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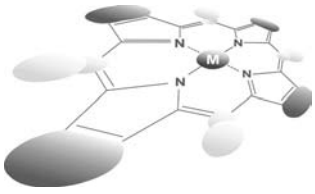

A Bis-Au(III) [28]hexaphyrin triphenylphosphine adduct

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Dedicated to Professor Tomas Torres on the occasion of his 65th birthday

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ABSTRACT: Triphenylphosphine was added regioselectively at the C(3) position of bis-Au(III) complex of [26]hexaphyrin **5** in the presence of trifluoroacetic acid to produce [28]hexaphyrin triphenylphosphine adduct **6** in 62% yield, which has been fully characterized by NMR, UV-vis/NIR absorption, and MS spectroscopies, and X-ray diffraction analysis. The rigid planar structure forces **6** to take Hückel antiaromaticity, which has been supported by its ^{1}H NMR spectrum. Curiously, the detailed structural analysis elucidated that the triphenylphosphine moiety exists as a phosphorane form in the solid state. A plausible mechanism *via* a double protonated **5** is proposed, which can explain the observed regioselectivity.

KEYWORDS: expanded porphyrin, hexaphyrin, triphenylphosphine, phosphonium ylide, phosphorane.

INTRODUCTION

In the last two decades, considerable efforts have been devoted to the development of expanded porphyrins that consist of more than five pyrroles, which are ring extended porphyrin analogs, since they display intriguing optical, electronic, and structural properties that significantly differ from those of porphyrin [1]. In particular, expanded porphyrins have been demonstrated to realize Hückel and Möbius (anti)aromaticity [2, 3], anion receptors [4], various metal complexes [5], near-infrared (NIR) absorption dyes [6], and stable organic radicals [7]. In addition to these unique properties, the reactivity of expanded porphyrin has been studied and discovered sometimes in an unprecedented manner, such as skeleton rearrangement [8], cell division like splitting reaction [9], pericyclic reaction [10], electrophilicity [11], and nucleophilicity [12]. Previously, we have reported that nucleophilic addition of triphenylphosphine to [26]hexaphyrin free base **1** and palladium complex **3** gave the corresponding [28]hexaphyrin triphenylphosphine adducts **2** and **4**, respectively [11] (Scheme 1). These reactions caused conformational changes from planar Hückel form to twisted Möbius-strip like form. Characteristically, triphenylphosphine moiety dominantly exists as a phosphorane form **2b** in free base **2** while a phosphonium ylide form **4a** is more important in palladium complex **4**. Inspired by these results, we herein tried the reaction of bis-Au(III) [26]hexaphyrin **5** [13] with triphenylphosphine. Addition of triphenylphosphine proceeded regioselectively to furnish bis-Au(III) [28]hexaphyrin triphenylphosphine adduct **6** in a good yield. The structural rigidity of **5** did not allow large conformational change observed for the free base [26]hexaphyrin and its Pd complex, and the adduct **6** displayed Hückel antiaromaticity. In addition, the triphenylphosphine moiety was found to exist as a phosphorane contribution in the solid state.

RESULTS AND DISCUSSION

The reaction of bis-Au(III) complex of [26]hexaphyrin **5** with 1 equivalent of triphenylphosphine in the presence of trifluoroacetic acid (TFA) gave [28]hexaphyrin triphenylphosphine adduct **6** in 62% yield along with formation of [28]hexaphyrin **7** in 29% yield (Scheme 2). The high-resolution electrospray-ionization time-of-flight (HR-ESI-TOF) mass spectrum of **6** indicated the parent ion peak at m/z = 2109.0477 $[M - H]^-$ (calcd. for

◊ SPP full member in good standing

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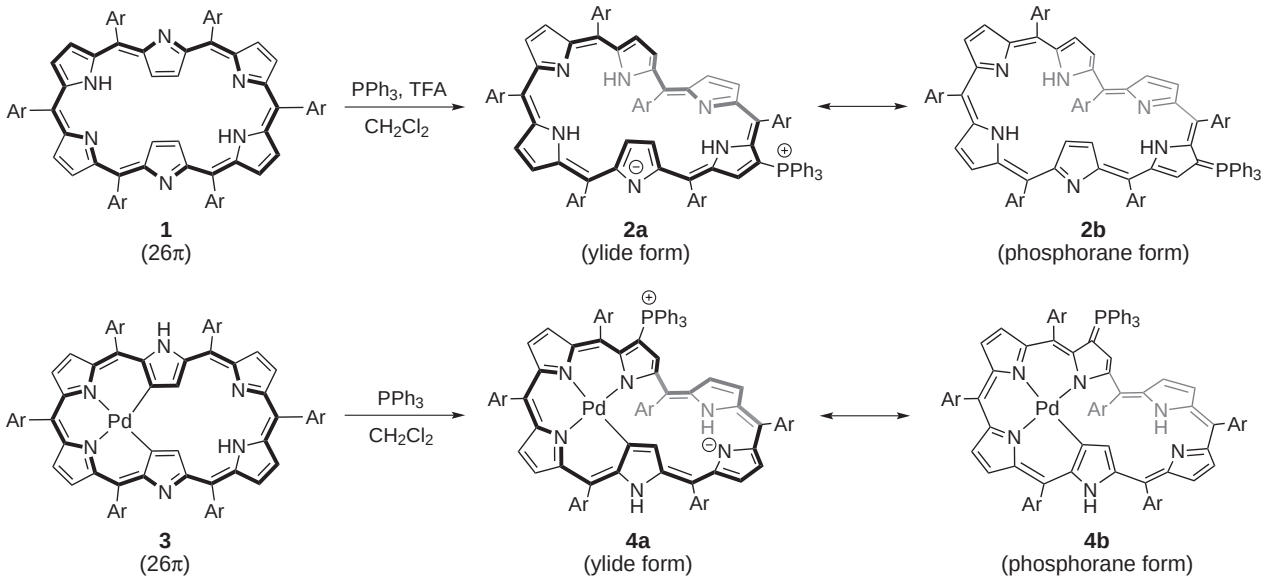
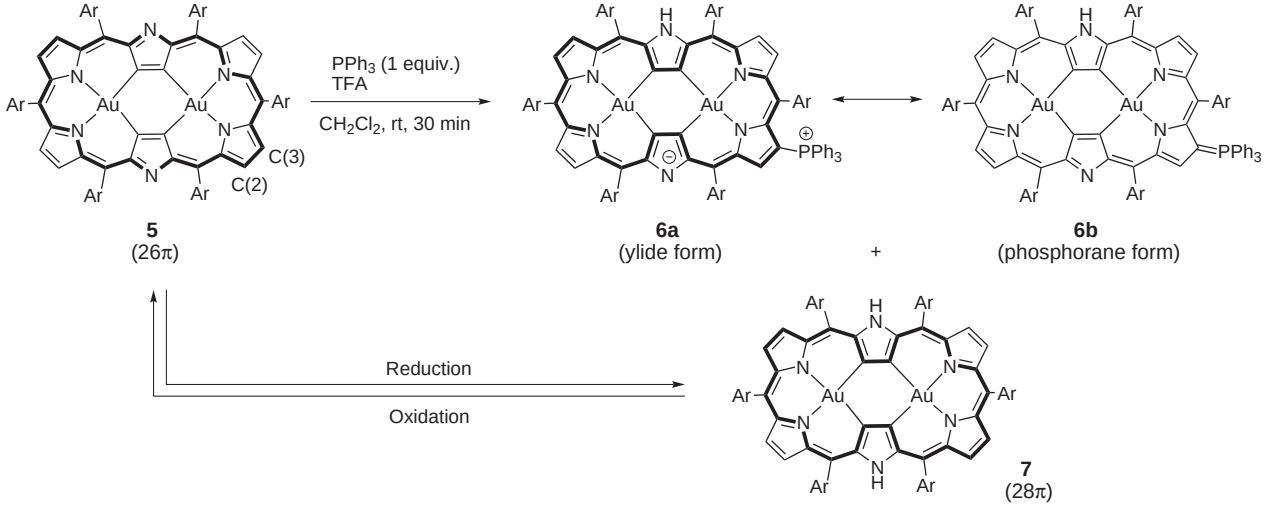


Scheme 1. Synthesis of [28]hexaphyrin triphenylphosphine adducts **2** and **4** and possible resonance between phosphonium ylide **a** and phosphorane **b** in **2** and **4**. Ar = pentafluorophenyl. The bold line represents a conjugated circuit



Scheme 2. Synthesis of a bis-Au(III) [28]hexaphyrin triphenylphosphine adduct **6** and possible resonance between phosphonium ylide **6a** and phosphorane **6b**. Ar = pentafluorophenyl. The bold line represents a conjugated circuit

2109.0490, $C_{84}H_{22}N_6F_{30}PAu_2$). It is thought that there are two kinds of triphenylphosphine adducts since there are two reactive positions C(2) and C(3) in **5**. However, only one isomer was obtained, indicating the reaction proceeded regioselectively.

The structure of **6** has been unambiguously determined by X-ray diffraction analysis, which revealed the addition of triphenylphosphine reacted at the C(3) position (Fig. 1). The bond length of P–C(3) is 1.77 Å (1.77 Å), which is shorter than a typical bond length of P–C (1.82 Å) observed in β-diphenylphosphine-substituted porphyrins [14]. The angle of C–N–C in the pyrrole C is 110.0° (109.0°), while that in the pyrrole F is 103.9° (104.3°), implying that the pyrrole C is amino-type pyrrole and the pyrrole F is imino-type pyrrole. While ylide form **6a** and phosphorane form **6b** are resonance hybrid contributors of **6**, these observations indicated that **6b** is more important than **6a** in the solid state.

The ^{1}H NMR spectrum of **6** revealed that signals due to the outer β protons are observed in the range of 2.62–3.43 ppm and the outer NH proton is observed at 2.45 ppm. These data indicate a strong paratropic ring current, and hence antiaromaticity for **6**, similarly to [28]hexaphyrin **7**. The nuclear independent chemical shift (NICS) values of **6** at the center of gravity exhibited positive values (NICS(+1) = +19.4 ppm and NICS(-1) = +21.7 ppm), also suggesting the antiaromaticity [15].

In the absorption spectrum of **6**, an intense absorption band was observed at 572 nm and weak absorption

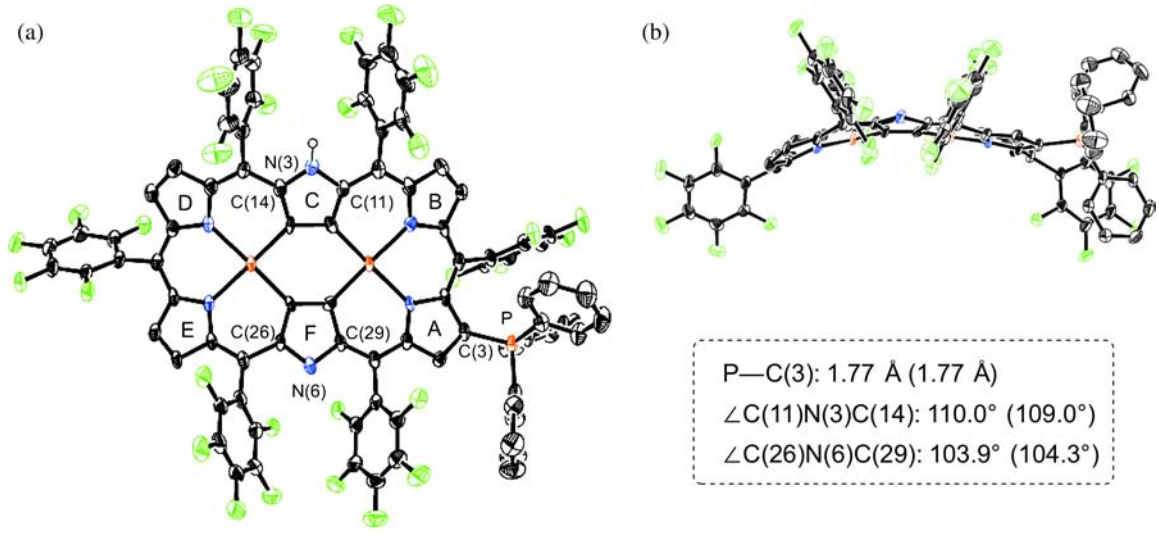


Fig. 1. X-ray crystal structure of **6**. (a) Top view. (b) Side view. The thermal ellipsoids are scaled to 50% probability level. Solvent molecules and hydrogen atoms except for NH are omitted for clarity. One of two independent structures in the lattice is shown

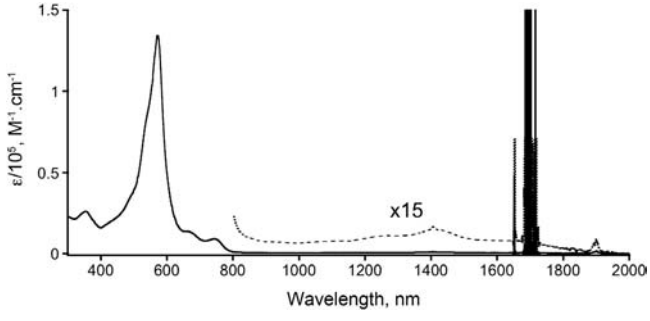


Fig. 2. UV-vis/NIR absorption spectrum of **6** in CH_2Cl_2

bands at 665 and 743 nm. The broad and quite weak absorption band that reached around 2000 nm was also detected because of the transition to the dark state, which was characteristic of antiaromatic porphyrinoids [16] (Fig. 2).

A plausible reaction mechanism was shown in Scheme 3. Addition of triphenylphosphine to **5** proceeded smoothly in the presence of TFA but did not occur in the absence of TFA, indicating that protonated [26]hexaphyrin would be a key intermediate. Thus, we took doubly protonated species **5H** as a reaction intermediate and calculated its molecular orbitals by the density functional theory (DFT) method. Curiously, the lowest unoccupied molecular orbital (LUMO) of **5H** shown in Scheme 3b nicely explains the observed highly regioselective addition of triphenylphosphine at the C(3) position. Rearomatization of **5P** and subsequent deprotonation of **6H** furnished the final adduct **6**. The doubly protonated hexaphyrin could be easily reduced to afford **7**, and thus it is conceivable that the reduction of the protonated [26]hexaphyrin **5H** competes with the nucleophilic attack of triphenylphosphine.

EXPERIMENTAL

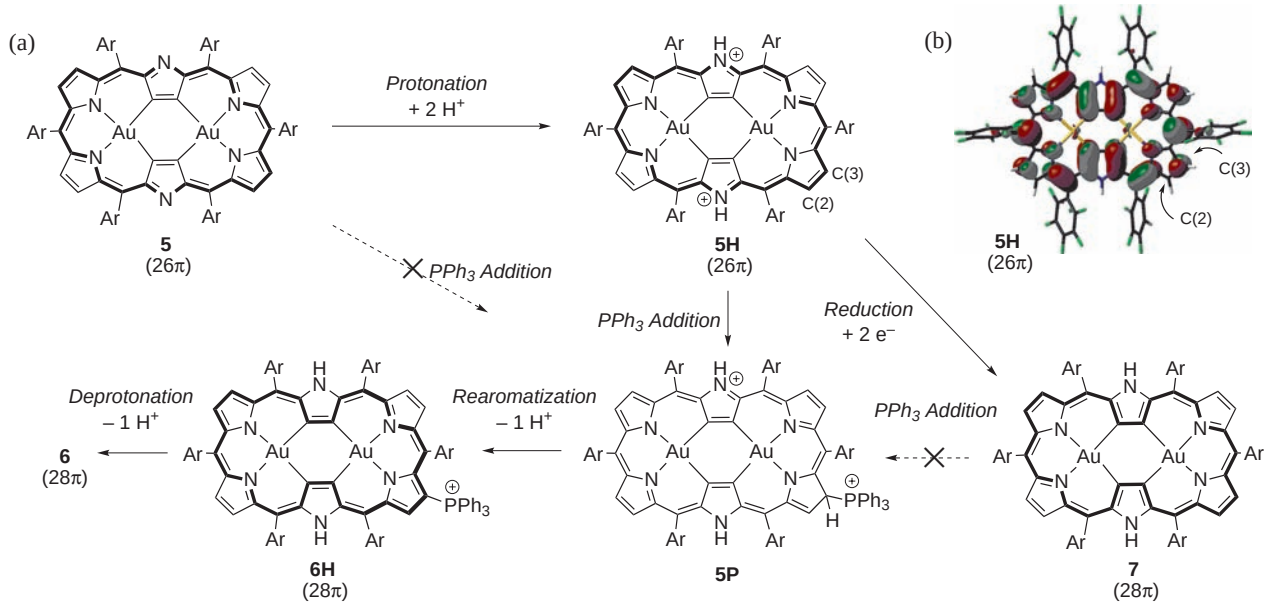
General

All reagents were of the commercial reagent grade and were used without further purification except where noted. Silica gel column chromatography was performed on Wakogel C-300. UV-vis/NIR absorption spectra were recorded on a Shimadzu UV-3600PC spectrometer. ^{1}H, ^{19}F, and ^{31}P NMR spectra were recorded on a JEOL ECA-600 spectrometer (operating as 600.17 MHz for ^{1}H, 564.73 MHz for ^{19}F, and 242.95 MHz for ^{31}P) using the residual solvent as the internal reference for ^{1}H (δ = 7.26 ppm in $CDCl_3$), hexafluorobenzene as the external reference for ^{19}F (δ = -162.9 ppm), and 85% phosphoric acid as the external reference for ^{31}P (δ = 0.00 ppm). NMR signals were assigned from the ^{1}H–^{1}H COSY spectrum, and the comparison with the spectra in the presence of D_2O (signals assigned for NH protons disappear in the presence of D_2O). High-resolution electrospray-ionization time-of-flight mass spectroscopy (HR-ESI-TOF-MS) was recorded on a BRUKER micrOTOF model using negative mode for acetonitrile solutions of samples.

Crystal data

X-ray crystallographic data were collected on a Rigaku XtaLAB P200 apparatus at -180 °C using graphite-monochromated CuKα radiation (λ = 1.54187 Å). The structures were solved by direct method SIR-97 and refined by SHELXL-97 program.

6. $2(C_{84}H_{23}N_6F_{30}Au_2P)\cdot 3.5(C_8H_{18})\cdot 1.69(C_7H_8)$, M_w = 4776.88, monoclinic, space group *C*2/*c* (no. 15), a = 41.025(7) Å, b = 27.969(3) Å, c = 36.794(8) Å, β = 120.951(5)°, V = 36207(11) Å^3, T = 93 K, ρ_{calcd} = 1.753



Scheme 3. (a) A plausible mechanism of the nucleophilic addition of triphenylphosphine to **6**. (b) LUMO of **5H**. Ar = pentafluorophenyl. The bold line represents a conjugated circuit

g.cm^{-3}, Z = 8, R_1 = 0.0635 ($I > 2\sigma$ (I)), R_w = 0.1780 (all data), GOF = 1.055.

Synthesis

Bis-Au(III) [26]hexaphyrin(1.1.1.1.1.1) 5. The titled compound was synthesized according to the literature [13c].

Bis-Au(III) [28]hexaphyrin(1.1.1.1.1.1) triphenylphosphine adduct 6. Bis-Au(III) [26]hexaphyrin **5** (20 mg, 11 μmol) and PPh_3 (2.5 mg, 1 equiv.) were dissolved in CH_2Cl_2 (1.0 mL) under inert atmosphere. One drop of TFA was added to the solution and the color of the solution immediately changed from green to purple. After stirred for 30 min, the resulting mixture was quenched by addition of aqueous $NaHCO_3$ solution. Then, the mixture was washed with water, extracted with CH_2Cl_2, and dried over Na_2SO_4. The residual solvent was removed under reduced pressure. Silica gel column chromatography using CH_2Cl_2/AcOEt (20/1) as an eluent afforded bis-Au(III) [28]hexaphyrin **7** (5.8 mg, 29%) [13a] as the first red fraction and the titled compound **6** (14 mg, 62%) as a purple fraction. ^{1}H NMR (600.17 MHz; $CDCl_3$): δ_H, ppm 7.63 (t, J = 7.4 Hz, 3H; phenyl), 7.52 (m, 6H; phenyl), 7.18 (m, 6H; phenyl), 3.43 (d, J = 5.0 Hz, 1H; β), 3.36 (d, J = 5.5 Hz, 1H; β), 3.31 (d, J = 5.5 Hz, 2H; β), 3.20 (d, J = 5.9 Hz, 1H; β), 3.13 (d, J = 5.5 Hz, 1H; β), 2.62 (d, J_{H-P} = 8.3 Hz, 1H; β) and 2.45 (s, 1H; NH). ^{19}F NMR (564.73 MHz; $CDCl_3$; hexafluorobenzene): δ_F, ppm -131.6 (d, J = 18.6 Hz, 2F; *ortho*-C_6F_5), -137.3 (m, 4F; *ortho*-C_6F_5), -138.3 (m, 4F; *ortho*-C_6F_5), -138.6 (m, 2F; *ortho*-C_6F_5), -151.5 (t, J = 22.0 Hz, 1F; *para*-C_6F_5), -152.2 (t, J = 23.4 Hz, 1F; *para*-C_6F_5), -153.4 (t, J = 23.4 Hz, 1F; *para*-C_6F_5), -154.1 (t, J = 21.4 Hz, 1F; *para*-C_6F_5), -157.3 (m, 2F; *para*-C_6F_5), -158.7 (t, J = 22.0 Hz, 2F; *meta*-C_6F_5), -159.4 (t, J = 17.5 Hz, 2F; *meta*-C_6F_5), -159.9 (t, J = 22.0 Hz, 2F; *meta*-C_6F_5), -160.4 (m, 2F; *meta*-C_6F_5), -164.3 (t, J = 22.0 Hz, 2F; *meta*-C_6F_5), and -164.5 (t, J = 21.5 Hz, 2F; *meta*-C_6F_5). ^{31}P NMR (242.95 MHz; $CDCl_3$; 85% phosphoric acid): δ_P, ppm 14.0 (s, 1P; *decoupled with* ^{13}C). MS (ESI-TOF-MS): *m/z* 2109.0477 [*M*–H]$^-$ (calcd. for 2109.0490. $C_{84}H_{23}N_6F_{30}PAu_2$). UV-vis ($CH_2Cl_2$): λ, nm (ε) 354 (26100), 572 (134400), 665 (13700), 743 (9100), and 1405 (1200).

CONCLUSION

In conclusion, the reaction of bis-Au(III) [26]hexaphyrin **5** with triphenylphosphine in the presence of TFA afforded [28]hexaphyrin triphenylphosphine adduct **6**, which was fully characterized by NMR and UV-vis/NIR absorption spectroscopy and X-ray diffraction analysis. Judging from the ^{1}H NMR and absorption spectroscopies, adduct **6** has been assigned as a distinct Hückel antiaromatic macrocycle. It was found that the phosphorane form **6b** is more important in the solid state. A plausible reaction mechanism *via* a doubly protonated species was suggested for the regioselective addtion of triphenylphosphine to **5**.

Acknowledgements

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Supporting information

The chart of NMR and MS spectra, crystallographic details, and theoretical calculations (Figs S1–S4, Tables S1–S2) are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

Crystallographic data for compound **6** have been deposited at the Cambridge Crystallographic Data Center (CCDC) under number CCDC-1437331. Copies can be obtained on request, free of charge, *via* www.ccdc.cam.ac.uk/data_request/cif or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223-336-033 or email: data_request@ccdc.cam.ac.uk).

REFERENCES

1. (a) Jasat A and Dolphin D. *Chem. Rev.* 1997; **97**: 2267. (b) Misra R and Chandrashekar TK. *Acc. Chem. Res.* 2008; **41**: 265. (c) Sessler JL and Seidel D. *Angew. Chem. Int. Ed.* 2003; **42**: 5134. (d) Stępień M, Sprutta N and Latos-Grażyński L. *Angew. Chem. Int. Ed.* 2011; **50**: 4288. (e) Saito S and Osuka A. *Angew. Chem. Int. Ed.* 2011; **50**: 4342.
2. For Hückel (anti)aromaticity, see (a) Shin JY, Furuta H, Yoza K, Igarashi S and Osuka A. *J. Am. Chem. Soc.* 2001; **123**: 7190. (b) Sung YM, Yoon MC, Lim JM, Rath H, Naoda K, Osuka A and Kim D. *Nat. Chem.* 2015; **7**: 418.
3. For Möbius (anti)aromaticity, see (a) Stępień M, Latos-Grażyński L, Sprutta N, Chwalisz P and Szterenberg L. *Angew. Chem. Int. Ed.* 2007; **46**: 7869. (b) Sankar J, Mori S, Saito S, Rath H, Suzuki M, Inokuma Y, Shinokubo H, Kim KS, Yoon ZS, Shin JY, Lim JM, Matsuzaki Y, Matsushita O, Muranaka A, Kobayashi N, Kim D and Osuka A. *J. Am. Chem. Soc.* 2008; **130**: 13568. (c) Higashino T, Lim JM, Miura T, Saito S, Shin JY, Kim D and Osuka A. *Angew. Chem. Int. Ed.* 2010; **49**: 4950.
4. (a) Sessler JL, Mody TD, Ford DA and Lynch V. *Angew. Chem. Int. Ed. Engl.* 1992; **31**: 452. (b) Köhler T, Seidel D, Lynch V, Arp FO, Ou Z, Kadish KM and Sessler JL. *J. Am. Chem. Soc.* 2003; **125**: 6872.
5. (a) Sessler JL and Tomat E. *Acc. Chem. Res.* 2007; **40**: 371. (b) Shimizu S and Osuka A. *Eur. J. Inorg. Chem.* 2006: 1319.
6. (a) Tanaka T, Aratani N, Lim JM, Kim KS, Kim D and Osuka A. *Chem. Sci.* 2011; **2**: 1414. (b) Naoda K, Mori H, Aratani N, Lee BS, Kim D and Osuka A. *Angew. Chem. Int. Ed.* 2012; **51**: 9850. (c) Mori H, Tanaka T, Lee S, Lim JM, Kim D and Osuka A. *J. Am. Chem. Soc.* 2015; **137**: 2097.
7. (a) Koide T, Furukawa K, Shinokubo H, Shin JY, Kim KS, Kim D and Osuka A. *J. Am. Chem. Soc.* 2010; **132**: 7246. (b) Gopalakrishna TY, Reddy JS and Anand VG. *Angew. Chem. Int. Ed.* 2014; **53**: 10984. (c) Hisamune Y, Nishimura K, Isakari K, Ishida M, Mori S, Karasawa S, Kato T, Lee S, Kim D and Furuta H. *Angew. Chem. Int. Ed.* 2015; **54**: 7323.
8. (a) Vogel E, Michels M, Zander L, Lex J, Tuzun NS and Houk KN. *Angew. Chem. Int. Ed.* 2003; **42**: 2857. (b) Yoneda T, Saito S, Yorimitsu H and Osuka A. *Angew. Chem. Int. Ed.* 2011; **50**: 3475. (c) Tanaka Y, Mori H, Koide, T, Yorimitsu H, Aratani N and Osuka A. *Angew. Chem. Int. Ed.* 2011; **50**: 11460.
9. (a) Tanaka Y, Hoshino W, Shimizu S, Youfu K, Aratani N, Maruyama N, Fujita S and Osuka A. *J. Am. Chem. Soc.* 2004; **126**: 3046. (b) Saito S, Kim KS, Yoon ZS, Kim D and Osuka A. *Angew. Chem. Int. Ed.* 2007; **46**: 5591.
10. (a) Hata H, Shinokubo H and Osuka A. *Angew. Chem. Int. Ed.* 2005; **44**: 932. (b) Hata H, Kamimura Y, Shinokubo H and Osuka A. *Org. Lett.* 2006; **8**: 1169.
11. (a) Youfu K and Osuka A. *Org. Lett.* 2005; **7**: 4381. (b) Inoue M, Yoneda T, Youfu K, Aratani N and Osuka A. *Chem. Eur. J.* 2011; **17**: 9028.
12. (a) Suzuki M and Osuka A. *Chem. Commun.* 2005: 3685. (b) Yoneda T and Osuka A. *Chem. Eur. J.* 2013; **19**: 7314.
13. (a) Mori S and Osuka A. *J. Am. Chem. Soc.* 2005; **127**: 8030. (b) Mori S, Kim KS, Yoon ZS, Noh SB, Kim D and Osuka A. *J. Am. Chem. Soc.* 2005; **127**: 8030. (c) Naoda K, Mori H and Osuka A. *Chem. Lett.* 2013; **42**: 2224.
14. Fujimoto K, Yoneda T, Yorimitsu H and Osuka A. *Angew. Chem. Int. Ed.* 2014; **53**: 1127.
15. (a) Schleyer PvR, Maerker C, Dransfeld A, Jiao H and Hommes NJRvE. *J. Am. Chem. Soc.* 1996; **118**: 6317. (b) Chen Z, Wannere CS, Corminboeuf C, Puchta R and Schleyer PvR. *Chem. Rev.* 2005; **105**: 3842.
16. Shin JY, Kim KS, Yoon MC, Lim JM, Yoon, ZS, Osuka A and Kim D. *Chem. Soc. Rev.* 2010; **39**: 2751.
17. Gaussian 09, Revision A.02, Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V, Mennucci B, Petersson GA, Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF, Bloino J, Zheng G, Sonnenberg JL, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Vreven T, Montgomery JA, Jr., Peralta JE, Ogliaro F, Bearpark M, Heyd JJ, Brothers E, Kudin KN, Staroverov VN, Kobayashi R, Normand J, Raghavachari K, Rendell A, Burant JC, Iyengar SS, Tomasi J, Cossi M, Rega N, Millam JM, Klene M, Knox JE, Cross JB, Bakken V, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Martin RL, Morokuma K, Zakrzewski VG, Voth GA, Salvador P, Dannenberg JJ, Dapprich S, Daniels AD, Farkas O, Foresman JB, Ortiz JV, Cioslowski J and Fox DJ. Gaussian, Inc., Wallingford CT, 2009.