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Singly and doubly β -to- β platinum-bridged porphyrin dimers and their reductive eliminations†

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2-Borylated porphyrins reacted with $\text{Pt}(\text{cod})\text{Cl}_2$ to give β -to- β platinum-bridged porphyrin dimers, which were converted to β -to- β directly linked porphyrin dimers through triphenylphosphine-mediated reductive elimination. Similar reactions of 2,18-diborylated $\text{Ni}(\text{II})$ -porphyrin and $\text{Zn}(\text{II})$ -porphyrin gave the corresponding doubly β -to- β platinum-bridged porphyrin dimers. Treatment of the doubly β -to- β platinum-bridged $\text{Ni}(\text{II})$ -porphyrin dimer with triphenylphosphine caused a single reductive elimination to produce a $\text{Ni}(\text{II})$ -porphyrin dimer possessing a β -to- β platinum bridge and a β -to- β direct C–C bond.

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.^{1–4} 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.⁵ Representative examples are shown in Chart 1. The doubly 2,6-pyridylene-bridged $\text{Ni}(\text{II})$ -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.^{4e} *meso*-Diphenylphosphanyl $\text{Zn}(\text{II})$ -porphyrin facilitated palladation and platination at the adjacent β -position to produce dimer **B**, which shows β -to- β *trans*-coordination of the two porphyrins.^{2b,c} Platinum-bridged dimer **C** formed from complexation of β -(pyrid-2-yl)-substituted $\text{Ni}(\text{II})$ -porphyrin with $(\text{Bu}_4\text{N})_2\text{PtCl}_6$ possesses *meso*-to-*meso* *cis*-coordination and shows intriguing conformational slippage upon two-electron reduction at the bridging platinum metal.^{4d}

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

preferred *cis*-geometry of the platinum-bridged nanoring intermediates, which causes molecular curvature, as a favorable structural feature for nanoring formation.^{7,8} In this paper, we examined the reactions of 2-borylporphyrins and 2,18-diborylporphyrins with $\text{Pt}(\text{cod})\text{Cl}_2$ to get information on the structural and electronic details of platinum-bridged porphyrin dimers. Actually, these reactions afforded singly and doubly β -to- β 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 $\text{Ni}(\text{II})$ porphyrin **1Ni** was treated with 0.5 equiv. $\text{Pt}(\text{cod})\text{Cl}_2$ in the presence of cesium fluoride and 1,5-cyclo-octadiene (*cod*) in refluxing THF under an argon atmosphere to give β -to- β platinum-bridged porphyrin dimer **2Ni** in 84% yield as a stable solid (Scheme 1).⁹ Matrix-assisted laser desorption/ion-

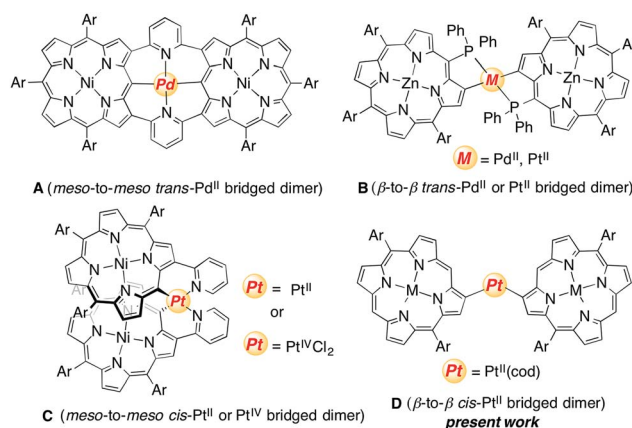


Chart 1 Examples of directly metal-bridged porphyrin dimers.

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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

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 β -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 ($\angle C\beta-Pt-C\beta$) of 88.18° and 86.33° , respectively. In addition, the two porphyrins in **2H** and **2Zn** take offset arrangements, as seen in their top views. The $C\beta-Pt$ 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 $C_{meso}-Pt$ bonds in *meso*-to-*meso* *cis*-Pt(II) bridged Ni(II) porphyrin dimer **C** (1.933 Å).^{4c} Treatment of **2Ni**, **2H** and **2Zn** with triphenylphosphine induced reductive elimination to yield directly β - β -linked porphyrin dimers **3Ni**, **3H** and **3Zn** in 81, 76 and 78% yields, respectively. X-ray diffraction analysis of **3Zn** has revealed a β -to- β direct C-C bond with a bond distance of 1.462 Å and a dihedral angle of the two porphyrins of 57.51° . The structures of **3Ni**, **3H** and **3Zn** are fully consistent with their spectroscopic data (ESI†).¹⁰ 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 Pt(cod)Cl₂ in 1,4-dioxane under similar conditions, which afforded doubly β -to- β 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 $C_{132}H_{152}N_8^{58}Ni_2^{192}Pt_2 = 2357.02 [M-cod]^+$). The 1H NMR

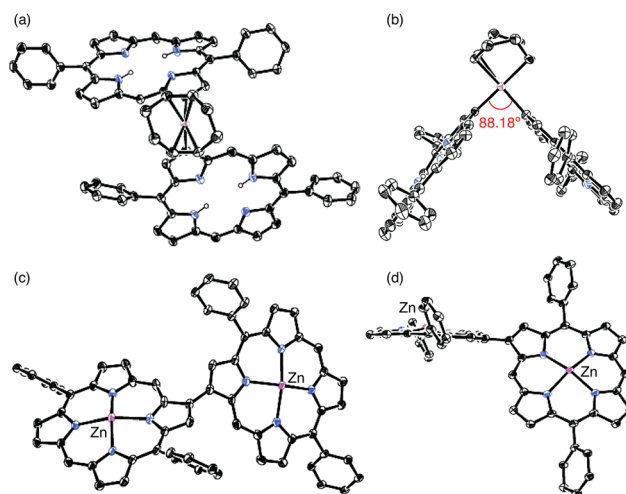
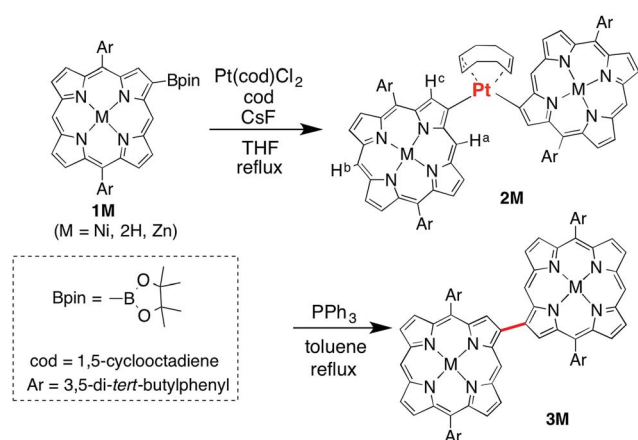


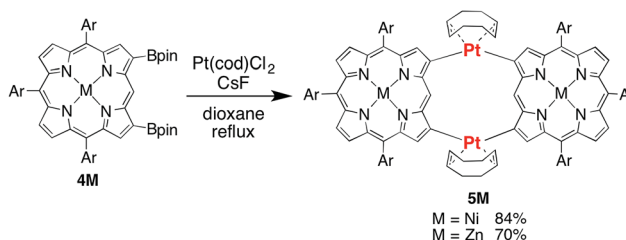
Fig. 1 X-ray crystal structures of **2H** and **3Zn**. *tert*-Butyl groups, solvent molecules including pyridines coordinated to Zn ions, and hydrogen atoms (except for inner NHs) are omitted for clarity. The thermal ellipsoids are scaled to 30% probability. (a) Top view of **2H**. (b) Side view of **2H**. (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 β -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 $C\beta-Pt$ 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° and 89.89° . In addition, the two Ni(II) porphyrins take on saddle conformations 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 Pt(cod)Cl₂ 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 Pt(cod)Cl₂ 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 β -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 β -to- β direct C–C bond with a bond distance of 1.486 Å. Owing to the structural constraint imposed by this direct β -to- β connection, the platinum bridge has now a *trans* coordination geometry with a large C_β –Pt– C_β angle of 159.04° and slightly longer C_β –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 β -to- β 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 ($\lambda_{max} = 412$ nm) of 5,15-diaryl Ni(II)-porphyrin,¹¹ 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

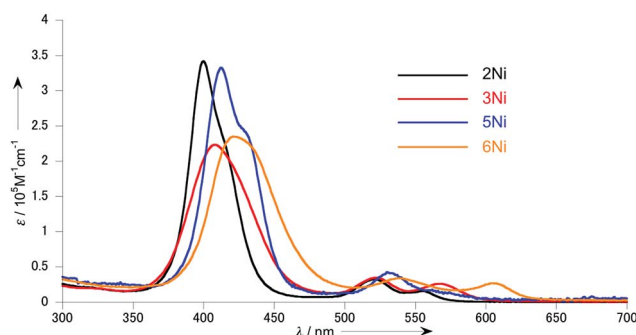


Fig. 3 UV/vis absorption spectra of **2Ni**, **3Ni**, **5Ni** and **6Ni** in CH_2Cl_2 .

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 (ΔE_{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– π antibonding interactions.^{2c,4c} In other words, the platinum bridge works as an electron-donating substituent to Ni(II) porphyrin. In contrast, the direct C_β – C_β connection results in split frontier molecular orbitals due to interporphyrin π -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 ΔE_{HL} value of **6Ni** is smaller than those of **2Ni** and **5Ni**, in line with their UV/vis absorption spectral data.

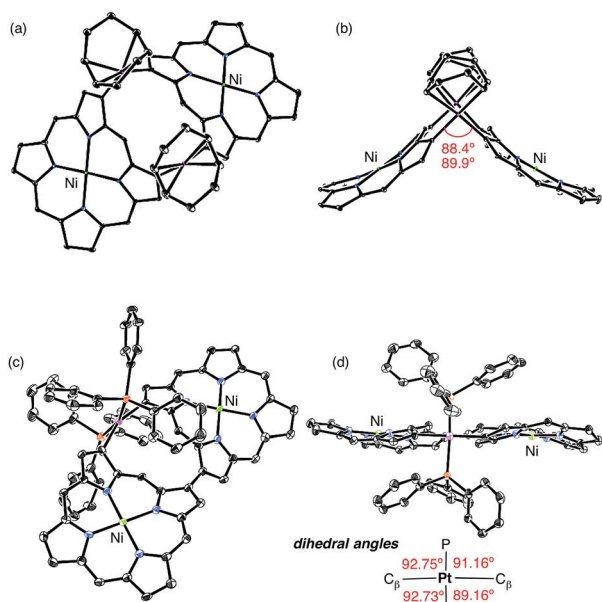


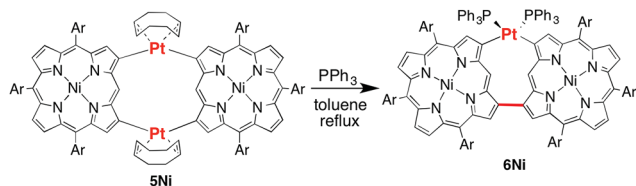
Fig. 2 X-ray crystal structures of **5Ni** and **6Ni**. 3,5-Di-*tert*-butylphenyl groups, solvent molecules, and hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled to 30% probability. (a) Perspective view of **5Ni**. (b) Side view of **5Ni**. (c) Perspective view of **6Ni**. (d)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

Table 1 Summary of the electrochemical potentials^a

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

^a Conditions; nBu_4NPF_6 electrolyte 0.1 M in PhCN, Ag/AgClO₄ 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). ^b ΔE_{HL} = electrochemical HOMO–LUMO gap ($= E_{ox1}^{1/2} - E_{red1}^{1/2}$ [eV]). ^c 5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrinatonicel(II). ^d Irreversible peaks.





Scheme 3 Synthesis of 6Ni from 5Ni.

Conclusions

2-Borylporphyrins reacted with Pt(cod)Cl₂ in the presence of cesium fluoride to produce β-to-β platinum-bridged porphyrin dimers, which were converted to β-β directly linked porphyrin dimers through triphenylphosphine-mediated reductive elimination. A similar reaction of 2,18-diborylated Ni(II)-porphyrin gave a doubly β-to-β platinum-bridged Ni(II)-porphyrin dimer, which was converted to a Ni(II)-porphyrin dimer bearing a β-to-β platinum-bridge and a β-to-β 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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