Porphyrin Wheels

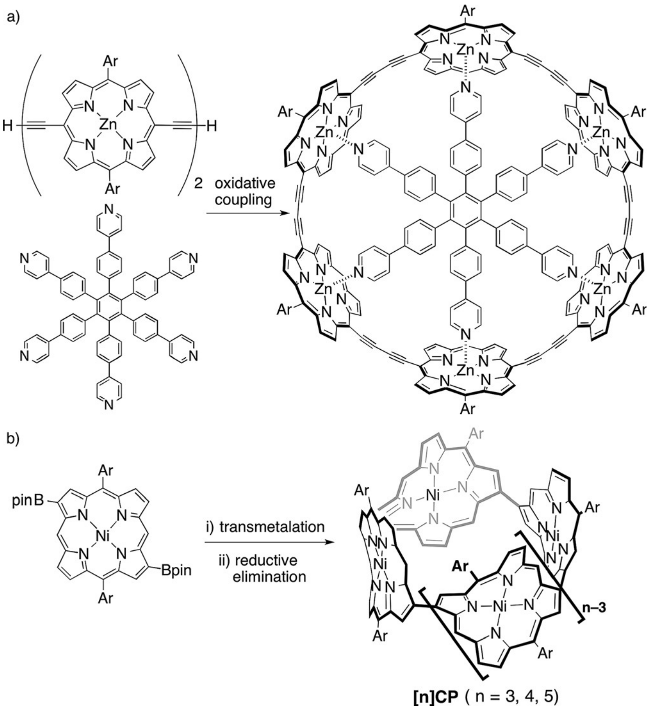
International Edition: DOI: 10.1002/anie.201507822
German Edition: DOI: 10.1002/ange.201507822

Synthesis of [*n*]Cyclo-5,15-porphyrinylene-4,4′-biphenylenes Displaying Size-Dependent Excitation-Energy Hopping

Hua-Wei Jiang, Takayuki Tanaka, Taeyeon Kim, Young Mo Sung, Hirotaka Mori, Dongho Kim, and Atsuhiro Osuka**

Abstract: *A set of 5,15-biphenylene-bridged porphyrin wheels, namely, [n]cyclo-5,15-porphyrinylene-4,4′-biphenylenes* ***[n]CPB****, have been synthesized through the platination of 5,15-bis(4-(pinacolboranyl)phenyl) nickel(II) porphyrin and subsequent reductive elimination of Pt^{II}(cod)-bridged cyclic porphyrin intermediates. The calculated strain energies for* ***[3]CPB****,* ***[4]CPB****,* ***[5]CPB****, and* ***[6]CPB*** *are 49.3, 32.9, 23.5, and 16.0 kcal mol^{-1}, respectively. UV/Vis absorption spectra and cyclic voltammetry indicated characteristic ring-size-dependent absorption-peak shifts and redox-potential shifts, which presumably reflect the degree of strain in the π-systems. Excitation-energy hopping (EEH) times were determined to be 5.1, 8.0, 8.0, and 9.6 ps for* ***[3]CPB****,* ***[4]CPB****,* ***[5]CPB****, and* ***[6]CPB****, respectively, in a pump-power-dependent TA experiment.*

Cyclic porphyrin arrays have been explored extensively as hosts for molecular recognition, models of artificial photosynthetic antenna complexes, and scaffolds for efficient hole delocalization.[1] In most cases, bent structural motifs, such as 1,3-phenylene bridges, were incorporated to construct porphyrin wheels.[2,3] In recent years, new synthetic strategies have been invented for the synthesis of porphyrin wheels from linear precursors. One strategy developed by Anderson and co-workers involves template-assisted oxidative coupling of *meso*-ethynyl zinc(II) porphyrins, which were thought not to be suitable as precursors for porphyrin wheels. Various 1,3-butadiyne-bridged cyclic oligomers were elegantly synthesized by this method (Scheme 1).[4] Later, this synthetic method was extended to include the Vernier template strategy, which has enabled the synthesis of specific large porphyrin wheels from linear oligomers through the use of a suitable templating host molecule, thus highlighting its effectiveness in overcoming the entropic disadvantages and inherent structural strain associated with cyclization.[4c]



Scheme 1. a) Template-assisted synthesis of butadiyne-bridged cyclic porphyrin oligomers. b) Two-step synthesis of **[*n*]CP** oligomers by platination and subsequent reductive elimination.

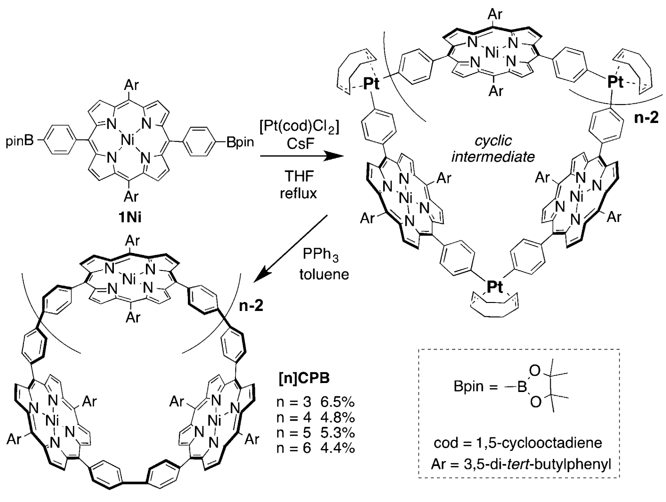
Another strategy makes use of a sequence of platinum(II) bridging and reductive elimination. This strategy was initially employed to synthesize cyclic 2,5-oligothiophenes and [*n*]cycloparaphenylenes ([*n*]CPP),[5–7] and has been used for the synthesis of nickel(II) [*n*]cyclo-2,12-porphyrinylenes **[*n*]CP** from 2,12-diborylated Ni^{II} porphyrins (Scheme 1 b).[8] An important factor in these syntheses is a preferred *cis* geometry of the platinum-bridged nanoring intermediates, which causes molecular curvature as a favorable structural feature for nanoring formation. To prove the generality of this strategy, we examined the synthesis of [*n*]cyclo-5,15-porphyrinylene-4,4′-biphenylenes (**[*n*]CPB**) as larger porphyrin wheels from a linear 5,15-bis(4-(pinacolboranyl)phenyl) Ni^{II} porphyrin precursor.

A solution of 5,15-bis(4-(pinacolboranyl)phenyl) nickel(II) porphyrin (**1Ni**) and [Pt(cod)Cl_2] in THF was heated at reflux in the presence of cesium fluoride (6 equiv) for 24 h to afford a mixture containing platinum-bridged cyclic porphyrin intermediates.[9] After the solvent had been changed to toluene, the mixture was refluxed in the presence of PPh_3 to promote reductive elimination (Scheme 2). Separation of the products by repeated recycling preparative gel permeation chromatography (GPC) with $CHCl_3$ as the eluent, followed by recrystallization, afforded cyclic oligomers: the cyclic trimer **[3]CPB**, tetramer **[4]CPB**, pentamer **[5]CPB**, and

---

[*] Dr. H.-W. Jiang, Dr. T. Tanaka, H. Mori, Prof. Dr. A. Osuka
Department of Chemistry, Graduate School of Science
Kyoto University
Sakyo-ku, Kyoto 606-8502 (Japan)
E-mail: osuka@kuchem.kyoto-u.ac.jp
T. Kim, Y. M. Sung, Prof. Dr. D. Kim
Spectroscopy Laboratory for Functional π-Electronic Systems and
Department of Chemistry, Yonsei University
Seoul 120-749 (Korea)
E-mail: dongho@yonsei.ac.kr

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201507822.



Scheme 2. Synthesis of **[*n*]CPB** oligomers.

hexamer **[6]CPB** in 6.5, 4.8, 5.3, and 4.4% yield, respectively.[10] The parent-ion peaks of **[*n*]CPB** were observed at $m/z = 2677.23$ (calcd for $C_{180}H_{174}N_{12}{}^{58}Ni_3$: 2677.20, $[M]^+$) for **[3]CPB**, at $m/z = 3569.53$ (calcd for $C_{240}H_{232}N_{16}{}^{58}Ni_4$: 3569.60, $[M]^+$) for **[4]CPB**, at $m/z = 4462.16$ (calcd for $C_{300}H_{290}N_{20}{}^{58}Ni_5$: 4462.01, $[M]^+$) for **[5]CPB**, and at $m/z = 5354.42$ (calcd for $C_{360}H_{348}N_{24}{}^{58}Ni_6$: 5354.41, $[M]^+$) for **[6]CPB** by matrix-assisted laser desorption–ionization time-of-flight mass spectrometry (MALDI-TOF MS). When the platination reaction was conducted at room temperature for 4 days with the intention of facilitating the formation of larger oligomers, oligomers larger than **[7]CPB** were detected by MALDI-TOF MS (see Figures S4–S10 in the Supporting Information). However, poor yields and low solubility have hampered the isolation of such large wheels, and the yields of **[*n*]CPB** wheels with $n = 3$–6 were even lower under these conditions. None of the corresponding **[*n*]CPB** rings were obtained from either Zn^{II} or free-base porphyrin precursors under similar conditions, thus suggesting that a Ni^{II} porphyrin scaffold is of vital importance for the successful formation of porphyrin nanorings, in analogy with the formation of **[*n*]CP** systems.[8]

In line with the symmetrical (D_{nh}) structures of the **[*n*]CPB** nanorings, their ^{1}H and ^{13}C NMR spectra display a single set of signals for the porphyrin and biphenylene bridge. In the aromatic region of the ^{1}H NMR spectra of the **[*n*]CPB** oligomers (Figure 1), two doublets due to the porphyrinic β-hydrogen atoms (H^c and H^d), two doublets due to the hydrogen atoms of the biphenylene bridge (H^a and H^b), and signals due to the aromatic hydrogen atoms of the 3,5-di-*tert*-butylphenyl groups (H^e and H^f) are observed. The chemical shifts of the signals for H^a and H^b are progressively shifted downfield, nearer to the position of the signals of the reference monomer **1Ni**, as the ring size increases. These shifts may be ascribed to the bending effect (for angles θ^1 and θ^2, see the Supporting Information), as seen in the case of [*n*]CPP.[7b] The chemical shift of H^c remains at a rather constant position, but that of H^d is shifted downfield as the ring size increases. The observed chemical-shift change of H^d may be explained in terms of increasing aromaticity and thus an increase in the diatropic ring current of the Ni^{II} porphyrin, since the Ni^{II} porphyrin is more distorted in the small wheel. The chemical shift of H^c is dependent upon both the diatropic ring current of the Ni^{II} porphyrin and the anisotropy of the *meso*-phenylene group. These two factors may compensate each other in the case of H^c. The H^e atoms in **[3]CPB** and **[4]CPB** are observed as broad signals, probably owing to restriction of the free rotation of the *meso*-aryl groups on the ^{1}H NMR timescale.

The structure of the most distorted nanoring, **[3]CPB**, was determined by X-ray diffraction analysis, which showed a wheel structure with a diameter of 15–16 Å (Figure 2).[11] The Ni^{II} porphyrins were severely ruffled with mean-plane-deviation (MPD) values of 0.373–0.420 Å, which are slightly

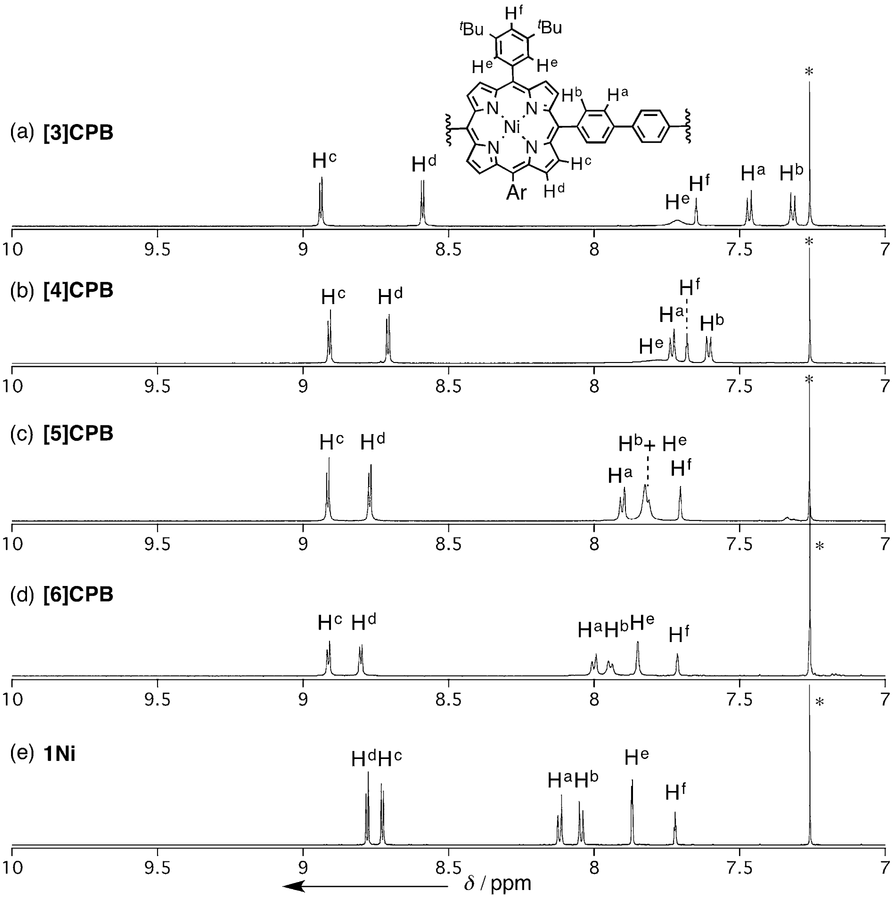


Figure 1. ^{1}H NMR spectra of a) **[3]CPB**, b) **[4]CPB**, c) **[5]CPB**, d) **[6]CPB**, and e) **1Ni** in CDCl$_3$ at room temperature.

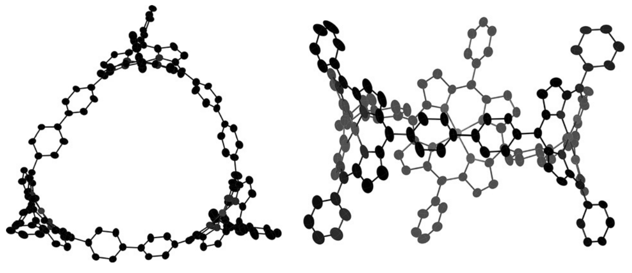


Figure 2. X-ray crystal structures of **[3]CPB**, top view (left) and side view (right). The asymmetric unit contains two molecules. *tert*-Butyl groups, solvent molecules, and hydrogen atoms have been omitted for clarity. The ellipsoids are scaled to 30% probability.

larger than those of *meso*-tetraaryl Ni^{II} porphyrin monomers (0.2–0.3 Å).[12] Structural optimization of **[3]CPB** was performed by Gaussian09, starting either from the crystal structure (C_1 symmetry) or with the assumption of D_3 symmetry.[13,14] The D_3 conformer was found to be only slightly higher in energy than the C_1 form (ca. 1.2 kcal mol^{-1}). Therefore, we used the structures optimized on the basis of the assumption of D_n symmetry (Table 1) for further consideration. The strain energy was calculated by the homodesmotic reaction model[13] to be 49.3, 32.9, 23.5, and 16.0 kcal mol^{-1} for **[3]CPB**, **[4]CPB**, **[5]CPB**, and **[6]CPB**, respectively. As the number of porphyrin units increases, the dihedral angle α between the *p*-phenylene and Ni^{II} porphyrin units becomes larger, whereas the dihedral angle β between two *p*-phenylene units decreases.

Table 1: Structures of **[*n*]CPB**, as calculated by Gaussian09 at the level of B3LYP/6-31G(d) (for C,H,N) + LANL2DZ (Ni) with the assumption of D_n symmetry.

Compound	Diameter [Å]	MPD [Å][a]	α [°][b]	β [°][c]	ΔH [kcal mol^{-1}][d]
[3]CPB	16.0	0.376	63.1	56.2	49.3
[4]CPB	22.4	0.331	66.3	47.1	32.9
[5]CPB	26.9	0.300	67.9	43.5	23.5
[6]CPB	33.1	0.274	68.9	41.4	16.0

[a] Mean-plane deviation defined by the average distance between the mean plane of 24 core atoms and each atom. [b] Dihedral angle between the Ni^{II} porphyrin plane and the *p*-phenylene unit. The porphyrin plane was defined by the connecting *meso*-carbon atom and two neighboring carbon atoms. [c] Dihedral angle between the two *p*-phenylene planes. [d] Strain energy calculated by the homodesmotic reaction model (for calculation details, see the Supporting Information).

Demetalation of the **[*n*]CPB** oligomers was examined by treatment with sulfuric acid in trifluoroacetic acid. The corresponding free bases were obtained and characterized by MALDI-TOF MS and ^{1}H NMR spectroscopy (see the Supporting Information). However, these free-base porphyrins were found to be rather unstable under ambient conditions, which hampered their full characterization.[15] Indeed, DFT calculations revealed the strain energy of the corresponding free bases to be much higher than that of the Ni^{II} complexes (67.2, 49.0, 41.2, and 32.6 kcal mol^{-1} for the free-base derivatives of **[3]CPB**, **[4]CPB**, **[5]CPB**, and **[6]CPB**, respectively). Furthermore, the strain energies of the corresponding Zn^{II} complexes were calculated to be even larger. These results again indicate the particular suitability of Ni^{II} porphyrin scaffolds for accommodating the strained cyclic structures.

Soret-like bands were observed at 435, 430, 428, and 427 nm and Q-like bands at 559 and 600 nm, 549 and 587 nm, 542 and 586 nm, and 540 and 586 nm in the UV/Vis absorption spectra of **[3]CPB**, **[4]CPB**, **[5]CPB**, and **[6]CPB**, respectively (Figure 3). Both the Soret and the Q-like bands were red-shifted and broadened as the ring size decreased. This trend can be explained on the basis of the dihedral angle α. As the angle α becomes smaller, the porphyrin unit becomes more conjugated to the biphenylene segment, thus resulting in the red-shifts of the absorption bands. Furthermore, a bent porphyrin chromophore itself shows red-shifted absorption bands.[16]

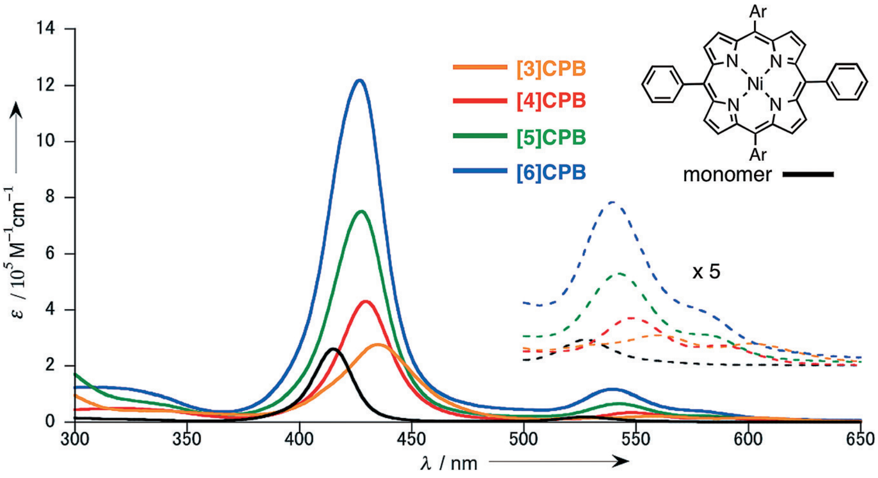


Figure 3. UV/Vis absorption spectra of **[*n*]CPB** oligomers and the monomer in CH_2Cl_2.

Cyclic voltammetry (CV) and differential-pulse voltammetry (DPV) experiments were conducted for the **[*n*]CPB** oligomers (see the Supporting Information). The electrochemical HOMO–LUMO gaps (ΔE_{HL}) become smaller as the ring size decreases, probably as a result of increased structural distortion. DFT molecular-orbital energy calculations reproduced this tendency (see Figure S7-2). In both the HOMO and the LUMO, the orbital coefficients are localized on the porphyrin moiety, and the interaction between two porphyrin units through the biphenylene linker is negligible (see Figure S7-3). The first oxidation and reduction potentials of **[6]CPB** are similar to those of the Ni^{II} porphyrin monomer.

To examine the excited-state dynamics of the **[*n*]CPB** systems, we measured their femtosecond transient absorption (fs-TA) spectra (see the Supporting Information). The TA spectra exhibited broad excited-state absorption (ESA) bands at the initial stage, and subsequent rapid spectral changes led to sharp derivative-like TA spectra as a result of the formation of a Ni^{II} ^{3}(d,d) state. These spectral features are characteristic of Ni^{II} porphyrin derivatives.[17] Generally, it was previously reported that the excited Ni^{II} porphyrin returns to the ground state by three main dynamic pathways. First, upon photoexcitation, the excited Ni^{II} porphyrin molecules in the $^1(\pi,\pi^*)$ state undergo energy transfer within a sub-picosecond time frame to a Ni^{II}-centered $^3(d_{z^2},d_{x^2-y^2})$ state, hereinafter referred to as the ^{3}(d,d) state, owing to a strong electronic interaction between the $^1(\pi,\pi^*)$ state and the ^{3}(d,d) state. Next, a vibrational cooling process from the vibrationally hot ^{3}(d,d) state to the relaxed ^{3}(d,d) state proceeds in 5–25 ps, followed by ground-state recovery with a time constant of approximately 200 ps. Accordingly, the TA decay profiles of the **[*n*]CPB** series are in good agreement with these dynamics, and the time constants varied slightly depending on the degree to which the structures were ruffled, which directly affects their electronic energy levels.

To explore the excitation-energy migration processes occurring in **[*n*]CPB**, we measured the pump-power-dependent TA spectra by varying the averaged pump power (1, 2, and 4 mW; Figure 4). The pump-power-dependent TA decay profiles provide strong evidence for exciton–exciton annihilation processes. Upon photoexcitation with high-density photons, two or more excitons are generated within a molecule. Then, adjacent excitons interact to form a doubly excited state, which rapidly relaxes to the S_1 state. The exciton–exciton annihilation process occurs due to the migration-limited process (Figure 4; see also Table S7).[16] In this regard, we evaluated the time constant of the EEH dynamics by extracting the hopping time (τ_h) from the exciton–exciton annihilation time (τ_a) according to Equation (1):[2d,18,19]

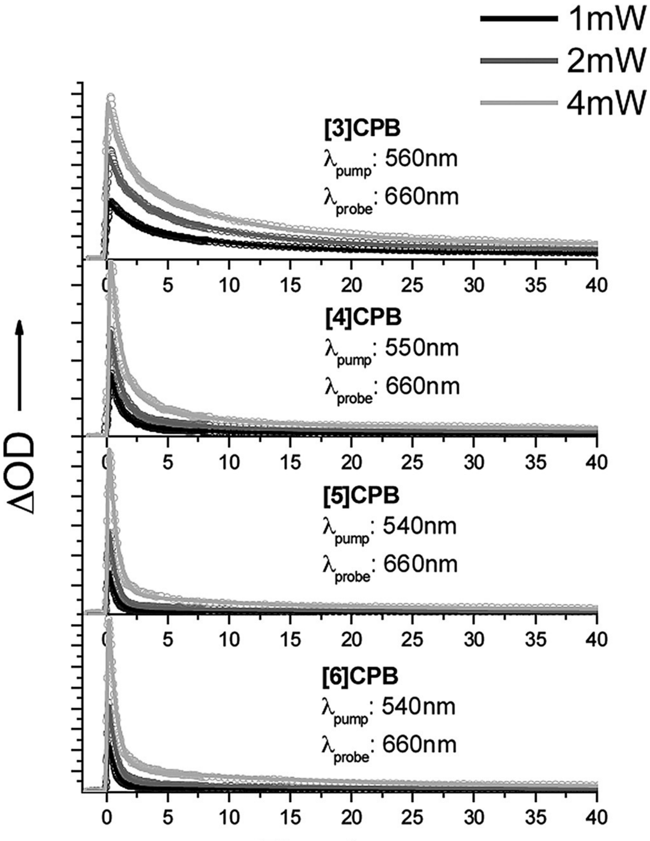


Figure 4. Pump-power-dependent TA decay profile of **[*n*]CPB** oligomers in toluene.

$$\tau_a = (\tau_h(N^2-1))/24 \qquad (1)$$

Thus, the pump-power-dependent TA decay profiles were fitted with three decay components as described above. In the **[*n*]CPB** series, except in the case of **[3]CPB**, the fastest decay component is regarded as the transition from $^1(\pi,\pi^*)$ to the ^{3}(d,d) state, because this decay process does not show power-dependent behavior. In contrast, **[3]CPB** exhibits pump-power dependence in the fastest decay component (1.3 ps), which indicates that **[3]CPB** exhibits competition between the transition $^1(\pi,\pi^*)\rightarrow{}^3$(d,d) and the exciton–exciton annihilation process in the $^1(\pi,\pi^*)$ state. On the basis of the annihilation times of 1.3, 5, 8, and 13 ps observed for **[3]CPB**, **[4]CPB**, **[5]CPB**, and **[6]CPB**, we determined τ_h times of 5.1, 8.0, 8.0, and 9.6 ps for **[3]CPB**, **[4]CPB**, **[5]CPB**, and **[6]CPB**, respectively, by using Equation (1). The trend of a slower EEH process for a larger **[*n*]CPB** ring may be directly related to the increased distance between Ni^{II} porphyrin units. These results are similar to our previous findings on the EEH times in **[*n*]CP**.[8]

In summary, we synthesized a series of oligomers **[*n*]CPB** through PPh_3-mediated reductive elimination from Pt^{II}(cod)-bridged intermediates. These novel cyclic porphyrin arrays have moderate ring-strain energies. UV/Vis absorption spectra and cyclic voltammetry indicated characteristic ring-size-dependent absorption-peak shifts and redox-potential shifts. Furthermore, EEH dynamics in **[*n*]CPB** were analyzed in pump-power dependent TA experiments. Denickelation of **[*n*]CPB** gave the corresponding free-base porphyrins, which were rather unstable, thus indicating that a Ni^{II} porphyrin scaffold is of vital importance for the successful formation of the porphyrin nanorings.

Acknowledgements

The research at Kyoto University was supported by JSPS KAKENHI Grants (numbers 25220802 and 25620031). We thank Professor Dr. Hiromitsu Maeda and Dr. Yuya Bando (Ritsumeikan University) for MALDI-TOF MS measurements. We thank Dr. H. Sato (Rigaku) for his help in refinement of the crystal structure. The research at Yonsei University was supported by the Global Research Laboratory (GRL) Program (2013K1A1A2A02050183) of the Ministry of Education, Science and Technology (MEST) of Korea.

Keywords: energy transfer · nickel · platination · porphyrinoids · porphyrin wheels

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 15197–15201
Angew. Chem. **2015**, *127*, 15412–15416

[1] a) S. Anderson, H. L. Anderson, J. K. M. Sanders, *Acc. Chem. Res.* **1993**, *26*, 469; b) A. Satake, Y. Kobuke, *Tetrahedron* **2005**, *61*, 13; c) Y. Nakamura, N. Aratani, A. Osuka, *Chem. Soc. Rev.* **2007**, *36*, 831; d) C. Maeda, T. Kamada, N. Aratani, A. Osuka, *Coord. Chem. Rev.* **2007**, *251*, 2743; e) T. Hori, Y. Nakamura, N. Aratani, A. Osuka, *J. Organomet. Chem.* **2007**, *692*, 148; f) N. Aratani, D. Kim, A. Osuka, *Acc. Chem. Res.* **2009**, *42*, 1922; g) N. Aratani, A. Osuka, *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1.

[2] a) J. Li, A. Ambroise, S. I. Yang, J. R. Diers, J. Seth, C. R. Wack, D. F. Bocian, D. Holten, J. S. Lindsey, *J. Am. Chem. Soc.* **1999**, *121*, 8927; b) X. Peng, N. Aratani, A. Takagi, T. Matsumoto, T. Kawai, I.-W. Hwang, T. K. Ahn, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2004**, *126*, 4468; c) A. Kato, K. Sugiura, H. Miyasaka, H. Tanaka, T. Kawai, M. Sugimoto, M. Yamashita, *Chem. Lett.* **2004**, *33*, 578; d) Y. Nakamura, I.-W. Hwang, N. Aratani, T. K. Ahn, D. M. Ko, A. Takagi, T. Kawai, T. Matsumoto, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2005**, *127*, 236; e) T. Hori, N. Aratani, A. Takagi, T. Matsumoto, T. Kawai, M.-C. Yoon, Z. S. Yoon, S. Cho, D. Kim, A. Osuka, *Chem. Eur. J.* **2006**, *12*, 1319; f) S. Rucareanu, A. Schuwey, A. Gossauer, *J. Am. Chem. Soc.* **2006**, *128*, 3396; g) N. Aratani, A. Osuka, *Chem. Commun.* **2008**, 4076; h) J. Song, N. Aratani, H. Shinokubo, A. Osuka, *J. Am. Chem. Soc.* **2010**, *132*, 16356; i) H.-W. Jiang, S. Ham, N. Aratani, D. Kim, A. Osuka, *Chem. Eur. J.* **2013**, *19*, 13328.

[3] a) R. Takahashi, Y. Kobuke, *J. Am. Chem. Soc.* **2003**, *125*, 2372; b) Y. Kuramochi, A. Satake, Y. Kobuke, *J. Am. Chem. Soc.* **2004**, *126*, 8668; c) I.-W. Hwang, T. Kamada, T. K. Ahn, D. M. Ko, T. Nakamura, A. Tsuda, A. Osuka, D. Kim, *J. Am. Chem. Soc.* **2004**, *126*, 16187; d) C. Maeda, P. Kim, S. Cho, J. K. Park, J. M. Lim, D. Kim, J. Vura-Weis, M. R. Wasielewski, H. Shinokubo, A. Osuka, *Chem. Eur. J.* **2010**, *16*, 5052.

[4] a) M. Hoffmann, C. J. Wilson, B. Odell, H. L. Anderson, *Angew. Chem. Int. Ed.* **2007**, *46*, 3122; *Angew. Chem.* **2007**, *119*, 3183; b) M. Hoffmann, J. Kärnbratt, M.-H. Chang, L. M. Herz, B. Albinsson, H. L. Anderson, *Angew. Chem. Int. Ed.* **2008**, *47*, 4993; *Angew. Chem.* **2008**, *120*, 5071; c) M. C. O'Sullivan, J. K. Sprafke, D. V. Kondratuk, C. Rinfray, T. D. W. Claridge, A. Saywell, M. Blunt, J. N. O'Shea, P. H. Beton, M. Malfois, H. L. Anderson, *Nature* **2011**, *469*, 72; d) J. K. Sprafke, D. V. Kondratuk, M. Wykes, A. L. Thompson, M. Hoffmann, R. Drevinskas, W.-H. Chen, C. K. Yong, J. Kärnbratt, J. E. Bullock, M. Malfois, M. R. Wasielewski, B. Albinsson, L. M. Herz, D. Zigmantas, D. Beljonne, H. L. Anderson, *J. Am. Chem. Soc.* **2011**, *133*, 17262; e) D. V. Kondratuk, L. M. A. Perdigao, M. C. O'Sullivan, S. Svatek, G. Smith, J. N. O'Shea, P. H. Beton, H. L. Anderson, *Angew. Chem. Int. Ed.* **2012**, *51*, 6696; *Angew. Chem.* **2012**, *124*, 6800; f) D. V. Kondratuk, J. K. Sprafke, M. C. O'Sullivan, L. M. A. Perdigao, A. Saywell, M. Malfois, J. N. O'Shea, P. H. Beton, A. L. Thompson, H. L. Anderson, *Chem. Eur. J.* **2014**, *20*, 12826; g) P. Neuhaus, A. Cnossen, J. Q. Gong, L. M. Herz, H. L. Anderson, *Angew. Chem. Int. Ed.* **2015**, *54*, 7344; *Angew. Chem.* **2015**, *127*, 7452.

[5] a) H. Omachi, Y. Segawa, K. Itami, *Acc. Chem. Res.* **2012**, *45*, 1378; b) E. S. Hirst, R. Jasti, *J. Org. Chem.* **2012**, *77*, 10473; c) T. J. Sisto, R. Jasti, *Synlett* **2012**, 483; d) S. Yamago, E. Kayahara, T. Iwamoto, *Chem. Rec.* **2014**, *14*, 84; e) R. Jasti, J. Bhattacharjee, J. B. Neaton, C. R. Bertozzi, *J. Am. Chem. Soc.* **2008**, *130*, 17646; f) H. Takaba, H. Omachi, Y. Yamamoto, J. Bouffard, K. Itami, *Angew. Chem. Int. Ed.* **2009**, *48*, 6112; *Angew. Chem.* **2009**, *121*, 6228.

[6] a) F. Zhang, G. Götz, H. D. F. Winkler, C. A. Schalley, P. Bäuerle, *Angew. Chem. Int. Ed.* **2009**, *48*, 6632; *Angew. Chem.* **2009**, *121*, 6758; b) K. Asai, A. Fukazawa, S. Yamaguchi, *Chem. Commun.* **2015**, *51*, 6096; c) M. Ball, B. Fowler, P. Li, L. A. Joyce, F. Li, T. Liu, D. Paley, Y. Zhong, H. Li, S. Xiao, F. Ng, M. L. Steigerwald, C. Nuckolls, *J. Am. Chem. Soc.* **2015**, *137*, 9982.

[7] a) S. Yamago, Y. Watanabe, T. Iwamoto, *Angew. Chem. Int. Ed.* **2010**, *49*, 644; *Angew. Chem.* **2010**, *122*, 654; b) T. Iwamoto, Y. Watanabe, Y. Sakamoto, T. Suzuki, S. Yamago, *J. Am. Chem. Soc.* **2011**, *133*, 8354; c) E. Kayahara, Y. Sakamoto, T. Suzuki, S. Yamago, *Org. Lett.* **2012**, *14*, 3284; d) E. Kayahara, T. Iwamoto, T. Suzuki, S. Yamago, *Chem. Lett.* **2013**, *42*, 621; e) T. Iwamoto, E. Kayahara, N. Yasuda, T. Suzuki, S. Yamago, *Angew. Chem. Int. Ed.* **2014**, *53*, 6430; *Angew. Chem.* **2014**, *126*, 6548; f) S. Hitosugi, T. Yamasaki, H. Isobe, *J. Am. Chem. Soc.* **2012**, *134*, 12442; g) T. Matsuno, S. Kamata, S. Hitosugi, H. Isobe, *Chem. Sci.* **2013**, *4*, 3179.

[8] H.-W. Jiang, T. Tanaka, H. Mori, K. H. Park, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2015**, *137*, 2219.

[9] The intermediates were not identified in the current study, but we determined the structures and properties of Pt^{II}(cod)-bridged porphyrin dimers very recently: H.-W. Jiang, T. Tanaka, A. Osuka, *Chem. Sci.* **2015**, *6*, 6102.

[10] The major products were linear oligomers. The solubility of long linear oligomers was very poor, and these compounds were readily removed by precipitation and separated on a short silica-gel column.

[11] Crystallographic data for **[3]CPB**: $C_{360}H_{348}N_{24}Ni_6$; $M_w = 5362.78\ \mathrm{g\,mol^{-1}}$; monoclinic; $P2_1/c$ (No. 14); $a = 33.8505(6)$, $b = 36.5556(7)$, $c = 33.6745(7)$ Å; $\beta = 96.1655(18)°$; $V = 41428.7(14)$ Å^3; $Z = 4$; $D_{calcd} = 0.860\ \mathrm{g\,cm^{-3}}$; $R_1 = 0.1226$ [$I > 2\sigma(I)$]; $wR_2 = 0.3952$ (all data); GOF = 1.230. CCDC 1419552 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. The contributions to the scattering arising from the presence of disordered solvent molecules in the crystal were removed by use of the utility SQUEEZE in the PLATON software package.[20]

[12] R. Scheidt in *The Porphyrin Handbook*, *Vol. 3* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), Academic Press, San Diego, **2000**, pp. 49–112.

[13] In the case of [12]CPP, 15 stable conformations have been computed, and the most stable form was a D_{2d}-symmetric conformation with a dihedral angle of 33° between each biphenylene unit: Y. Segawa, H. Omachi, K. Itami, *Org. Lett.* **2010**, *12*, 2262.

[14] M. J. Frisch et al., Gaussian 09, Revision A.03, Gaussian, Inc., Wallingford, CT, **2009**.

[15] The observed instability of the free-base porphyrin wheels may be ascribed to large strain associated with the ring structures. Thus, the Ni^{II} porphyrin appears to be important for the ring structures.

[16] a) A. B. J. Parusel, T. Wondimagegn, A. Ghosh, *J. Am. Chem. Soc.* **2000**, *122*, 6371; b) R. E. Haddad, S. Gazeau, J. Pécaut, J.-C. Marchon, C. J. Medforth, J. A. Shelnutt, *J. Am. Chem. Soc.* **2003**, *125*, 1253; c) J. S. Evans, R. L. Musselman, *Inorg. Chem.* **2004**, *43*, 5613.

[17] X. Zhang, E. C. Wasinger, A. Z. Muresan, K. Attenkofer, G. Jennings, J. S. Lindsey, L. X. Chen, *J. Phys. Chem. A* **2007**, *111*, 11736.

[18] S. E. Bradforth, R. Jimenez, F. Vanmourik, R. Vangrondelle, G. R. Fleming, *J. Phys. Chem.* **1995**, *99*, 16179.

[19] J. Yang, M.-C. Yoon, H. Yoo, P. Kim, D. Kim, *Chem. Soc. Rev.* **2012**, *41*, 4808.

[20] a) A. L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht, The Netherlands, **2005**; b) P. van der Sluis, A. L. Spek, *Acta Crystallogr. Sect. A* **1990**, *46*, 194.

Received: August 21, 2015