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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 Pt(cod)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 Ni(II)–porphyrin and Zn(II)–porphyrin gave the corresponding doubly β-to-β platinum-bridged porphyrin dimers. Treatment of the doubly β-to-β platinum-bridged Ni(II)–porphyrin dimer with triphenylphosphine caused a single reductive elimination to produce a Ni(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 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.[4e] *meso*-Diphenylphosphanyl Zn(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 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.[4d]

Recently, we reported the synthesis of cyclic 2,12-porphyrinylene nanorings by following Yamago's synthetic strategy.[6,7] 2,12-Diborylated Ni(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 Pt(cod)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 Ni(II) porphyrin **1Ni** was treated with 0.5 equiv. Pt(cod)Cl_2 in the presence of cesium fluoride and 1,5-cyclooctadiene (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/

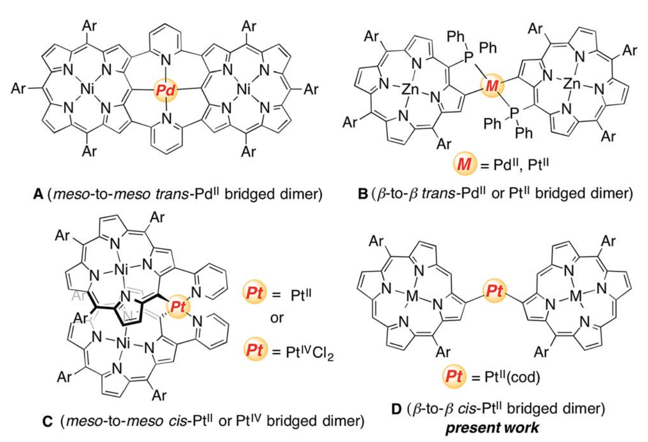

Chart 1 Examples of directly metal-bridged porphyrin dimers.

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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 ^{1}H 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 (∠Cβ–Pt–Cβ) 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_β–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)Cl_2 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 $C_{132}H_{152}N_8{}^{58}Ni_2{}^{192}Pt_2 = 2357.02$ $[M\text{-cod}]^+$). The ^{1}H NMR 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_β–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 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 Pt(cod)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 Pt(cod)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 $m/z =$

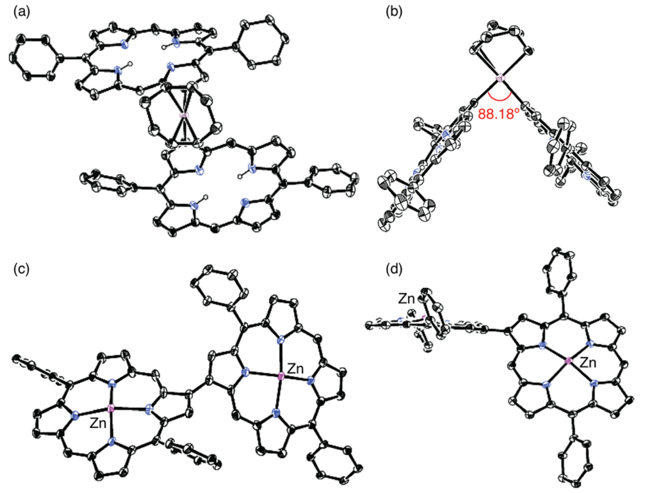
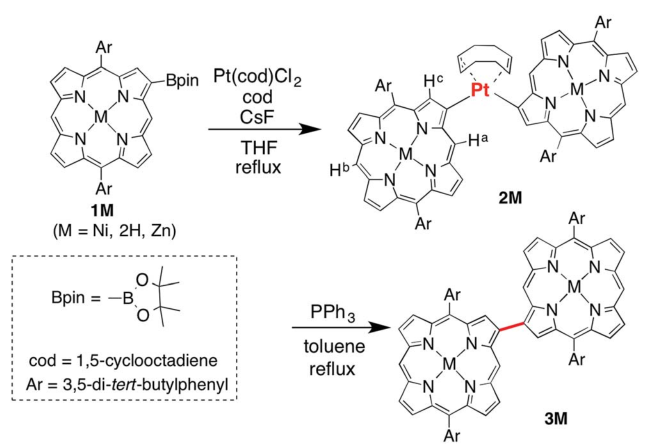
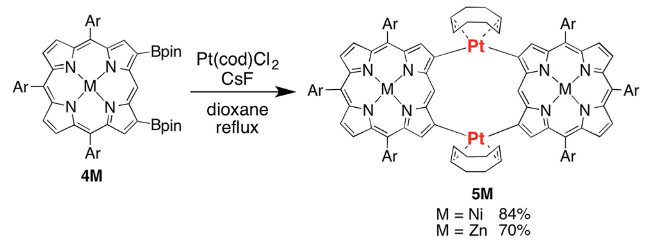


Fig. 1 X-ray crystal structures of **2H** and **3Zn**. *tert*-Butyl groups, solvent molecules including pyridines coordinated to Zn ions, and hydrogen atoms (except for inner NHs) are omitted for clarity. The thermal ellipsoids are scaled to 30% probability. (a) Top view of **2H**. (b) Side view of **2H**.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



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 ^{1}H 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 (λ_{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

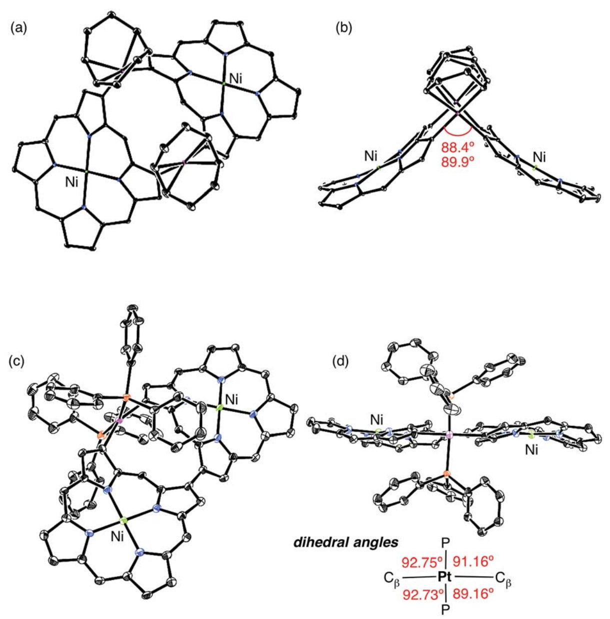


Fig. 2 X-ray crystal structures of 5Ni and 6Ni. 3,5-Di-*tert*-butylphenyl groups, solvent molecules, and hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled to 30% probability. (a) Perspective view of 5Ni. (b) Side view of 5Ni. (c) Perspective view of 6Ni. (d) Side view of 6Ni.

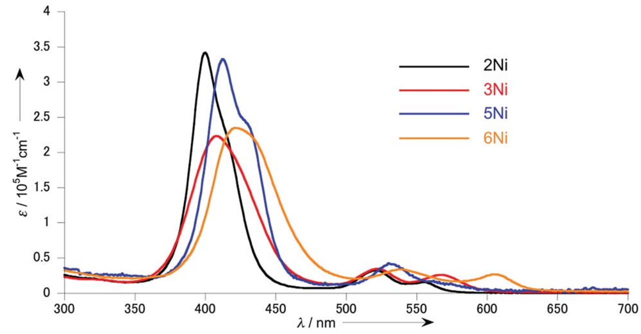


Fig. 3 UV/vis absorption spectra of **2Ni**, **3Ni**, **5Ni** and **6Ni** in CH_2Cl_2.

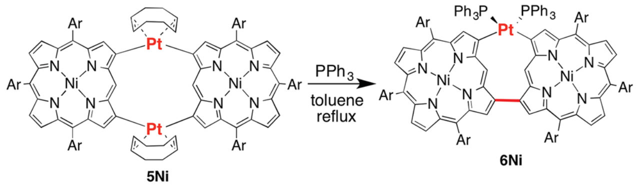
absorption spectrum of **5Ni** displays a split Soret band at 412 and 435 nm probably as a consequence of increased exciton coupling due to its fixed conformation by the double Pt bridges. Naturally, the absorption spectrum of **6Ni** exhibits a much broader Soret band at 421 nm and the most red-shifted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

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$_4$NPF$_6$ electrolyte 0.1 M in PhCN, Ag/AgClO$_4$ 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)porphyrinatonickel(II). [d] Irreversible peaks.



Scheme 3 Synthesis of **6Ni** from **5Ni**.

Conclusions

2-Borylporphyrins reacted with $Pt(cod)Cl_2$ 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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