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## Introduction

In the past decade, porphyrins bearing a metal fragment directly at their peripheries have been actively explored in light of their characteristic optical and electronic properties and catalytic reactivity.<sup>1–4</sup> As an extension of these species, directly metal-bridged porphyrin dimers have also been developed, which display intriguing structural features and characteristic electronic interactions between the porphyrin units through the metal bridge.<sup>5</sup> Representative examples are shown in Chart 1. The doubly 2,6-pyridylene-bridged Ni(II)-porphyrin dimer underwent smooth palladation to give dimer A, in which the two porphyrin units have *meso*-to-*meso* *trans*-coordination to the palladium metal, and the incorporated palladium metal increases both the electronic interaction and molecular curvature.<sup>4e</sup> *meso*-Diphenylphosphanyl Zn(II)-porphyrin facilitated palladation and platination at the adjacent  $\beta$ -position to produce dimer B, which shows  $\beta$ -to- $\beta$  *trans*-coordination of the two porphyrins.<sup>2b,c</sup> Platinum-bridged dimer C formed from complexation of  $\beta$ -(pyrid-2-yl)-substituted Ni(II)-porphyrin with  $(Bu_4N)_2PtCl_6$  possesses *meso*-to-*meso* *cis*-coordination and shows intriguing conformational slippage upon two-electron reduction at the bridging platinum metal.<sup>4d</sup>

Recently, we reported the synthesis of cyclic 2,12-porphyrinylene nanorings by following Yamago's synthetic strategy.<sup>6,7</sup> 2,12-Diborylated Ni(II)-porphyrins were transformed to platinum-bridged oligomeric porphyrin rings, which reacted with triphenylphosphine to induce reductive elimination.<sup>6</sup> A key factor in the synthesis of such porphyrin nanorings is a

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† Electronic supplementary information (ESI) available: Experimental and computational details, as well as X-ray crystallographic data for 2H, 2Zn, 3Zn, 5Ni and 6Ni are available. CCDC 1406329–1406332 and 1406343. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c5sc02553b

## Singly and doubly $\beta$ -to- $\beta$ platinum-bridged porphyrin dimers and their reductive eliminations†

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2-Borylated porphyrins reacted with Pt(cod)Cl<sub>2</sub> to give  $\beta$ -to- $\beta$  platinum-bridged porphyrin dimers, which were converted to  $\beta$ -to- $\beta$  directly linked porphyrin dimers through triphenylphosphine-mediated reductive elimination. Similar reactions of 2,18-diborylated Ni(II)-porphyrin and Zn(II)-porphyrin gave the corresponding doubly  $\beta$ -to- $\beta$  platinum-bridged porphyrin dimers. Treatment of the doubly  $\beta$ -to- $\beta$  platinum-bridged Ni(II)-porphyrin dimer with triphenylphosphine caused a single reductive elimination to produce a Ni(II)-porphyrin dimer possessing a  $\beta$ -to- $\beta$  platinum bridge and a  $\beta$ -to- $\beta$  direct C–C bond.

preferred *cis*-geometry of the platinum-bridged nanoring intermediates, which causes molecular curvature, as a favorable structural feature for nanoring formation.<sup>7,8</sup> In this paper, we examined the reactions of 2-borylporphyrins and 2,18-diborylporphyrins with Pt(cod)Cl<sub>2</sub> to get information on the structural and electronic details of platinum-bridged porphyrin dimers. Actually, these reactions afforded singly and doubly  $\beta$ -to- $\beta$  platinum-bridged porphyrin dimers, both of which possess *cis*-coordination geometries (dimer D) and thus undergo reductive elimination upon treatment with triphenylphosphine.

## Results and discussion

2-Borylated Ni(II) porphyrin **1Ni** was treated with 0.5 equiv. Pt(cod)Cl<sub>2</sub> in the presence of cesium fluoride and 1,5-cyclooctadiene (cod) in refluxing THF under an argon atmosphere to give  $\beta$ -to- $\beta$  platinum-bridged porphyrin dimer **2Ni** in 84% yield as a stable solid (Scheme 1).<sup>9</sup> Matrix-assisted laser desorption/

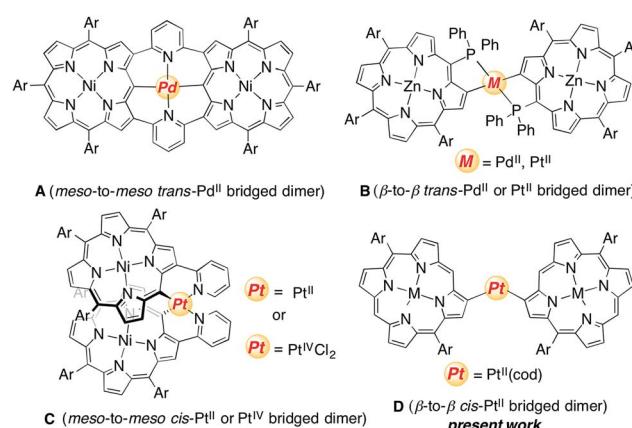


Chart 1 Examples of directly metal-bridged porphyrin dimers.



ionization time-of-flight mass spectrometry (MALDI-TOF-MS) detected the parent ion peak at  $m/z = 1782.73$  (calcd for  $C_{104}H_{114}N_8^{58}Ni_2^{192}Pt = 1782.75 [M]^{+}$ ). The  $^1H$  NMR spectrum of **2Ni** showed singlets due to the *meso*-protons at 10.66 ppm ( $H^a$ ) and 9.67 ppm ( $H^b$ ) and a singlet due to the  $\beta$ -proton ( $H^c$ ) at 9.12 ppm. Under the same reaction conditions, 2-borylporphyrins **1H** and **1Zn** were dimerised to give **2H** and **2Zn** in 60 and 82% yields, respectively. In these reactions, 1,5-cyclooctadiene ligand was found to be crucial, since the reactions with platinum salts with other ligands such as 1,3-bis(diphenylphosphino)propane, ethylenediamine, 2,2'-bipyridine and 2,5-norbornadiene did not give platinum-bridged dimers. The structures of **2H** and **2Zn** have been unambiguously confirmed by X-ray diffraction analysis (Fig. 1 and ESI†). Both dimers **2H** and **2Zn** display *cis*-arrangements of the two porphyrins at the platinum bridge with bite angles ( $\angle C\beta\text{-Pt-C}\beta$ ) of  $88.18^\circ$  and  $86.33^\circ$ , respectively. In addition, the two porphyrins in **2H** and **2Zn** take offset arrangements, as seen in their top views. The  $C\beta\text{-Pt}$  bond lengths are 2.024 and 2.036 Å in **2H**, and 2.002 and 2.032 Å in **2Zn**, which are longer than the  $C_{\text{meso}}\text{-Pt}$  bonds in *meso*-to-*meso* *cis*-Pt(II) bridged Ni(II) porphyrin dimer C (1.933 Å).<sup>4c</sup> Treatment of **2Ni**, **2H** and **2Zn** with triphenylphosphine induced reductive elimination to yield directly  $\beta$ - $\beta$ -linked porphyrin dimers **3Ni**, **3H** and **3Zn** in 81, 76 and 78% yields, respectively. X-ray diffraction analysis of **3Zn** has revealed a  $\beta$ -to- $\beta$  direct C-C bond with a bond distance of 1.462 Å and a dihedral angle of the two porphyrins of  $57.51^\circ$ . The structures of **3Ni**, **3H** and **3Zn** are fully consistent with their spectroscopic data (ESI†).<sup>10</sup> It is worthy to mention that *meso*-platinum-bridged porphyrin dimers were not obtained from *meso*-borylporphyrins under similar conditions, probably due to serious steric hindrance at the *meso*-position.

In the next step, we examined the reaction of 2,18-diborylated Ni(II)-porphyrin **4Ni** with an equimolar amount of  $\text{Pt}(\text{cod})\text{Cl}_2$  in 1,4-dioxane under similar conditions, which afforded doubly  $\beta$ -to- $\beta$  platinum-bridged porphyrin dimer **5Ni** as a stable compound in 84% yield (Scheme 2). MALDI-TOF-MS showed the mass ion peak of **5Ni** at  $m/z = 2356.95$  (calcd. for  $C_{132}H_{152}N_8^{58}Ni_2^{192}Pt_2 = 2357.02 [M\text{-cod}]^{+}$ ). The  $^1H$  NMR

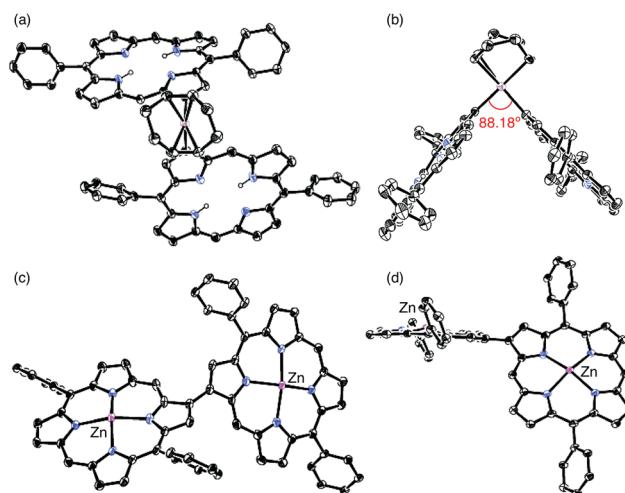
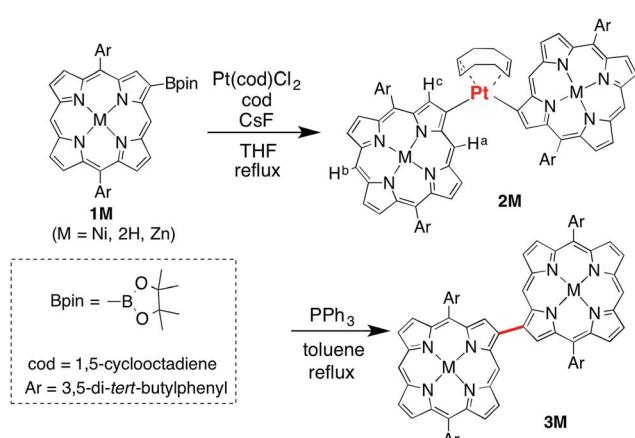


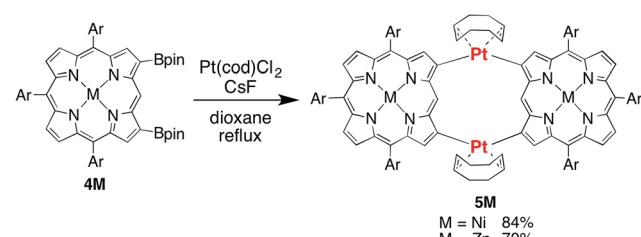
Fig. 1 X-ray crystal structures of **2H** and **3Zn**. *tert*-Butyl groups, solvent molecules including pyridines coordinated to Zn ions, and hydrogen atoms (except for inner NHs) are omitted for clarity. The thermal ellipsoids are scaled to 30% probability. (a) Top view of **2H**. (b) Side view of **2H**. (c) Top view of **3Zn**. (d) Side view of **3Zn**.

spectrum of **5Ni** exhibited a singlet at 11.86 ppm due to the *meso*-protons and a singlet at 8.76 ppm due to the  $\beta$ -protons adjacent to the platinum linkage. The doubly bridged structure of **5Ni** has been confirmed by X-ray analysis, in which the two porphyrins take *cis*-coordination geometries with  $C\beta\text{-Pt}$  bond lengths of 2.020, 2.044, 2.021 and 2.033 Å (Fig. 2). Therefore, the two porphyrins are held in an oblique arrangement with bite angles of  $88.41^\circ$  and  $89.89^\circ$ . In addition, the two Ni(II) porphyrins take on saddle confirmations with mean-plane deviations of 0.306 Å. This is the first example of doubly and directly metal-bridged porphyrin dimer. The reaction of **4Zn** with  $\text{Pt}(\text{cod})\text{Cl}_2$  under the same conditions gave **5Zn** in 70% yield. This complex was found to decompose slowly under ambient conditions but could be stored without serious deterioration under an inert atmosphere at low temperature. In contrast, the reactions of **4H** with  $\text{Pt}(\text{cod})\text{Cl}_2$  gave complicated mixtures under all conditions we tested.

Finally, the reductive elimination of **5Ni** was attempted by the reaction with triphenylphosphine in refluxing toluene, which gave rise to a single platinum elimination as well as a ligand replacement of 1,5-cyclooctadiene with two triphenylphosphines to provide dimer **6Ni** in 78% yield (Scheme 3). MALDI-TOF-MS showed the parent ion peak of **6Ni** at  $m/z =$



Scheme 1 Synthesis of **2M** and **3M**.



Scheme 2 Synthesis of doubly platinum-bridged porphyrin dimer **5M**.



2579.21 (calcd for  $C_{160}H_{170}N_8^{58}Ni_2P_2^{192}Pt = 2579.14 [M]^{+}$ ). The  $^1H$  NMR spectrum of **6Ni** exhibited a singlet at 11.79 ppm due to the *meso*-protons and singlets at 9.00 and 8.01 ppm due to the  $\beta$ -protons adjacent to the platinum bridge and the direct C-C linkage. The structure of **6Ni** has been determined by X-ray analysis, and shows a  $\beta$ -to- $\beta$  direct C-C bond with a bond distance of 1.486 Å. Owing to the structural constraint imposed by this direct  $\beta$ -to- $\beta$  connection, the platinum bridge has now a *trans* coordination geometry with a large  $C_{\beta}$ -Pt- $C_{\beta}$  angle of 159.04° and slightly longer  $C_{\beta}$ -Pt bond lengths of 2.059 and 2.084 Å as compared with those of **5Ni**. The two porphyrins of **6Ni** show slightly larger mean-plane deviations of 0.322 and 0.329 Å. Further reductive elimination of **6Ni** was attempted under stronger reaction conditions but ended in failure. This failure may be ascribed to the *trans*-coordination of **6Ni** and severe steric hindrance in the expected doubly  $\beta$ -to- $\beta$  connected porphyrin dimer due to the closely located *meso*-hydrogen atoms. The reductive elimination of **5Zn** was attempted but resulted in the production of a complicated mixture. These results suggest that the central metal in the porphyrin pocket plays a vital role in these reactions.

Fig. 3 shows the UV-vis absorption spectra of **2Ni**, **3Ni**, **5Ni** and **6Ni** in  $CH_2Cl_2$ . As compared with the sharp Soret band ( $\lambda_{\text{max}} = 412$  nm) of 5,15-diaryl Ni(II)-porphyrin,<sup>11</sup> the Soret band of **2Ni** becomes considerably broadened with a substantial blue shift to 400 nm, reflecting the exciton coupling and the influence of the platinum-bridge. The Soret band of **3Ni** is observed as a much broader band at 408 nm as a consequence of the increased exciton coupling as well as the through-bond electronic interactions. The UV-vis

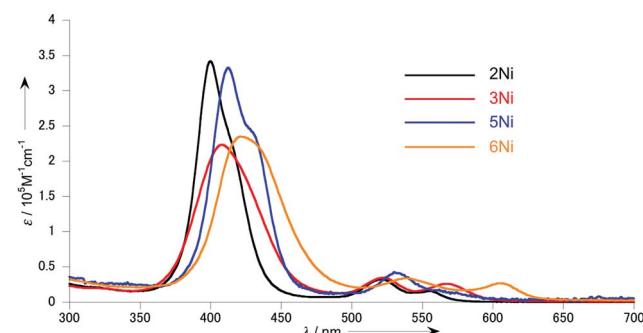


Fig. 3 UV-vis absorption spectra of **2Ni**, **3Ni**, **5Ni** and **6Ni** in  $CH_2Cl_2$ .

absorption spectrum of **5Ni** displays a split Soret band at 412 and 435 nm probably as a consequence of increased exciton coupling due to its fixed conformation by the double Pt bridges. Naturally, the absorption spectrum of **6Ni** exhibits a much broader Soret band at 421 nm and the most red-shifted Q-band at 604 nm.

The electrochemical properties of **2Ni**, **3Ni**, **5Ni** and **6Ni** have been investigated by cyclic voltammetry and differential pulse voltammetry in benzonitrile (Table 1). The reference Ni(II) porphyrin exhibits an oxidation potential at 0.53 V and a reduction potential at -1.76 V, which leads to the estimation of an electrochemical HOMO-LUMO gap ( $\Delta E_{\text{HL}}$ ) of 2.29 eV. The platinum-bridged dimers display negatively shifted oxidation and reduction potentials, at 0.36 and -1.87 V for **2Ni** and 0.28 and -1.97 V for **5Ni**. The DFT molecular orbital calculations have revealed that the presence of C-Pt bonds substantially raises the MO energy levels due to d- $\pi$  antibonding interactions.<sup>2c,4c</sup> In other words, the platinum bridge works as an electron-donating substituent to Ni(II) porphyrin. In contrast, the direct  $C_{\beta}$ - $C_{\beta}$  connection results in split frontier molecular orbitals due to interporphyrin  $\pi$ -orbital interaction. It is thus expected that the LUMO of **6Ni** is stabilised by the electronic interaction between the two Ni(II)-porphyrins, but the HOMO is destabilised due to the electronic interaction between the two Ni(II)-porphyrins as well as the antibonding interaction with the platinum bridge. Consequently, the  $\Delta E_{\text{HL}}$  value of **6Ni** is smaller than those of **2Ni** and **5Ni**, in line with their UV-vis absorption spectral data.

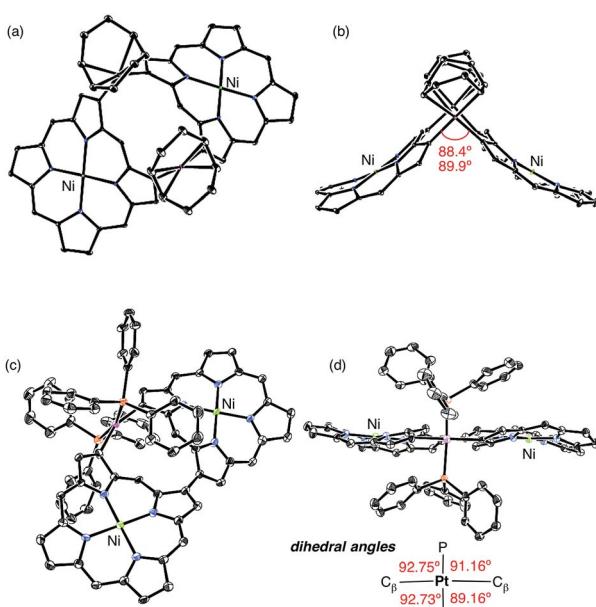


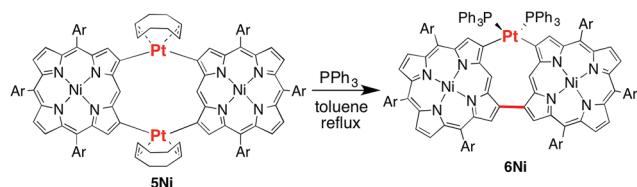
Fig. 2 X-ray crystal structures of **5Ni** and **6Ni**. 3,5-Di-*tert*-butylphenyl groups, solvent molecules, and hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled to 30% probability. (a) Perspective view of **5Ni**. (b) Side view of **5Ni**. (c) Perspective view of **6Ni**. (d) Side view of **6Ni**.

Table 1 Summary of the electrochemical potentials<sup>a</sup>

|                               | $E_{\text{ox2}}^{1/2}$ | $E_{\text{ox1}}^{1/2}$ | $E_{\text{red1}}^{1/2}$ | $E_{\text{red2}}^{1/2}$ | $\Delta E_{\text{HL}}^b$ |
|-------------------------------|------------------------|------------------------|-------------------------|-------------------------|--------------------------|
| Ni(II) porphyrin <sup>c</sup> |                        | 0.53 <sup>d</sup>      | -1.76                   |                         | 2.29                     |
| <b>2Ni</b>                    | 0.36 <sup>d</sup>      |                        | -1.87                   |                         | 2.23                     |
| <b>3Ni</b>                    | 0.62 <sup>d</sup>      | -1.69                  |                         | -1.80                   | 2.31                     |
| <b>5Ni</b>                    | 0.28 <sup>d</sup>      | -1.97                  |                         |                         | 2.25                     |
| <b>6Ni</b>                    | 0.50                   | 0.32                   | -1.87                   | -2.07 <sup>d</sup>      | 2.19                     |

<sup>a</sup> Conditions:  $nBu_4NPF_6$  electrolyte 0.1 M in PhCN, Ag/AgClO<sub>4</sub> reference electrode, Pt working electrode, Pt wire counter electrode, scan rate 0.05 V  $s^{-1}$ . All values were determined by differential pulse voltammetry (in V). <sup>b</sup>  $\Delta E_{\text{HL}} = \text{electrochemical HOMO-LUMO gap} (= E_{\text{ox1}}^{1/2} - E_{\text{red1}}^{1/2}$  [eV]). <sup>c</sup> 5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrinatonicke(II). <sup>d</sup> Irreversible peaks.





Scheme 3 Synthesis of 6Ni from 5Ni.

## Conclusions

2-Borylporphyrins reacted with Pt(cod)Cl<sub>2</sub> in the presence of cesium fluoride to produce  $\beta$ -to- $\beta$  platinum-bridged porphyrin dimers, which were converted to  $\beta$ - $\beta$  directly linked porphyrin dimers through triphenylphosphine-mediated reductive elimination. A similar reaction of 2,18-diborylated Ni(II)-porphyrin gave a doubly  $\beta$ -to- $\beta$  platinum-bridged Ni(II)-porphyrin dimer, which was converted to a Ni(II)-porphyrin dimer bearing a  $\beta$ -to- $\beta$  platinum-bridge and a  $\beta$ -to- $\beta$  direct C-C bond *via* similar reductive eliminations. These platinum-bridged porphyrin dimers display characteristic electronic and optical properties. Further extension of this strategy to longer porphyrin arrays is now in progress in our laboratory.

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