Porphyrin dimers bridged by a platinum–diacetylide unit†

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A series of butadiyne- and platinum diacetylide-bridged conjugated porphyrin dimers have been prepared; electrochemical and UV-vis absorption measurements on these compounds show that the butadiyne-bridge confers stronger porphyrin–porphyrin conjugation than the platinum diacetylide-bridge.

The synthesis of porphyrin arrays continues to attract attention due to their peculiar properties. One of the most active subjects in porphyrin arrays over the last decade focuses on the design and construction of molecular-scale electronic devices.[1] To control the individual porphyrin units in well-defined shape and dimensions, a variety of functional groups have been used as the bridges, including saturated and π-conjugated units.[2,3] These multiporphyrin systems continue to provide valuable information regarding the mechanisms of electron and energy transfer processes. Numerous metal bis(acetylide) complexes have been synthesized via σ coordination of two acetylide ligands to a metal center.[4] Platinum–acetylide π-conjugated oligomers and polymers have received much attention because of their potential applications in electronic and optoelectronic devices.[5] Examples of platinum complexes with σ-bonded porphyrinylethynyl are rare.[6] Russo et al. reported the synthesis of this type of porphyrin oligomers in 1998.[6] However, some of these complexes were not well characterized.

It has been shown that the nature of the bridges significantly influences the extent of the interchromophore electronic and exciton coupling in multiporphyrins.[2,3] However, platinum diacetylide-bridged bisporphyrins have not been synthesized and the issue concerning the effects of the platinum bridge that enhance or disrupt the π-conjugation between the porphyrin units has not been addressed. Here we report the construction of porphyrin dimers in which the porphyrin subunits are connected through a platinum bis(σ-acetylide) moiety and their electrochemical properties are described. For comparison, the bisporphyrins linked by a butadiyne group, which has been shown to promote electronic coupling between the porphyrin rings, were also synthesized.

As shown in Scheme 1, platinum-bridged bisporphyrins Ni$_2$1 and Zn$_2$1 were prepared in good yields by the reaction of Ni4 and Zn4, respectively, with trans-[Pt(PEt$_3$)$_2$Cl$_2$] in
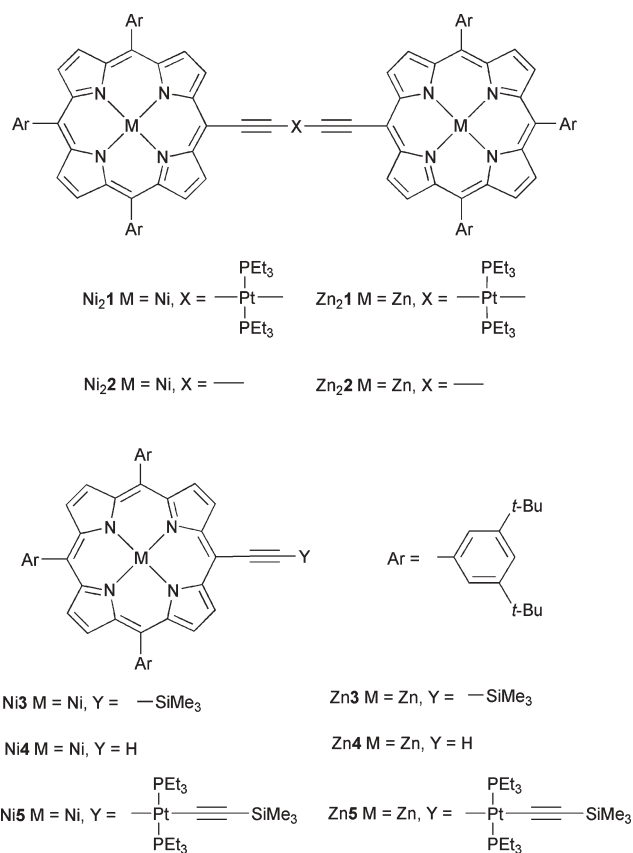
Scheme 1   Structures of porphyrins studied in this work.

diethylamine. It should be noted that the use of CuI catalyst leads to the formation of butadiyne-bridged porphyrins, thus resulting in a decrease in the yields of the desired platinum-bridged products. The reference bisporphyrin Zn$_2$2[7] were synthesized by the coupling reaction of Zn4 catalyzed by CuI in CH$_2$Cl$_2$ under air.[8] Demetallation of Zn$_2$2 with aqueous HCl solution gave the corresponding free base, which was then treated with Ni(OAc)$_2$ in refluxing DMF to give the dinickel porphyrin Ni$_2$2. Reference compounds Ni5 and Zn5 were synthesized by the reaction of Ni4 and Zn4, respectively, with trans-[Pt(PEt$_3$)$_2$Cl$_2$], followed by treatment with trimethylsilylacetylene.

The absorption spectrum of Ni$_2$1 shows peak-broadening and red shift of the Soret band and slight red shift of Q(0,0) band with respect to those of the reference compound Ni5 (Table 1). The full width at half maximum (FWHM) is 1421 cm^{-1} for Ni$_2$1, which is about 30% larger than that for Ni5 (FWHM = 1026 cm^{-1}). These spectral features suggest electronic

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Table 1 Redox and absorption data in CH_2Cl_2

Redox data[a]		Absorption (cm^{-1})		
$E_{1/2}$(ox)	$E_{1/2}$(red)	Neutral form	Monocation[c]	Dication[c]
Ni$_2$**1** +0.70, +0.83, +1.19	−1.37[b]	22272, 18116, 16807	22883, 18382, 17123, 15385, 11173, 3964	23148, 21645, 18904, 15385, 10471
Zn$_2$**1** +0.50, +0.56, +1.01	−1.47	22523, 17422, 16234	22676, 18939, 17637, 16340, 15129, 1058	23041, 21739, 18939, 15129, 10417
Ni$_2$**2** +0.93, +1.10, +1.30	−1.14[b]	22321, 21186, 18215, 15773	24096, 19608, 12034, 3957	24096, 13793, 12034
Zn$_2$**2** +0.69, +0.78, +1.24	−1.22	22222, 20790, 17699, 15873, 14749	23640, 21551, 15873, 14749, 11123, 4026	23981, 21786, 10363
Ni**3** +0.97, +1.21	−1.26	23419, 18484, 17422		
Zn**3** +0.78, +1.16	−1.31	23202, 17794, 16529		
Ni**5** +0.70, +1.19	−1.44[b]	22624, 18116, 17007		
Zn**5** +0.48, +0.95	−1.53[b]	22421, 17361, 16181		

[a] The electrochemical reactions were carried out in CH_2Cl_2 containing 0.1 M TBAPF$_6$ at a scan rate of 100 mV s^{-1}. Potentials (V) are reported *vs.* Ag/AgCl and referenced to the Fc/Fc$^+$ couple which occurs at $E_{1/2}$ = +0.43 V *vs.* Ag/AgCl. [b] Irreversible reactions. [c] The mono- and dications were generated *in situ* by reacting the neutral molecules with 1 and 2 eq. [(p-BrC$_6$H$_4$)$_3$N][SbCl$_6$], respectively.

interactions between the porphyrin units *via* the bridge. It should be pointed out that the red shift of the Q band on comparing Ni$_2$**1** with Ni**5** of 200 cm^{-1} is very much less than the red shift of the Q band on comparing Ni$_2$**2** with Ni**3** of 1649 cm^{-1}, suggesting that the butadiyne-bridge confers stronger porphyrin–porphyrin conjugation than the platinum diacetylide-bridge. In contrast, the absorption spectrum of Zn$_2$**1** show slight blue shift of the Soret and Q bands as compared to Zn**5**, and the FWHM of the Soret band is 593 cm^{-1} for both Zn$_2$**1** and Zn**5**. This indicates that the platinum bridge disrupts the electronic interaction between the two porphyrin units in Zn$_2$**1**.

The identities and conformations of bisporphyrins Zn$_2$**2** and Ni$_2$**1** were further confirmed by their crystal structures.‡ As expected for Zn$_2$**2**, the individual porphyrin rings are in a coplanar arrangement (Fig. 1(a)). This is similar to the structure of a *meso*-butadiyne-linked porphyrin dimer reported by Anderson *et al.*[8] The ORTEP drawing of compound Ni$_2$**1** is shown in Fig. 1(b). To our knowledge, this is the first crystal structure of a platinum diacetylide-bridged bisporphyrin. The geometry of the platinum ion does not exhibit significant deviation from that expected for a square-planar arrangement. Notably, the porphyrin rings adopt a

Fig. 1 Crystal structure of (a) Zn$_2$**2** and (a) Ni$_2$**1** drawn at 50% probability ellipsoids. Additional "A" letters in the atom labels denote atoms at equivalent position ($-x$, $-y$, $-z$). Aryl groups and H atoms were omitted for clarity. Selected distances (Å) and angles (°): Zn$_2$**2**: C20–C21 1.427(3), C21–C22 1.202(4), C22–C22A 1.371(5), Zn–O1 2.158(2), O1···O2 2.664; ∠C20–C21–C22 176.0(3), ∠C21–C22–C22A 179.2(4); Ni$_2$**1**: C20–C21 1.432(7), C21–C22 1.204(7), Pt–C22 1.995(5), Pt–P1 2.286(1); ∠C22–Pt–P1 92.08(14).

nonplanar conformation and the two individual porphyrin mean planes are nearly coplanar. The nitrogen and nickel atoms only slightly deviate from the porphyrin mean plane. The average deviations from the mean plane are 0.561, 0.322 and 0.218 Å for *meso*-, α- and β-carbon atoms, respectively. It should be noted that both complexes have crystallographically imposed inversion symmetry.

The electronic coupling of the porphyrin units in these porphyrin dimers were investigated by electrochemical methods. The electrochemical data are listed in Table 1. In the case of the reference compound Zn$_2$**2**, the cyclic voltammogram shows two overlapping 1-e$^-$ couples at $E_{1/2}$ = 0.69 and 0.78 V, which can be resolved by differential pulse voltammetry, and one 2-e$^-$ process at $E_{1/2}$ = 1.24 V. The first and second 1-e$^-$ processes can be assigned to the first electron abstraction from the two porphyrin units, suggesting interporphyrin communication in the molecule. Similarly, compound Zn$_2$**1** undergoes two overlapping 1-e$^-$ reversible oxidations at $E_{1/2}$ = 0.50 and 0.56 V. Comparing with Zn$_2$**2**, compound Zn$_2$**1** exhibits smaller separation of the first and second oxidation processes ($\Delta E_{1/2}$ = 60 mV). This may be ascribed to the longer distance between porphyrin units or/and to inclusion of a platinum ion. In the nickel porphyrin dimers, the electronic coupling between the porphyrin units is more pronounced. Three oxidation processes can be resolved for compound Ni$_2$**1**, with the respective redox potentials being at $E_{1/2}$ = 0.70 (1-e$^-$), 0.83 (1-e$^-$) and 1.19 (2-e$^-$) V. The stepwise oxidations demonstrate that the porphyrin units are electrochemically coupled with each other *via* the platinum–diacetylide bridge and that insertion of a platinum atom into an alkynyl–alkynyl unit does not completely disrupt the electronic delocalization of the π-conjugation. The separation of 170 mV for the first two successive oxidations in Ni$_2$**2** is larger by 40 mV than that in Ni$_2$**1** because the bridge length of 9.253 Å in Ni$_2$**1** is much longer (by about 2.6 Å) than that in Ni$_2$**2**. In a conjugated dimer of nickel octaethylporphyrin linked by an ethyne–phenylene–ethyne unit,[9] with an estimated bridge length of about 10.9 Å, the redox potentials for the first electron abstraction from the porphyrin rings were observed at 0.91 and 0.96 V *vs.* Ag/AgCl at 293 K. The separation of these two successive oxidations, about 50 mV, is much smaller than that observed in Ni$_2$**1**. These results suggest that the platinum–diacetylide can be an alternative bridge, which provides a conductive pathway for charge-transport, for the construction of conjugated multiporphyrins, although platinum–diacetylide is less conjugated as compared with butadiyne. Comparing with Zn$_2$**1**, compound Ni$_2$**1** shows electronic communication between the chromophores.
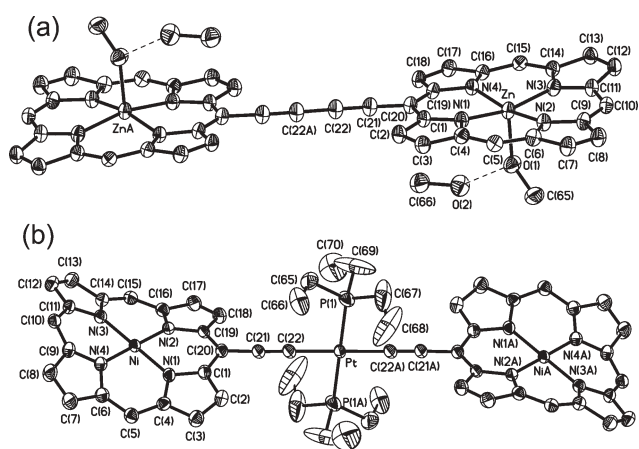
Extensive studies of the strongly coupled butadiyne-bridged bisporphyrin systems showed that the bisporphyrin monoanion and monocation exhibit an intense intervalence charge transfer (IVCT) band in the near-IR region.[9] It has been pointed out that the term "IVCT" is not suitable for a class III system (Robin and Day's classification).[9,10] The absorption in the near-IR region might be termed a "charge resonance band" for a class III system.[10] Since the term "charge resonance band" is not widely used, in keeping with convention, we use the term IVCT to describe this near-IR band. In all cases except dimer $Zn_2\mathbf{1}$, a broad band in the near-IR region for their corresponding monocations was observed. Fig. 2 shows absorption spectra of the neutral forms and mono- and dications of the dinickel porphyrins $Ni_2\mathbf{1}$ and $Ni_2\mathbf{2}$. The monocations and dications, generated *in situ* by reacting the neutral molecules with stoichiometric amounts of $[(p\text{-}BrC_6H_4)_3N][SbCl_6]$, are stable under the chemical oxidation conditions. Upon one-electron oxidation, the broad IVCT bands for $Ni_2\mathbf{1}^+$ and $Ni_2\mathbf{2}^+$ were observed at 3964 and 3957 cm^{-1}, respectively. The IVCT band disappears upon further oxidation by $[(p\text{-}BrC_6H_4)_3N][SbCl_6]$ to generate the corresponding dication. In monocations $Ni_2\mathbf{1}^+$ and $Ni_2\mathbf{2}^+$, the existence of the IVCT bands confirms the interporphyrin electronic communication. Based on the fact that the IVCT band is narrow and asymmetric, the radical cation and anion of the butadiyne bisporphyrin has been described by a fully delocalized class III system.[9] For the platinum bisacetylide-bridged porphyrin dimers, the shape of the IVCT band for $Ni_2\mathbf{1}^+$ cannot be completely determined since the low-energy side of this band is out of the limit of our instrument. Analysis of this IVCT band shows that the band width is broad and the intensity is relatively weak, suggesting that the monocation $Ni_2\mathbf{1}^+$ can be described by an intermediate coupling system (class II). The monocation $Zn_2\mathbf{1}^+$ can be classified by a localized system (class I), since such a IVCT band in the near-IR region was not observed for this monocation. Based on the electrochemical measurements and analysis of absorption spectra of monocations $Ni_2\mathbf{1}^+$ and $Zn_2\mathbf{1}^+$, we proposed that the HOMOs for $Ni_2\mathbf{1}$ and $Zn_2\mathbf{1}$ are mainly contributed from the mixing of a_{2u} orbitals, based on Gouterman's four-orbital model and the π orbitals of the ethynyl groups. However, the d_{xz} orbital of the platinum ion more or less involves in the HOMO for $Ni_2\mathbf{1}$, whereas the d orbitals of the platinum bridge do not involve in the HOMO for $Zn_2\mathbf{1}$ (z-axis = P1A–Pt–P axis; x-axis = C22–Pt–C22A axis).
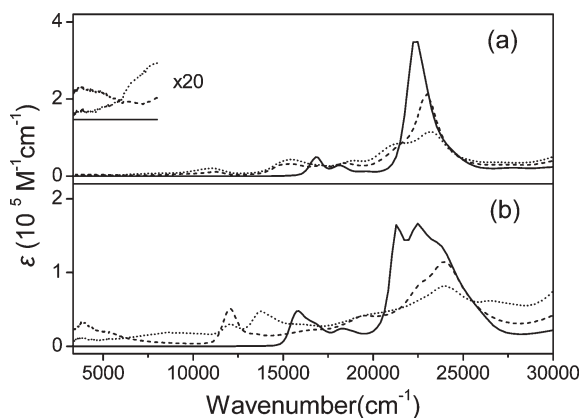
In summary, we have successfully synthesized novel platinum diacetylide-bridged porphyrin dimers. The two porphyrin units are essentially independent in $Zn_2\mathbf{1}$. In contrast, the chromophores exhibit electronic coupling *via* the bridge in dimer $Ni_2\mathbf{1}$. Theoretical calculations would be helpful to provide some insights into the d_{xz}–π orbital interaction in this new type of porphyrin dimers. Efforts along this line are in progress.

Notes and references

‡ *Crystal data*: $Ni_2\mathbf{1}$, crystals were grown from CHCl$_3$–MeOH. $Ni_2\mathbf{1}$·6CHCl$_3$, C$_{146}$H$_{178}$Cl$_{18}$N$_8$Ni$_2$P$_2$Pt, M = 3057.51, triclinic, space group $P\bar{1}$, T = 150(1) K, a = 9.7645(1), b = 19.8365(2), c = 22.0587(2) Å, α = 68.4657(6), β = 80.3541(6), γ = 89.0879(6)°, V = 3913.36(7) Å^3, Z = 1, μ = 1.505 mm^{-1}, 69469 reflections collected, 17970 independent, R_{int} = 0.0579, final residuals $R1$ = 0.0671, $wR2$ = 0.1922 [$I > 2\sigma(I)$]; $R1$ = 0.0807, $wR2$ = 0.2037 (all data). $Zn_2\mathbf{2}$, crystals were grown from CH$_2$Cl$_2$–MeOH. $Zn_2\mathbf{2}$·4CH$_3$OH·2CH$_2$Cl$_2$, C$_{134}$H$_{162}$Cl$_4$N$_8$O$_4$Zn$_2$, M = 2221.26, triclinic, space group $P\bar{1}$, T = 150(1) K, a = 13.8674(2), b = 14.9588(2), c = 16.0677(2) Å, α = 85.2430(8), β = 87.9895(9), γ = 68.9350(9)°, V = 3099.58(7) Å^3, Z = 1, μ = 0.528 mm^{-1}, 64819 reflections collected, 14190 independent, R_{int} = 0.0539, final residuals $R1$ = 0.0574, $wR2$ = 0.1551 [$I > 2\sigma(I)$]; $R1$ = 0.0885, $wR2$ = 0.1760 (all data). CCDC 285537 and 285538. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513921j

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Fig. 2 The absorption spectra of (a) $Ni_2\mathbf{1}$ (solid), $Ni_2\mathbf{1}^+$ (dashed) and $Ni_2\mathbf{1}^{2+}$ (dotted) and (b) $Ni_2\mathbf{2}$ (solid), $Ni_2\mathbf{2}^+$ (dashed) and $Ni_2\mathbf{2}^{2+}$ (dotted) in CH$_2$Cl$_2$.