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Singly and doubly  $\beta$ -to- $\beta$  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  $\beta$ -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  $\text{Ni}(\text{II})$ -porphyrin and  $\text{Zn}(\text{II})$ -porphyrin gave the corresponding doubly  $\beta$ -to- $\beta$  platinum-bridged porphyrin dimers. Treatment of the doubly  $\beta$ -to- $\beta$  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  $\beta$ -to- $\beta$  platinum bridge and a  $\beta$ -to- $\beta$  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.<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  $\text{Ni}(\text{II})$ -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.<sup>4e</sup> *meso*-Diphenylphosphanyl  $\text{Zn}(\text{II})$ -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  $\text{Ni}(\text{II})$ -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.<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  $\text{Ni}(\text{II})$ -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

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  $\text{Pt}(\text{cod})\text{Cl}_2$  to get information on the structural and electronic details of platinum-bridged porphyrin dimers. Actually, these reactions afforded singly and doubly  $\beta$ -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  $\text{Ni}(\text{II})$  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  $\beta$ -to- $\beta$  platinum-bridged porphyrin dimer **2Ni** in 84% yield as a stable solid (Scheme 1).<sup>9</sup> Matrix-assisted laser desorption/ion

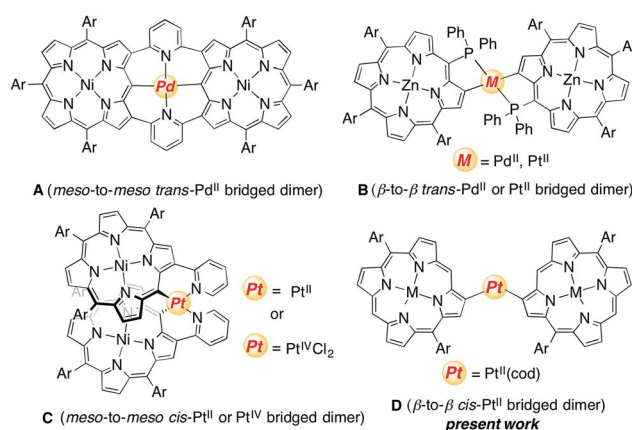


Chart 1 Examples of directly metal-bridged porphyrin dimers.

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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  $\beta$ -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 ( $\angle C\beta-Pt-C\beta$ ) 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).<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°. 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 Pt(cod)Cl<sub>2</sub> 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  $C_{132}H_{152}N_8^{58}Ni_2^{192}Pt_2 = 2357.02 [M-cod]^+$ ). The  $^1H$  NMR

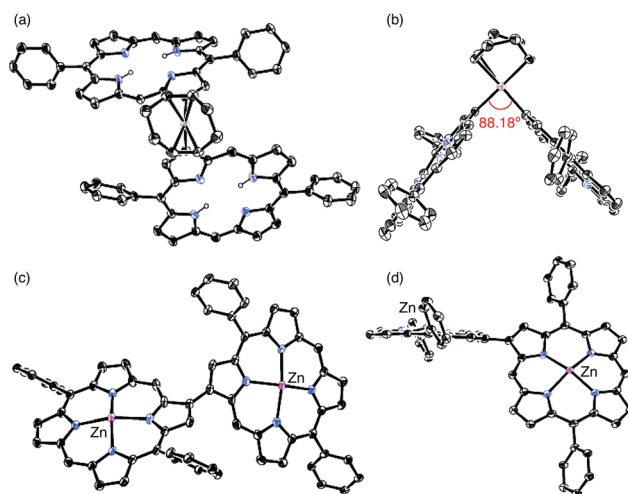
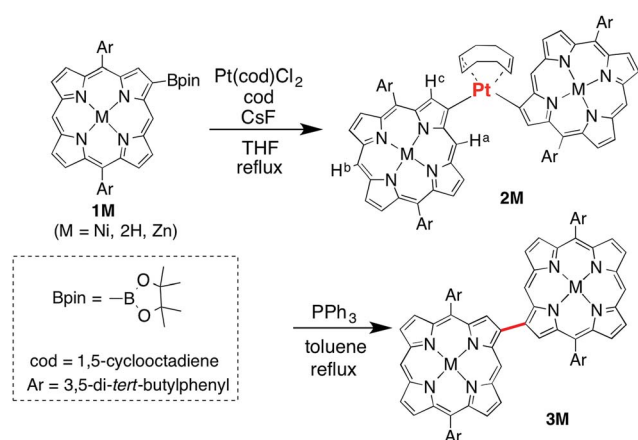


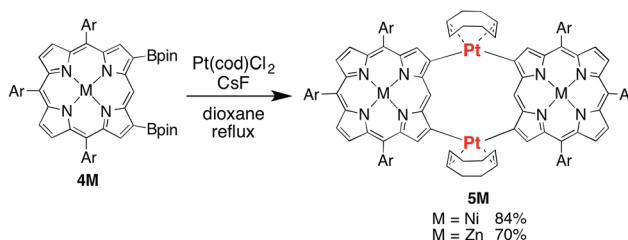
Fig. 1 X-ray crystal structures of **2H** and **3Zn**. *tert*-Butyl groups, solvent molecules including pyridines coordinated to Zn ions, and hydrogen atoms (except for inner NHs) are omitted for clarity. The thermal ellipsoids are scaled to 30% probability. (a) Top view of **2H**. (b) Side view of **2H**. (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  $C\beta-Pt$  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)Cl<sub>2</sub> 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<sub>2</sub> 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  $159.04^\circ$  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 ( $\lambda_{max} = 412$  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

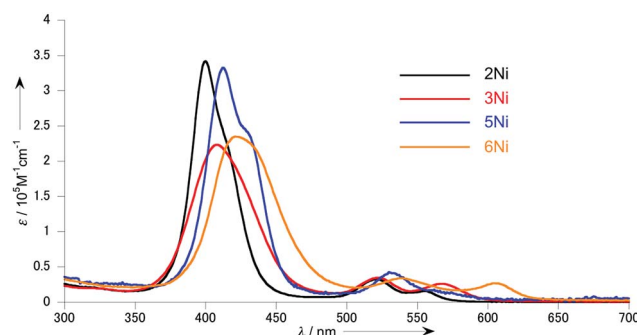


Fig. 3 UV/vis absorption spectra of **2Ni**, **3Ni**, **5Ni** and **6Ni** in  $CH_2Cl_2$ .

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 ( $\Delta E_{HL}$ ) 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  $\Delta E_{HL}$  value of **6Ni** is smaller than those of **2Ni** and **5Ni**, in line with their UV/vis absorption spectral data.

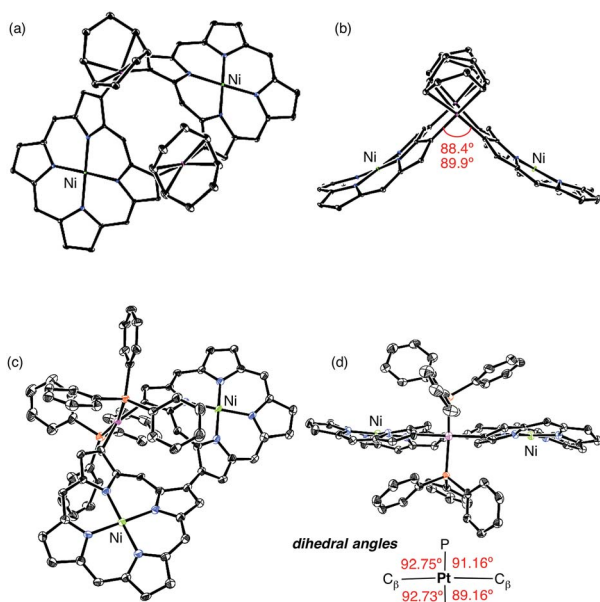


Fig. 2 X-ray crystal structures of **5Ni** and **6Ni**. 3,5-Di-*tert*-butylphenyl groups, solvent molecules, and hydrogen atoms are omitted for clarity. The thermal ellipsoids are scaled to 30% probability. (a) Perspective view of **5Ni**. (b) Side view of **5Ni**. (c) Perspective view of **6Ni**. (d)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

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

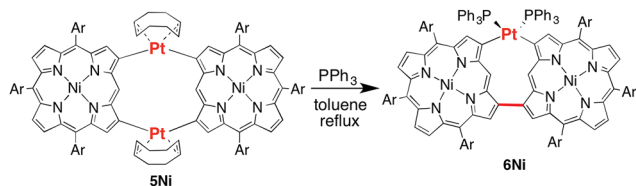
	$E_{ox2}^{1/2}$	$E_{ox1}^{1/2}$	$E_{red1}^{1/2}$	$E_{red2}^{1/2}$	$\Delta E_{HL}^b$
Ni(II) porphyrin <sup>c</sup>		0.53 <sup>d</sup>	$-1.76$		2.29
<b>2Ni</b>		0.36 <sup>d</sup>	$-1.87$		2.23
<b>3Ni</b>		0.62 <sup>d</sup>	$-1.69$	$-1.80$	2.31
<b>5Ni</b>		0.28 <sup>d</sup>	$-1.97$		2.25
<b>6Ni</b>	0.50	0.32	$-1.87$	$-2.07^d$	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<sup>−1</sup>. All values were determined by differential pulse voltammetry (in V). <sup>b</sup>  $\Delta E_{HL}$  = electrochemical HOMO–LUMO gap ( $= E_{ox1}^{1/2} - E_{red1}^{1/2}$  [eV]). <sup>c</sup> 5,15-Bis(3,5-di-*tert*-butylphenyl)porphyrinatonicel(II).

<sup>d</sup> Irreversible peaks.







Scheme 3 Synthesis of 6Ni from 5Ni.

## Conclusions

2-Borylporphyrins reacted with  $\text{Pt}(\text{cod})\text{Cl}_2$  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  $\text{Ni}(\text{II})$ -porphyrin gave a doubly  $\beta$ -to- $\beta$  platinum-bridged  $\text{Ni}(\text{II})$ -porphyrin dimer, which was converted to a  $\text{Ni}(\text{II})$ -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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## Notes and references

- (a) F. Atefi and D. P. Arnold, *J. Porphyrins Phthalocyanines*, 2008, **12**, 801; (b) B. M. J. M. Suijkerbuijk and R. J. M. Klein Gebbink, *Angew. Chem., Int. Ed.*, 2008, **47**, 7396; (c) H. Shinokubo and A. Osuka, *Chem. Commun.*, 2009, 1011; (d) H. Yorimitsu and A. Osuka, *Asian J. Org. Chem.*, 2013, **2**, 356.
- (a) D. P. Arnold, P. C. Healy, M. J. Hodgson and M. L. Williams, *J. Organomet. Chem.*, 2000, **607**, 41; (b) Y. Matano, K. Matsumoto, Y. Nakao, H. Uno, S. Sakai and H. Imahori, *J. Am. Chem. Soc.*, 2008, **130**, 4588; (c) Y. Matano, K. Matsumoto, H. Hayashi, Y. Nakao, T. Kumpulainen, V. Chukharev, N. Tkachenko, H. Lemmetyinen, S. Shimizu, N. Kobayashi, D. Sakamaki, A. Ito, K. Tanaka and H. Imahori, *J. Am. Chem. Soc.*, 2012, **134**, 1825; (d) R. D. Hartnell, T. Yoneda, H. Mori, A. Osuka and D. P. Arnold, *Chem.-Asian J.*, 2013, **8**, 2670.
- (a) K. M. Smith, K. C. Langry and O. Minnetian, *J. Org. Chem.*, 1984, **49**, 4602; (b) K. Sugiura, A. Kato, K. Iwasaki, H. Miyasaka, M. Yamashita, S. Hino and D. P. Arnold, *Chem. Commun.*, 2007, 2046.
- (a) S. Yamaguchi, T. Katoh, H. Shinokubo and A. Osuka, *J. Am. Chem. Soc.*, 2007, **129**, 6392; (b) J. Yamamoto, T. Shimizu, S. Yamaguchi, N. Aratani, H. Shinokubo and A. Osuka, *J. Porphyrins Phthalocyanines*, 2011, **15**, 534; (c) S. Yamaguchi, T. Katoh, H. Shinokubo and A. Osuka, *J. Am. Chem. Soc.*, 2008, **130**, 14440; (d) S. Yamaguchi, H. Shinokubo and A. Osuka, *Inorg. Chem.*, 2009, **48**, 795; (e) J. Song, N. Aratani, J. H. Heo, D. Kim, H. Shinokubo and A. Osuka, *J. Am. Chem. Soc.*, 2010, **132**, 11868; (f) K. Yoshida, S. Yamaguchi, A. Osuka and H. Shinokubo, *Organometallics*, 2010, **29**, 3997; (g) S. Yamaguchi, H. Shinokubo and A. Osuka, *J. Am. Chem. Soc.*, 2010, **132**, 9992; (h) K. Yoshida, T. Nakashima, S. Yamaguchi, A. Osuka and H. Shinokubo, *Dalton Trans.*, 2011, **40**, 8773; (i) S. Anabuki, H. Shinokubo, N. Aratani and A. Osuka, *Angew. Chem., Int. Ed.*, 2012, **51**, 3174; (j) K. Fujimoto, T. Yoneda, H. Yorimitsu and A. Osuka, *Angew. Chem., Int. Ed.*, 2014, **53**, 1127.
- T. Tanaka and A. Osuka, *Chem. Soc. Rev.*, 2015, **44**, 943.
- H.-W. Jiang, T. Tanaka, H. Mori, K. H. Park, D. Kim and A. Osuka, *J. Am. Chem. Soc.*, 2015, **137**, 2219.
- (a) S. Yamago, Y. Watanabe and T. Iwamoto, *Angew. Chem., Int. Ed.*, 2010, **49**, 757; (b) T. Iwamoto, Y. Watanabe, Y. Sakamoto, T. Suzuki and S. Yamago, *J. Am. Chem. Soc.*, 2011, **133**, 8354; (c) S. Yamago, E. Kayahara and T. Iwamoto, *Chem. Rec.*, 2014, **14**, 84; (d) S. Hitosugi, T. Yamasaki and H. Isobe, *J. Am. Chem. Soc.*, 2012, **134**, 12442; (e) T. Matsuno, S. Kamata, S. Hitosugi and H. Isobe, *Chem. Sci.*, 2013, **4**, 3179.
- (a) F. Zhang and P. Bäuerle, *J. Am. Chem. Soc.*, 2007, **129**, 3090; (b) F. Zhang, G. Götz, H. D. F. Winkler, C. A. Schalley and P. Bäuerle, *Angew. Chem., Int. Ed.*, 2009, **48**, 6632.
- H. Hata, H. Shinokubo and A. Osuka, *J. Am. Chem. Soc.*, 2005, **127**, 8264.
- Examples of  $\beta$ - $\beta$ -linked porphyrin dimers: (a) Y. Nakamura, N. Aratani, A. Tsuda, A. Osuka, K. Furukawa and T. Kato, *J. Porphyrins Phthalocyanines*, 2003, **7**, 264; (b) H. Uno, Y. Kitawaki and N. Ono, *Chem. Commun.*, 2002, 116; (c) Y. Deng, C. K. Chang and D. G. Nocera, *Angew. Chem., Int. Ed.*, 2000, **39**, 1066.
- A. Tsuda, A. Nakano, H. Furuta, H. Yamochi and A. Osuka, *Angew. Chem., Int. Ed.*, 2000, **39**, 558.

