ChemPubSoc Europe

DOI: 10.1002/chem.201600473

CHEMISTRY
A European Journal
Communication

Stereochemistry | *Hot Paper* |

Porphyrin Analogues of a Trityl Cation and Anion

Kenichi Kato,[a] Woojae Kim,[b] Dongho Kim,*[b] Hideki Yorimitsu,*[a] and Atsuhiro Osuka*[a]

Abstract: Porphyrin-stabilized *meso*- or β-carbocations were generated upon treatment of the corresponding bis(4-*tert*-butylphenyl)porphyrinylcarbinols with trifluoroacetic acid (TFA). Bis(4-*tert*-butylphenyl)porphyrinylcarbinols were treated with TFA to generate the corresponding carbocations stabilized by a *meso*- or β-porphyrinyl group. The *meso*-porphyrinylmethyl carbocation displayed more effective charge delocalization with decreasing aromaticity compared with the β-porphyrinylmethyl carbocation. A propeller-like porphyrin trimer, tris(β-porphyrinyl)carbinol, was also synthesized and converted to the corresponding cation that displayed a more intensified absorption reaching over the NIR region. *meso*-Porphyrinylmethyl carbanion was generated as a stable species upon deprotonation of bis(4-*tert*-butylphenyl)(*meso*-porphyrinyl)methane with potassium bis(trimethylsilyl)amide (KHMDS) and [18]crown-6, whereas β-porphyrinylmethyl anions were highly unstable.

Since its discovery as the first identified carbocation in 1901,[1] the triphenylmethyl cation has played an indispensable role in the understanding of a huge number of reaction mechanisms as well as the development of fundamental concepts about π-electronic delocalization. This unusually stable carbocation and its derivatives have found widespread usage as protecting groups, Lewis acids, and chromophores and fluorophores.[2]

With various important functions of porphyrins taken into consideration, porphyrin-stabilized carbocations are attractive molecules in terms of effective electronic delocalization and resultant low-energy absorption. Despite these promises, porphyrin-stabilized carbocations have been scarcely studied so far.[3] In these studies, strong absorptions were observed in NIR region for porphyrin-stabilized cations as a consequence of effective charge delocalization. It is desirable to develop more general synthetic methods to generate such cations. On the other hand, porphyrin-stabilized carbanions have not been characterized in the literature to the best of our knowledge. Herein, we disclose the effective generation of porphyrin analogues of a trityl cation by using porphyrinyllithium reagents. We also report the generation of a porphyrin analogue of a trityl anion.

Porphyrinyllithium reagents recently developed by us are useful reactive species possessing high nucleophilicity.[4] In fact, *meso*- and β-lithioporphyrins prepared from the corresponding iodoporphyrins[5] furnished the corresponding carbinols **1 OH** and **2 OH** by their reactions with 4,4′-di-*tert*-butylbenzophenone, respectively (Scheme 1). In the next step, we attempted to synthesize trisporphyrinylcarbinols by using lithioporphyrins and soon found that tris(*meso*-porphyrinyl)carbinol was very difficult to synthesize due to serious steric hindrance. On the other hand, tris(β-porphyrinyl)carbinol **3 OH** was formed in approximately 40 % yield by reaction of the β-lithioporphyrin with dimethyl carbonate, but the reaction was not very clean, hampering the isolation of **3 OH**. After further optimization, we found that **3 OH** was obtained in a better yield of 72 % when β-lithioporphyrin generated upon treatment of β-iodoporphyrin with 4-(*N*,*N*-dimethylamino)phenyllithium[6] was used for the reaction with dimethyl carbonate in the presence of LiCl. The addition of LiCl also improved the yield of **2 OH** significantly. (Scheme 1, conditions b,c). These carbinols **1 OH**, **2 OH**, and **3 OH** were reduced to the corresponding triarylmethanes **1 H**, **2 H**, and **3 H** by ionic hydrogenation reaction with $HBF_4{\cdot}OEt_2$ and $BH_3{\cdot}NEt_3$ in excellent to quantitative yield (Scheme 1, conditions d). These newly synthesized compounds have been characterized by high-resolution APCI- or MALDI-TOF-MS and NMR experiments (see the Supporting Information).

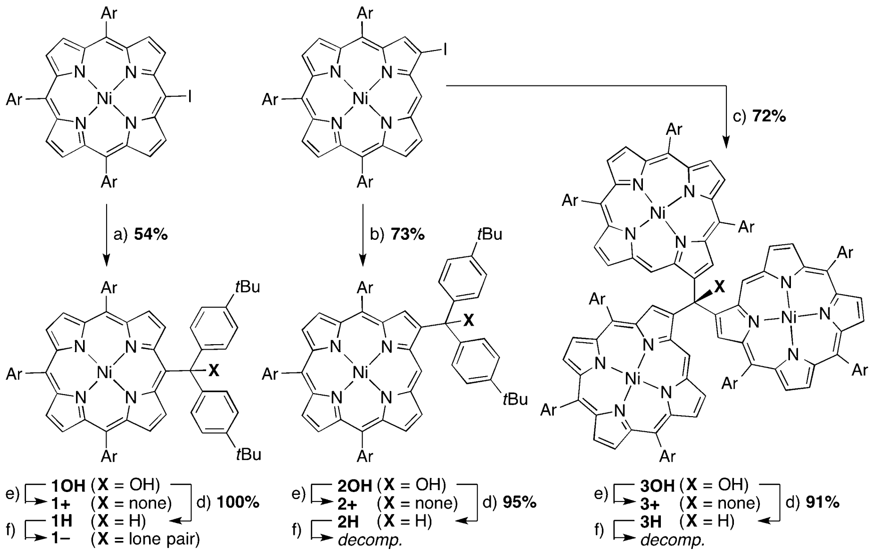
The structures of **1 OH** and **3 OH** have been revealed by single-crystal X-ray diffraction analysis to be diarylporphyrinyl carbinol and trisporphyrinylcarbinol, respectively (Figure 1 a–c). In **3 OH**, the three porphyrin moieties are tilted with dihedral angles of 40-55° in a propeller-like manner. The ^{1}H NMR spectrum of **1 OH** in $CDCl_3$ (Figure 2) was slightly broad at room temperature but became sharp at 60 °C, probably due to rotational hindrance at room temperature. On the other hand, that of **2 OH** was sharp even at room temperature, suggesting less rotational hindrance. The ^{1}H NMR spectrum of **3 OH** was rather broad at room temperature in $CDCl_3$ and did not become almost sharp until heating at 120 °C in $CDCl_2CDCl_2$, which indicated larger rotational hindrance (Supporting Information). When the measurement temperature was cooled at −60 °C, the ^{1}H NMR spectrum of **3 OH** became clear. A singlet at $\delta =$ 10.48 ppm due to the *meso*-protons, a broad singlet at $\delta =$

---

[a] K. Kato, Prof. Dr. H. Yorimitsu, Prof. Dr. A. Osuka
Department of Chemistry, Graduate School of Science
Kyoto University
Sakyo-ku Kyoto, 606-8502 (Japan)
E-mail: yori@kuchem.kyoto-u.ac.jp
osuka@kuchem.kyoto-u.ac.jp

[b] W. Kim, 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/chem.201600473.



Scheme 1. Synthesis of porphyrinylcarbinols and their conversions into the corresponding cations, hydrides, and anion. a) i) 1.5 equiv *n*BuLi, 3.0 equiv LiCl, THF, −98 °C, 30 min, ii) 2 equiv 4,4′-di-*tert*-butylbenzophenone, −98 °C to RT, 1 h; b) i) 1.5 equiv *n*BuLi, THF, −98 °C, 30 min, ii) 2 equiv 4,4′-di-*tert*-butylbenzophenone, −98 °C to RT, 1 h;. c) i) 1.00 equiv 4-(*N*,*N*-dimethylamino)phenyllithium, 3.0 equiv LiCl, THF, −98 °C, 30 min, ii) 0.28 equiv dimethyl carbonate, −98 °C to RT, 1 h; d) i) 10 equiv $HBF_4{\cdot}OEt_2$, CH_2Cl_2, RT, 10 miin, ii) 5.0 equiv $BH_3{\cdot}NEt_3$, RT, 10 min, e) TFA, CH_2Cl_2, RT, f) 20 equiv [18]crown-6, 20 equiv KHMDS, THF, RT. Ar = 3,5-di-*tert*-butylphenyl.

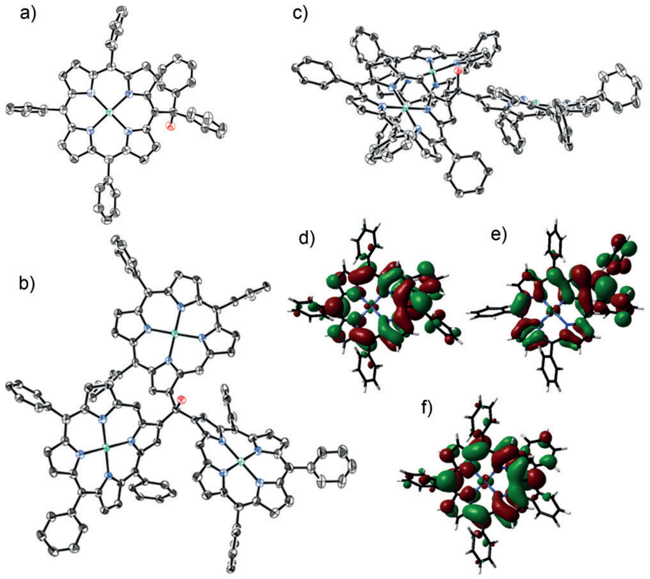


Figure 1. X-ray crystal structures of **1OH** and **3OH**. a) Top view of **1OH**. b) Top view and c) side view of **3OH** (one of two independent molecules is shown). The thermal ellipsoids are drawn at 50% probability. *tert*-Butyl groups, all hydrogen atoms, and solvent molecules are omitted for clarity. Kohn–Sham orbital representations on the optimized structures at the B3LYP/6-31G(d) level. LUMOs of d) **1+′** and e) **2+′**. f) HOMO of **1−′**.

5.63 ppm due to the hydroxyl proton, seven signals due to the pyrrolic β-protons, nine signals due to the *meso*-aryl protons, and six signals due to the protons of the *tert*-butyl groups indicated that rotations of the porphyrinyl groups and 3,5-di-*tert*-butylphenyl groups were frozen. On the other hand, the ^{1}H NMR spectrum of **3H** at room temperature showed sharp signals due to the pyrrolic β-protons and broad signals due to

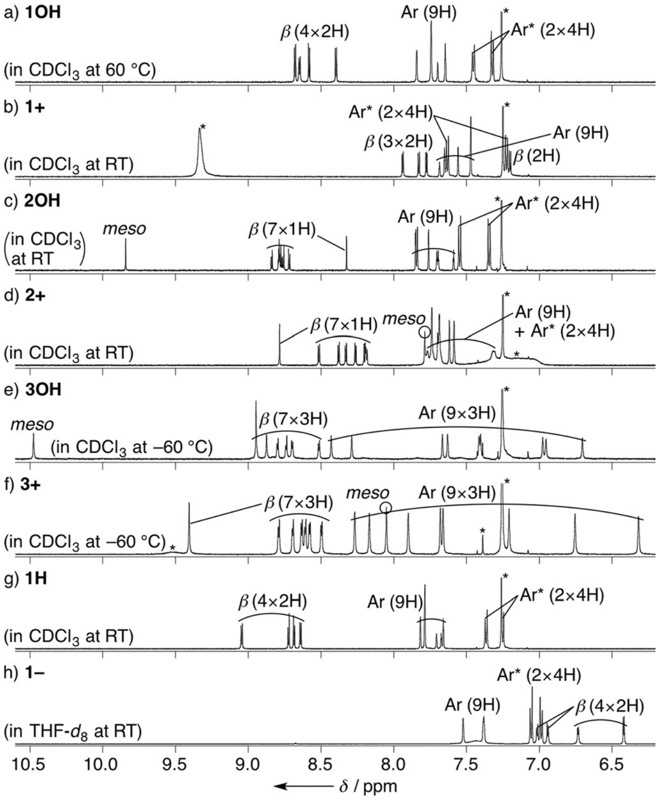


Figure 2. Aromatic region of the ^{1}H NMR spectra of a) **1OH**, b) **1+**, c) **2OH**, d) **2+**, e) **3OH**, f) **3+**, g) **1H**, and h) **1−**. Peaks marked with * are due to residual solvents and protonated water. Ar = 3,5-di-*tert*-butylphenyl and Ar* = 4-*tert*-butylphenyl.

the aryl protons, which have been ascribed to less rotational hindrance around the central carbon (Supporting Information).

Cations **1+**, **2+**, and **3+** were readily generated upon addition of trifluoroacetic acid (TFA) (ca. 0.5 %) to their solutions in CH_2Cl_2 or $CDCl_3$. In the ^{1}H NMR spectrum of **1+** taken at room temperature, the signals due to the pyrrolic protons were observed as sharp signals in an upfield region ($\delta = 7.95$–7.21 ppm) as compared with those ($\delta = 8.68$–8.40 ppm) of **1 OH**. Considering the positive charge at the periphery of the porphyrin, these upfield shifts were unexpected but can be rationalized in terms of decreased diatropic ring current associated with the effective charge delocalization onto the porphyrin π-system, which gives rise to an increased contribution of nonaromatic resonance contributor. Cation **1+** characteristically displayed a smeared Soret band at $\lambda = 424$ nm and a broad band around $\lambda = 713$ nm (Figure 3). Similarly, the pyrrolic protons of **2+** were upfield shifted ($\delta = 8.80$–8.20 ppm) from those ($\delta = 8.84$–8.32 ppm) of **2 OH** and the absorption spectrum of **2+** showed a smeared Soret band at $\lambda = 407$ nm and a broad band around $\lambda = 816$ nm. Upfield shifts of the pyrrolic β-protons were also observed for **3+** ($\delta = 9.41$–8.50 ppm) but their extents were much smaller compared with those of **1+** and **2+**. This may be explained by considering equal delocalization of the single positive charge over the three porphyrin units.[7] Namely, each porphyrin may receive one-third of the cation effect. In addition, the ^{1}H NMR spectrum of **3+** revealed substantial rotational hindrance of the porphyrinyl groups (Supporting Information). Different from **1+** and **2+**, **3+** displayed an absorption spectrum that contained a relatively sharp Soret band at $\lambda = 424$ nm and a broad band around $\lambda = 958$ nm.

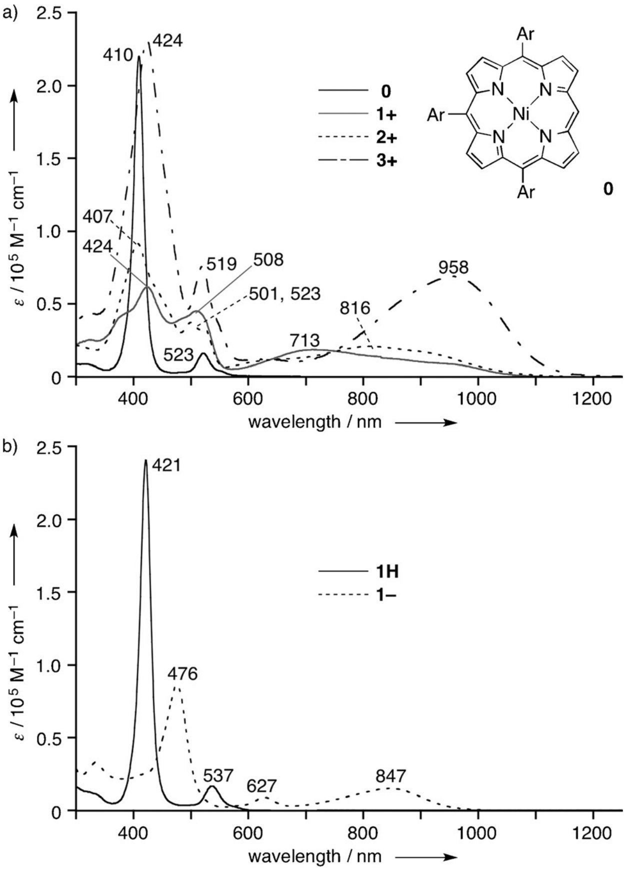


Figure 3. UV/vis/NIR absorption spectra of a) **0**, **1+**, **2+**, and **3+** in CH_2Cl_2 and b) **1 H** and **1−** in THF.

We have attempted to generate porphyrinylmethyl carbanions by treating **1 H**, **2 H**, and **3 H** with bases under various conditions. Treatment of **1 H** with potassium bis(trimethylsilyl)-amide (KHMDS) in THF at room temperature did not cause any change, but we found that in the presence of [18]crown-6,[8] the solution gave rise to an immediate vivid color change from red to green. The green solution showed a Soret band at $\lambda = 476$ nm, a Q-band at $\lambda = 627$ nm, and a broad band at $\lambda = 847$ nm. The ^{1}H NMR spectrum of the green species in [D$_8$]THF indicated signals due to the pyrrolic β-protons in the range of 6.99 ~ 6.39 ppm. We assigned the green species as *meso*-porphyrinylmethyl carbanion **1−**. In line with this assignment, addition of acetic acid to the green solution led to the recovery of exactly the same absorption spectrum as **1 H**. The absorption spectral features indicated that more porphyrinic character remained in **1−** as compared with cations **1+** and **2+**. Despite our extensive efforts, we could not find suitable conditions to generate anions **2−** and **3−** from **2 H** and **3 H**. Treatments of **2 H** and **3 H** with KHMDS and [18]crown-6 under the same conditions caused color changes but the solution colors changed rapidly to black in a minute, indicating rapid decomposition.

The observations discussed above were supported by DFT calculations at the B3LYP/6-31G(d) level[9] on **1+′**, **2+′**, and **1−′**, in which the *tert*-butyl groups are replaced by hydrogen atoms. The HOMO–LUMO gaps of **1+′**, **2+′**, and **1−′** have been calculated to be 1.93, 1.67, and 1.94 eV, respectively, which are roughly consistent with the optical HOMO–LUMO gaps estimated from the edges of the absorption spectra. It is conceivable that the vacant p-orbitals of the cations or the lone pair electrons of the anion are effectively conjugated with the porphyrinic electronic networks (Figure 1 d–f, Supporting Information). NICS(0) values[10] have also been calculated at the B3LYP/6-31G(d) and HF/6-31G(d) level (Supporting Information). These calculations indicated that the NICS(0) values were substantially decreased in **1+′** (−6.22 ~ −4.12), **2+′** (−13.28 ~ −9.47), and **1−′** (−10.57 ~ −8.59), compared those of **0′** (−19.55–−19.39), supporting our interpretations of ^{1}H NMR spectra.

Next, we have carried out femtosecond transient absorption (fs-TA) measurements in order to scrutinize the excited-state dynamics of tris(β-porphyrinyl)carbinol **3 OH**, and its cation **3+**. As shown in Figure 4 a, **3 OH** shows simultaneous peak shifts in the ground-state bleaching (GSB) and excited-state absorption (ESA) band on the subpicosecond timescale after photoexcitation. By using global analysis with singular value decomposition (SVD), we could obtain decay-associated spectra (DAS) of three transient components. The initial decay with $\tau = 0.76$ ps has been associated with the transition from the lowest-energy $^1(\pi,\pi^*)$ state of the porphyrin core to the Ni^{II}-centered

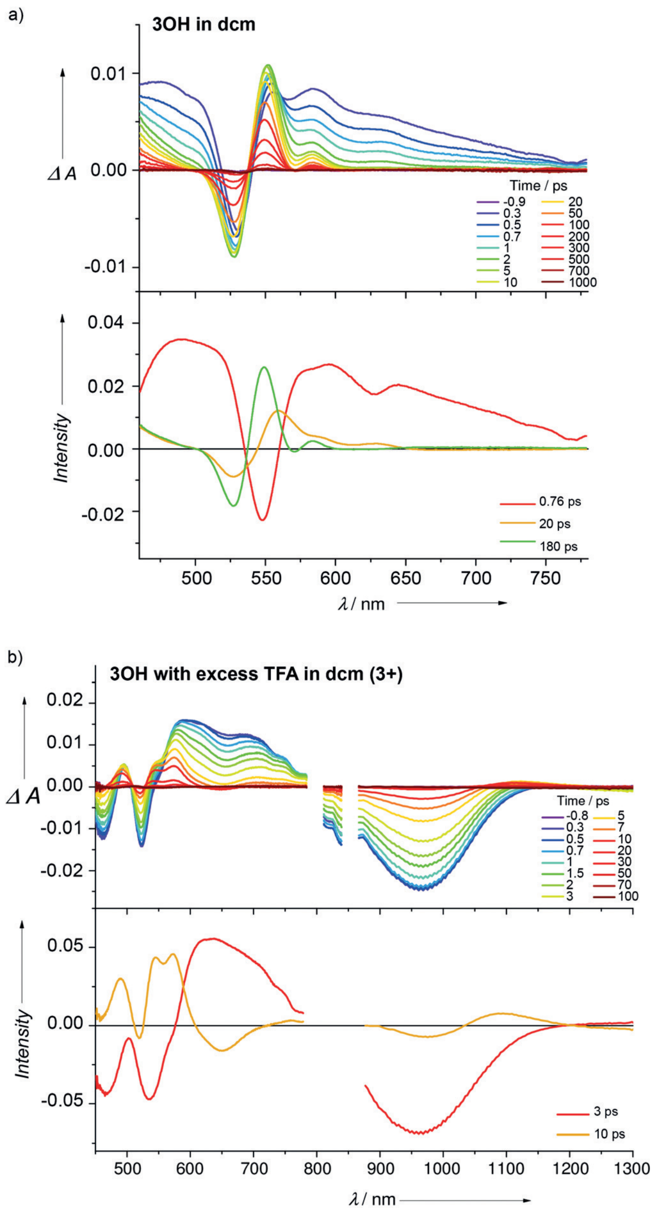


Figure 4. Transition absorption (top) and decay-associated spectra (bottom) of a) **3 OH**, and b) **3+** in CH_2Cl_2 after photoexcitation at 530 nm.

$^3(d,d)$ state and is responsible for TA spectral changes on the subpicosecond timescale. The second time constant with $\tau =$ 20 ps can be assigned as a vibrational cooling process from hot $^3(d,d)$ to the relaxed $^3(d,d)$ state. Following this process, the relaxed $^3(d,d)$ state decayed to the ground state with $\tau =$ 180 ps. The observed excited-state dynamics of **3 OH** were quite similar to those of **NiTPP** (Supporting Information),[11] which indicated that **3 OH** behaved like a monomer in the excited state. This is presumably due to negligible excitonic interactions between three porphyrin moieties, despite of their proximity. However, relaxation time constants of **3 OH** were slightly faster than those of **NiTPP**, which can be ascribed to the large flexibility of trimeric system. Moreover, the excited-state dynamics of triarylmethane **3 H**, were exactly the same as those of **3 OH** (Supporting Information). This implies the substituent on the sp^3 central carbon atom plays no measureable role in the excited state.

The spectral evolution of transient absorption and decay profiles of **3+** were entirely different from those of **3 OH** and **3 H** (Figure 4 b). Interestingly, we found that **3+** did not reveal any subpicosecond decay time constant, implying the fast deactivation from the $^1(\pi,\pi^*)$ state to the Ni^{II}-centered $^3(d,d)$ state did not occur in this case. In other words, the electron in the excited-state of **3+** was not localized within the nickel of one porphyrin unit. This observation can be a clear evidence that **3+** behaved as a single chromophore owing to its effective delocalization of the electrons and positive charge over the entire molecular framework both in the ground and excited state. Thus, we can directly assign a time constant with $\tau =$ 3 ps as a vibrational or structural relaxation process and $\tau =$ 10 ps as an excited-state lifetime of **3+**. The diminished lifetime of **3+** again indicates that the excited-state depopulation did not originate from the $^3(d,d)$ state and reflects the reduced HOMO–LUMO gap due to the effective delocalization and stabilization of the positive charge.

In summary, porphyrin analogues of the trityl cation and anion were generated and characterized with UV/vis/NIR absorption and NMR spectroscopies. Positive charge was delocalized more effectively to a *meso*-porphyrinyl group with decreasing aromatic characters of porphyrin than to a β-porphyrinyl group. The *meso*-porphyrinylmethyl carbanion displayed the absorption reflecting remaining porphyrinic nature, in contrast to the *meso*-porphyrinylmethyl carbocation. The charge-induced decreased aromaticity of porphyrin macrocycles was also supported by calculated NICS(0) values. We finally confirmed the effective delocalization and stabilization of the positive charge in **3+** by using fs-TA measurements, which showed entirely different excited-state dynamics in comparison to the neutral species.

Acknowledgements

The work at Kyoto was supported by a Grants-in-Aid from MEXT (no.: 25107002 "Science of Atomic Layers") and from JSPS (no.: 25220802 (Scientific Research (S)), 24685007 (Young Scientists (A)), 26620081 (Exploratory Research)), and by ACT-C, JST. The authors thank Prof. Dr. H. Maeda and Dr. Y. Bando (Ritsumeikan University) for MALDI-TOF-MS measurements. H.Y. thanks the Kansai Research Foundation for Technology Promotion and The Asahi Glass Foundation for financial support. 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: carbanions · carbocations · electronic structure · lithium · porphyrinoids

[1] a) J. F. Norris, *Am. Chem. J.* **1901**, *25*, 117; b) F. Kehrmann, F. Wentzel, *Chem. Ber.* **1901**, *34*, 3815.
[2] Books: a) *Carbonium Ions*: An Introduction (Eds.: D. Bethell, V, Gold), Academic Press, New York, **1967**; b) *Carbonium Ions, Vol. 1* (Eds.: G. A.

Olah, R. v. P. Schleyer), Wiley, New York, **1968**; c) *Carbocation Chemistry* (Eds.: G. A. Olah, G. K. S. Prakash), Wiley, Hobeken, NJ, **2004**. Selected reviews: d) G. A. Olah, *J. Org. Chem.* **2001**, *66*, 5943; e) R. R. Naredla, D. A. Klumpp, *Chem. Rev.* **2013**, *113*, 6905.

[3] a) Y. Xu, L. Jaquinod, A. Wickramasinghe, K. M. Smith, *Tetrahedron Lett.* **2003**, *44*, 7753; b) K. J. Thorley, J. M. Hales, H. L. Anderson, J. W. Perry, *Angew. Chem. Int. Ed.* **2008**, *47*, 7095; *Angew. Chem.* **2008**, *120*, 7203; c) K. J. Thorley, H. L. Anderson, *Org. Biomol. Chem.* **2010**, *8*, 3472.

[4] Porphyrinyllithium reagents were prepared from the corresponding iodoporphyrins by iodine–lithium exchange at −98 °C: a) K. Fujimoto, H. Yorimitsu, A. Osuka, *Chem. Eur. J.* **2015**, *21*, 11311; b) K. Kato, K. Fujimoto, H. Yorimitsu, A. Osuka, *Chem. Eur. J.* **2015**, *21*, 13522.

[5] Late-stage modification methods of porphyrin have recently developed rapidly. Selected reviews: a) M. O. Senge, *Chem. Commun.* **2011**, *47*, 1943; b) H. Yorimitsu, A. Osuka, *Asian J. Org. Chem.* **2013**, *2*, 356; selected articles: c) K. Fujimoto, H. Yorimitsu, A. Osuka, *Org. Lett.* **2014**, *16*, 972; d) K. Oda, M. Akita, S. Hiroto, H. Shinokubo, *Org. Lett.* **2014**, *16*, 1818; e) Q. Chen, Y.-Z. Zhu, Q.-J. Fan, S.-C. Zhang, J.-Y. Zheng, *Org. Lett.* **2014**, *16*, 1590; f) N. Fukui, H. Yorimitsu, A. Osuka, *Angew. Chem. Int. Ed.* **2015**, *54*, 6311; *Angew. Chem.* **2015**, *127*, 6409.

[6] The *meso*- and β-porphyrinyllithium prepared from the corresponding iodoporphyrins with 1.0 equiv 4-(*N*,*N*-dimethylamino)phenyllithium were quenched with D_2O to provide deuterated product, protonated compound, and starting iodoporphyrin (*meso*-lithiation: 53, 20, and 10 %; β-lithiation: 92, 8, and 0 %, respectively).

[7] One of the reviewers requested to report the chemical shifts of the cationic carbon atoms. We synthesized ^{13}C-enriched samples of **1+** and **2+** and determined the chemical shifts to be $\delta = 184.55$ and 179.87 ppm, respectively. The chemical shift of **3+** has been assigned on the basis of the ^{13}C NMR spectral pattern to be $\delta = 155.37$ ppm. The observed less lower chemical shift of **3+** has been also ascribed to the effective delocalization of the postive charge over the three porphyrins.

[8] For favorable effect of [18]crown-6 on deprotonation from arylmethanes, see: E. Buncel, B. Menon, *J. Am. Chem. Soc.* **1977**, *99*, 4457.

[9] a) M. J. Frisch et al. Gaussian09, revision A.02; Gaussian, Inc.; Wallingford, CT, **2009**; b) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 1372; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.

[10] a) P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. v. E. Hommes, *J. Am. Chem. Soc.* **1996**, *118*, 6317; b) Z. Chen, C. S. Wannere, C. Corminboeuf, R. Puchta, P. v. Ragué, *Chem. Rev.* **2005**, *105*, 3842.

[11] Excited-state dynamics of Ni^{II} porphyrin: C. M. Drain, C. Kirmaier, C. J. Medforth, D. J. Nurco, K. M. Smith, D. Holten, *J. Phys. Chem.* **1996**, *100*, 11984.

Received: February 1, 2016