

Dipyrrin–Porphyrin Hybrids: Potential π -Conjugated Platform to Fabricate Coordination Oligomers

Hiromitsu Maeda* and Miki Ito

Department of Bioscience and Biotechnology, Faculty of Science and Engineering,
Ritsumeikan University, Kusatsu 525-8577

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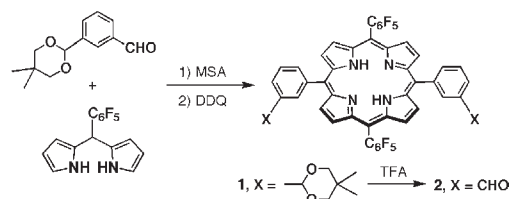
Bis-dipyrrin-appended porphyrin derivatives, potential building blocks for supramolecular coordination architectures, were synthesized and exhibited complexation at the two dipyrrin sites with BF_2 and $\text{Rh}(\text{CO})_2$.

Metal coordination enables organic ligands to form potential oligomers and nanospace applicable for materials science.¹ Among a variety of coordination assemblies, porphyrin platform is used as a functional π -conjugated system for versatile purposes.² Porphyrin squares and prism fabricated by *meso*-pyridyl units were achieved by coordination to metal cations like Pd^{II} .³ Contrasted with *neutral* ligands such as 2,2'-bipyridines, dipyrrin (dipyrromethene), a dye consisting of two pyrroles bridged by conjugated linkage, is an essential bidentate *monoanionic* ligand for metal ion in natural and artificial systems (Figure 1).⁴ Dipyrrin forms metal complexes in flexible coordination modes according to metal cations, due to the acyclic structure. Therefore, dipyrrin, a promising planar scaffolding for supramolecular architectures, would give discrete neutral coordination oligomers. Recently, Lindsey et al. reported dipyrrin metal complexes as bridging units for energy transfer systems consisting of porphyrins.⁵ Here synthesis of dipyrrin-substituted porphyrins as building units for promising coordination space is reported. Dipyrrin units chelate metal cations and analogs such as difluoroboron (BF_2) and $\text{Rh}(\text{CO})_2$ moieties.



Figure 1. Frameworks of 2,2'-bipyridine (left) and dipyrrin (right) as coordination ligands.

5,15-Di(*m*-formylphenyl)porphyrin (**2**), a key precursor for synthesis of dipyrrin-substituted porphyrin, was obtained in 13% yield by acid-catalyzed [2 + 2] condensation of protected aldehyde⁶ and *meso*-pentafluorophenyl (C_6F_5) dipyrromethane using methanesulfonic acid (MSA) and oxidation by DDQ, followed by deprotection of porphyrin **1** using TFA (Scheme 1). In order to avoid fragmentation and scrambling by acid catalyst under cyclization, electron-withdrawing substituent was used in the dipyrromethane unit. *m*-Formyl-substitution, which could be more useful and suitable for the construction of coordination space than *p*- and *o*-formyl substitutions, was derived from the corresponding protected aldehyde. The structures of porphyrins **1** and **2** were confirmed by ^1H NMR and FAB-MS. Although conformation of the two formyl moieties of **2** in solution was not determined, the moieties in the solid state orient in the *anti* conformation, not the *syn*, which was elucidated by X-ray single crystal structure analysis.⁷ The π -plane of **2** stacks at edge-to-edge of each other with the plane distance of 3.897 Å (Figure 2).



Scheme 1. Synthesis of *m*-formylphenyl-substituted porphyrin **2**.

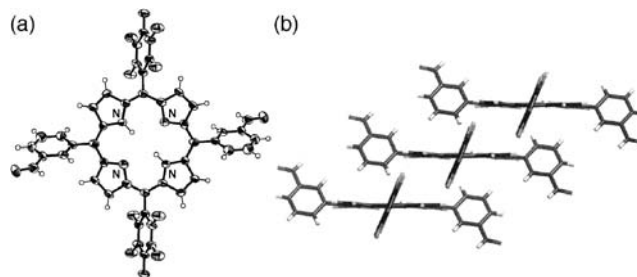
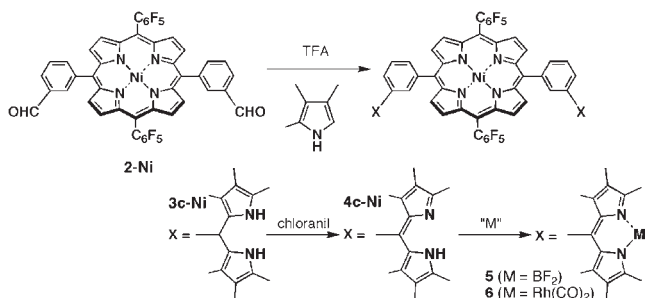


Figure 2. X-ray single crystal structure of porphyrin **2**, (a) top view (ORTEP drawing) and (b) π -stacking diagram from the side view. Thermal ellipsoids are scaled to the 50% probability level.

Under acidic conditions using TFA,⁸ formyl derivative (**2**) was transformed into dipyrromethane-appended porphyrins (**3a** and **3b**) as major products using α -free- and α -methylpyrrole,⁹ respectively (see the Supplemental Information). The derivative with unsubstituted pyrroles readily suffers the polymerization, possibly due to the remaining “free” pyrrolyl α - and β -positions. Without purification, **3a** and **3b** were converted to bisdipyrrin-porphyrin hybrids (**4a** and **4b**) by *p*-chloranil oxidation. The formation of **4b** was suggested by ^1H NMR, but the formation of other derivatives **3a**, **3b**, and **4a**, rather unstable compounds, was just inferred by MALDI-TOF-MS. For the efficient synthesis of stable dipyrromethane and dipyrrin derivatives, were examined two strategies: (i) metal coordination in the core to avoid trapping protons in the cavity and (ii) complete substitution of dipyrrin units to increase the stability. First, complexation of diamagnetic Ni^{II} , resistible to demetallation, was performed by the treatment with $\text{Ni}(\text{acac})_2$ hydrate in refluxing toluene for 8 h to afford **2-Ni** in 87% yield. Second, to obtain the derivative substituted totally except for N-positions, condensation of **2-Ni** with 2,3,4-trimethylpyrrole¹⁰ resulted in the rather stable dipyrromethane **3c-Ni** (Scheme 2). In ^1H NMR spectrum in CDCl_3 , the signal of formyl proton of **2-Ni** at 10.28 ppm completely disappeared, and, instead, that ascribable to *meso*-CH proton of **3c-Ni** appeared at 5.66 ppm. Dipyrromethane **3c-Ni**, gradually decomposed on silica gel chromatography, was stabi-



Scheme 2. Transformation of formyl groups into dipyrromethane and dipyrryn units, and coordination at the dipyrryn sites of **4c-Ni**.

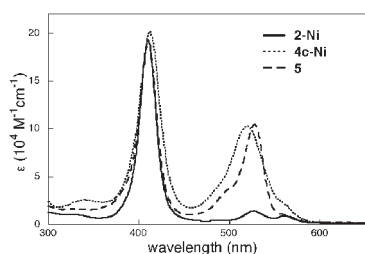


Figure 3. UV-vis absorption spectra of **2-Ni** (solid line), **4c-Ni** (dotted line), and BF_2 complex **5** (broken line) in CHCl_3 .

lized by dehydrogenation using *p*-chloranil to give a rather polar dipyrryn **4c-Ni** in 84% yield from **2-Ni**. The resonance of $\text{sp}^3\text{-CH}$ proton between dipyrromethane pyrroles in $^1\text{H NMR}$ (CDCl_3) was vanished and that of dipyrryn NH proton was observed at the downfield at 12.22 ppm, due to intramolecular hydrogen bonding. UV-vis absorption spectrum of **4c-Ni** in CHCl_3 shows a Soret-band at 412.0 nm and a large absorption at 519.5 nm, possibly due to the electronic interaction with dipyrryn units (Figure 3).

4c-Ni is the first example of phenylene-bridged bis-dipyrryn-appended porphyrin. So far, various porphyrin derivatives with a dipyrryn moiety have been reported by using long chain like phenylethynyl spacer,¹¹ and only two reports on the phenylene-bridged mono-dipyrryn derivatives have been reported.^{5,12} As mentioned above, the phenylene-bridged dipyrryn-porphyrin hybrids are less stable and, in order to avoid the decomposition, need the *protection* of pyrrole moieties in two dipyrryn units seen in **4c-Ni**.

Up to date, BF_2 complexes of dipyrryns have been reported as energy donor units seen in the synthetic photosynthetic models.¹³ In order to examine the chelation behavior, metal coordination chemistry of **4c-Ni** at the dipyrryn units were examined. When **4c-Ni** was treated with excess $\text{BF}_3 \cdot \text{OEt}_2$ (ca. 30 equiv.) in CHCl_3 with 5% Et_3N at reflux temperature, bis- BF_2 complex **5** was obtained in 52% yield (Scheme 2). $^1\text{H NMR}$ signals of dipyrryn NH in CDCl_3 disappeared. UV-vis absorption spectrum in CHCl_3 is found to show the Soret band at 411.5 nm and a large absorption at 527.5 nm, which is red-shifted at 8 nm as compared to that of metal-free **4c-Ni** (Figure 3), and fluorescence quenching infers the possibility of energy transfer from dipyrryn to porphyrin. Moreover, $[\text{RhCl}(\text{CO})_2]_2$ (1 equiv.) and NaOAc (10 equiv.) in refluxing CH_2Cl_2 gave bis- Rh^{I} complex **6** in 38% yield.¹⁴ MALDI-TOF-MS exhibits the peak of the species missing the carbonyl units. In contrast to **5** and **6**, treatment with

$\text{Zn}(\text{OAc})_2$ is found to show the MALDI-TOF-MS suggesting the formation of dimer ($m/z = 2738$, corresponding to $2 \times \text{4c-Ni} + 2 \times \text{Zn}^{2+}$; see the Supplemental Information) as a major product and trimetric and tetrametric structures as traces, which infers that the dipyrryn moieties behave as potential scaffolds for supramolecular coordination polymers. Further investigations to fabricate nanostructures based on the dipyrryn metal complexes are now in progress.

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- Crystal data for **2** (from $\text{CH}_2\text{Cl}_2/\text{CH}_2\text{ClCH}_2\text{Cl}/\text{hexane}$): $\text{C}_{46}\text{H}_{20}\text{N}_4\text{F}_{20}\text{O}_2$, $M_w = 850.67$, monoclinic, $a = 6.692(4)$, $b = 11.255(7)$, $c = 24.50(2)$ Å, $\beta = 91.02(2)^\circ$, $V = 1845(2)$ Å³, $T = 123(2)$ K, space group $P2_1/c$ (No. 14), $Z = 4$, $D_c = 1.531$ g/cm³, $\mu(\text{Mo K}\alpha) = 0.1299$ mm⁻¹, 17530 reflections measured, 17040 unique ($R_{\text{int}} = 0.131$), $R = 0.090$, $R_w = 0.126$, $\text{GOF} = 1.136$ ($I > 3\sigma(I)$). Crystallographic data for **2** has been deposited with Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-274878. Copy of the data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, 12, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).
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