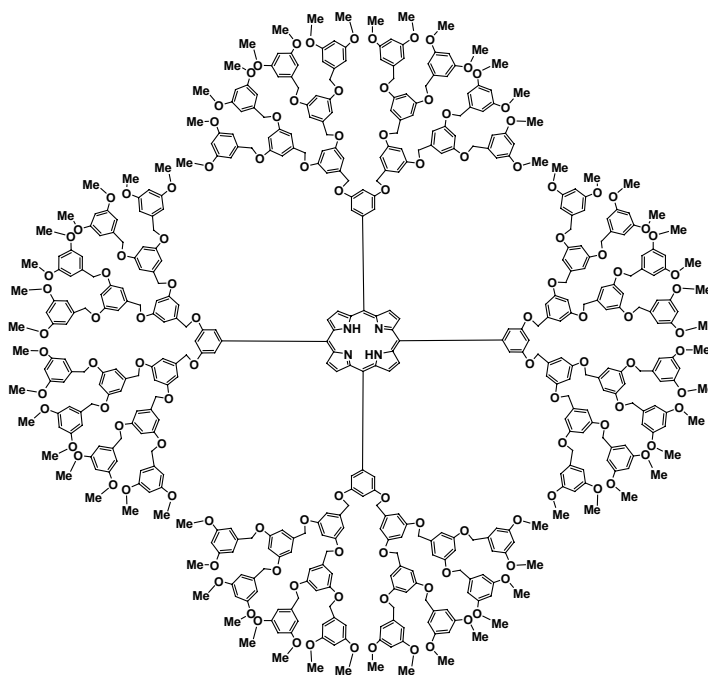
In 1991, we have reported the first example of dendrimer porphyrin **1** as a mimic of hemoproteins [3]. A series of such dendrimer porphyrins and their metal complexes allowed us to investigate chemical and physical properties of interior voids of dendritic macromolecules, photochemical properties of specially isolated dye molecules in regard to their morphology-dependent light harvesting functions, and their interesting potentials as artificial

hemoproteins [4–6]. Functionalization of their exterior surfaces with charged groups also allowed us to construct a cytochrome *C* mimic for the investigation of a core-to-exterior long-range electron transfer and to study electrostatic interaction between positively and negatively charged dendritic macromolecules via a core-to-core energy transfer [7,8]. More recently, in collaboration with Kataoka and coworkers, these water-soluble dendrimer porphyrins have been demonstrated to be highly useful for photodynamic cancer therapy [9–12]. Such broad applications of dendrimer porphyrins have prompted us to design a new class of bioinspired dendrimers.

In the present article, we highlight our recent efforts to construct several new bioinspired dendrimers and their self-organization by focusing attention on structure–function relationships.

2. Dendrimer cobalt porphyrin as a novel coenzyme B₁₂ Mimic

The well-defined hyperbranched structure of dendrimers has motivated chemists to explore



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