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# Platinum–acetylide dendrimers possessing a porphyrin core

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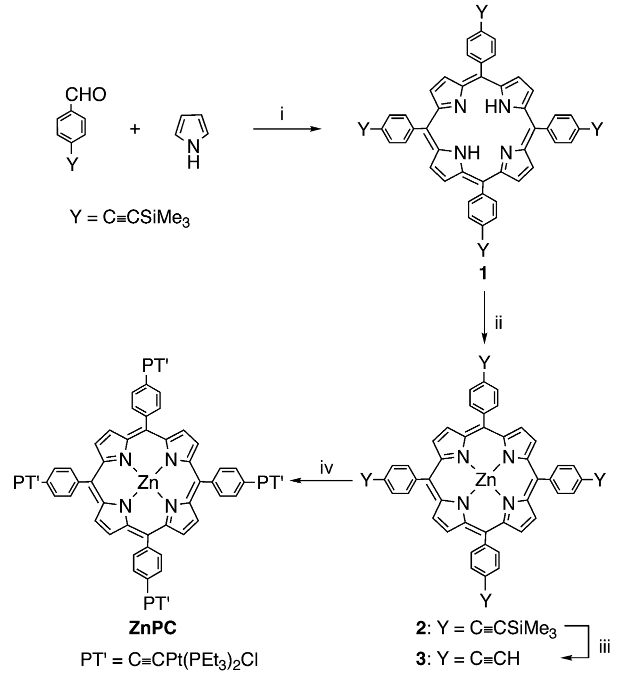
**Intramolecular energy transfer from platinum–acetylide moieties to the porphyrin core was observed in novel organometallic dendrimers that were prepared from a tetra(4-ethynylphenyl)porphyrin-bridged tetranuclear platinum–acetylide core and platinum–acetylide dendrons by a convergent method.**

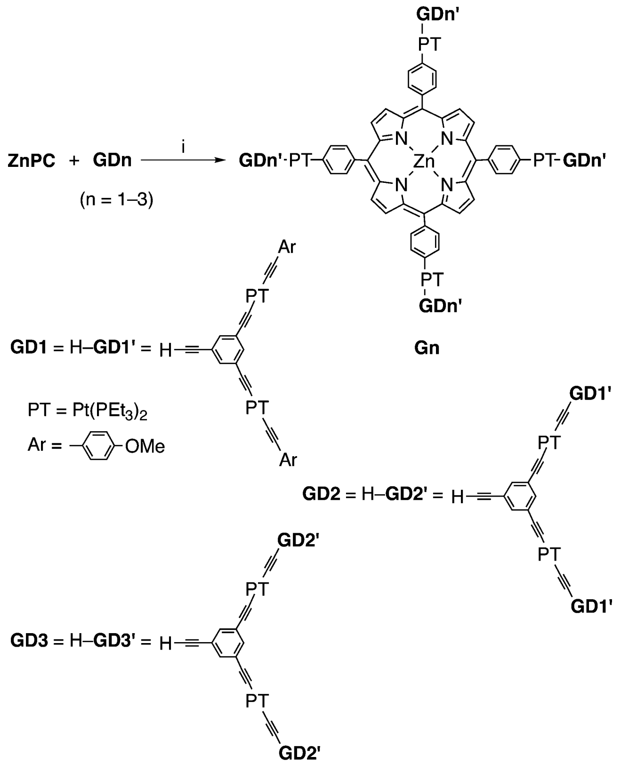
Dendrimers are regularly hyperbranched macromolecules that adopt well-defined nanostructures. Recently, increasing attention has been focused on the incorporation of functional units into such dendritic structures.[1] Dendritic porphyrins are promising molecules, since porphyrins are representative functional organic molecules and the local environment often affects their functionalities. Several types of dendritic porphyrin with organic dendrons have already been prepared, and some of them exhibit interesting properties due to the encapsulation of a porphyrin core in the interior of dendritic structures.[2] On the other hand, organometallic dendrimers are also promising as a new type of functional dendrimer due to their magnetic, electronic and photo-optical properties, as well their reactivity as catalysts.[3] Although dendritic porphyrins surrounded by an organometallic sphere are fascinating, only one example of such dendritic molecules has been prepared so far.[4] In the course of our study on organometallic dendrimers,[5] we developed an efficient route to platinum–acetylide dendrimers by a convergent method.[6,7] We present here the synthesis and properties of novel organometallic dendrimers composed of platinum–acetylide units and a porphyrin core.(Scheme 1)

The key intermediate in our convergent approach to the target dendrimers is a tetranuclear platinum complex (**ZnPC**) bridged by Zn(II) tetra(4-ethynylphenyl)porphyrin, which is the core of the present convergent approach. The reaction of 4-(trimethylsilylethynyl)benzaldehyde and pyrrole in refluxing propionic acid for 3 h gave tetra[4-(trimethylsilylethynyl)phenyl]porphyrin (**1**) in 33% yield. After metallation with $Zn(OAc)_2$, trimethylsilyl groups were removed by treatment with tetrabutylammonium fluoride (TBAF) to give Zn(II) tetra(4-ethynylphenyl)porphyrin (**3**). Platinum moieties were introduced by the reaction of **3** with 6 equiv. of $Pt(PEt_3)_2Cl_2$ in the presence of catalytic amounts of CuCl in a mixture of piperidine/dioxane (1/3 v/v) under reflux for 1 week to give **ZnPC** in 29% yield. Simple $^1$H-, $^{13}$C- and $^{31}$P NMR spectra of **ZnPC** are consistent with a highly symmetric structure.

A series of organometallic dendritic porphyrins was synthesized by the reaction of **ZnPC** with platinum–acetylide dendrons up to the third generation (Scheme 2). Platinum acetylide dendrons **GD1–GD3** were prepared as reported previously.[6] Reaction of **ZnPC** with 4 equiv. of first-generation dendron **GD1** catalyzed by CuCl in a mixture of THF/diethylamine (1/3 v/v) at room temperature produced the first-generation dendrimer **G1** along with small amounts of by-products, which were estimated to be defective dendrimers with less than three **GD1** based on $^{31}$P NMR and gel permeation chromatography (GPC) analyses. Therefore, **G1** was isolated in



**Scheme 1** *Reagents and conditions*: i, propionic acid, reflux, 3 h, 33%; ii, $Zn(OAc)_2$, $CHCl_3$, reflux, overnight, 97%; iii, TBAF, −78 °C to r.t., 1.5 h, 90%; iv, $Pt(PEt_3)_2Cl_2$ (6 eq.), CuCl cat., piperidine/dioxane (1 : 3 v/v), reflux, 1 week, 29%.



**Scheme 2** *Reagents and conditions*: i, CuCl cat., $Et_3N$/THF (1 : 3 v/v), r.t., 73% (**G1**); 67% (**G2**); 41% (**G3**).

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73% yield by preparative GPC followed by reprecipitation of a $CH_2Cl_2$ solution in hexane. Second- and third-generation dendrimers **G2** and **G3** were prepared by similar reactions of **4** with second- and third-generation dendrons **GD2** and **GD3** in yields of 67 and 41%, respectively. Although mass spectrometry is a powerful tool for the characterization of dendrimers, the molecular ions of platinum–acetylide dendrimers with more than four platinum moieties have never been observed, even in MALDI-TOF and ESI mass spectrometry. However, the platinum–acetylide dendrimers prepared in this study were fully characterized by NMR and GPC analyses in the same manner as was used for other platinum–acetylide dendrimers.[5–7] Since dendrimers **G1–G3** were synthesized by reaction between large molecules, the presence of products with a different composition is easily detected by GPC analysis. Narrow GPC profiles of **G1–G3** showed the absence of impurities with different molecular sizes. In the $^{31}P$ NMR spectra, no signals assignable to the $C{\equiv}CPt(PEt_3)_2Cl$ moieties were detected. The $^1H$ and $^{13}C$ NMR spectra are also consistent with the proposed structure of **G1–G3**.

The electronic absorption spectra of dendrimers **G1–G3** in THF are shown in Fig. 1 along with those of **3** and **ZnPC**. The higher energy bands ($\lambda$ = 300 nm) are due to $\pi$–$\pi^*$ transitions of the triethynylbenzene-bridges, and the absorption at about $\lambda_{max}$ = 341 nm is attributable to the MLCT band of platinum–acetylides.[8] The molar absorptivity ($\varepsilon$) of these absorptions remarkably increased with an increase in the generation of dendrimers. This phenomenon is due to the increase in platinum moieties in the molecules, since the spectra in this region based on platinum moieties resemble each other very closely. Dendritic porphyrins **G1–G3** and the core **ZnPC** showed a Soret band at about $\lambda_{max}$ = 435 nm, whereas that of **3** was observed at $\lambda_{max}$ = 426 nm. The $\varepsilon$ value of the Soret band decreased with an increase in the generation. Although the reason for this phenomenon is still unclear, it may be of interest since the Soret band is scarcely influenced by dendrons in dendritic porphyrins.[2,4] Two absorptions at about 560 and 600 nm characteristic of the Q band of zinc porphyrins were observed in the spectra of all of the samples.

When **G1** was excited at the MLCT band of platinum–acetylide units (341 nm), fluorescence peaks were observed at 381 and 617 nm (Fig. 2). Upon excitation at the Soret band (435 nm), **G1** emitted fluorescence at 617 nm, which is characteristic of the zinc porphyrin nucleus. Platinum–acetylide dendron **GD1** showed fluorescence at 384 nm upon excitation at 341 nm. Thus, the fluorescence spectrum of **G1** indicates energy transfer from platinum–acetylide dendrons to the porphyrin core. A mixture of **ZnPC** and **GD1** in a ratio of 1 : 4 did not show fluorescence from the porphyrin but rather from platinum–acetylide units by excitation at 343 nm, suggesting that energy transfer takes place intramolecularly. The intramolecular energy transfer was confirmed by the fluorescence spectra of **G2** and **G3**. Fluorescence from the porphyrin core at 617 nm appreciably decreased as the generation of dendrimers increased, while another fluorescence peak at 648 nm relatively increased. This is also a characteristic phenomenon of platinum–acetylide dendrimers, and studies on the reason of this phenomenon are in progress.

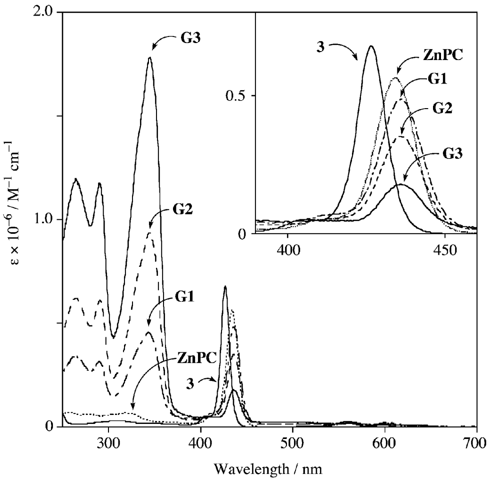

**Fig. 1** Electronic absorption spectra of **3**, **ZnPC**, **G1**, **G2** and **G3** in THF.

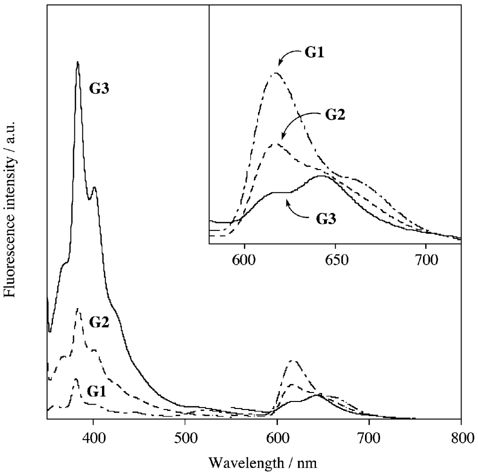

**Fig. 2** Fluorescence spectra of **G1** (excited at 341 nm), **G2** and **G3** (excited at 344 nm) in THF. The spectra were nomalized to the concentration of 8.9 × $10^{-8}$ M. The spectra were measured through a cut-off filter ($\lambda \leq$ 220 nm) in the region of $\lambda \leq$ 550 nm, and that ($\lambda \leq$ 450 nm) in the region of $\lambda \geq$ 550 nm.

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