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Subporphyrins with an Axial B–C Bond

Shun Saga,^[a] Shin-ya Hayashi,^[a] Kouta Yoshida,^[a] Eiji Tsurumaki,^[a] Pyosang Kim,^[b] Young Mo Sung,^[b] Jooyoung Sung,^[b] Takayuki Tanaka,^[a] Dongho Kim,^{*[b]} and Atsuhiro Osuka^{*[a]}

In recent years, subporphyrin, a ring-contracted porphyrin consisting of three pyrrole units cyclically arranged via three methine carbon atoms, has emerged as a new class of functional macrocycles that exhibit intriguing structural and electronic properties.^[1-4] Rational fabrication of subporphyrins allows the fine tuning of their properties, which has previously been accomplished by meso-substitution,^[1b,5] peripheral substitution,^[6] supramolecular assembling,^[7] and hydrogenation of the macrocyclic conjugated network.^[8] Functionalization of the boron atom at the nucleus of the subporphyrin is a very promising fabrication strategy that has yet to be fully explored. Along this line, subphthalocyanines^[9] bearing an axial B-C bond have recently been reported.^[10] On the other hand, there has been no report of subporphyrins bearing an axial B-C bond except our recent report describing the reaction of subporphyrin borenium cations with phenyllithium giving rise to B-phenylated subporphyrins.^[11] This method was effective but required tedious pre-isolation of subporphyrin borenium cations as a B-phenylation substrate. Here we report a more straightforward and convenient synthesis of subporphyrins bearing an axial B-C bond by reaction of B(methoxo)triphenylsubporphyrin 1 with Grignard reagents.

Treatment of a toluene solution of B-methoxo triphenylsubporphyrin (1) with phenylmagnesium bromide in THF produced B-phenyl subporphyrin 2 after usual hydrolytic workup and separation over a silica gel column or GPC column. To ensure complete conversion, an excess amount of Grignard reagent (ca. 20 equiv) was employed and the reaction mixture was heated at 100 °C for 1 h (Scheme 1).

- [a] S. Saga, S.-y. Hayashi, K. Yoshida, E. Tsurumaki, Dr. T. Tanaka, Prof. Dr. A. Osuka Department of Chemistry Graduate School of Science, Kyoto University Sakyo-ku, Kyoto 606-8502 (Japan) Fax: (+81)75-753-3970 E-mail: osuka@kuchem.kyoto-u.ac.jp
 [b] P. Kim, Y. M. Sung, J. Sung, Prof. Dr. D. Kim
- Spectroscopy Laboratory for Functional π-Electronic Systems and Department of Chemistry, Yonsei University Seoul 120-749 (Korea) Fax: (+82)2-2123-2434 E-mail: dongho@yonsei.ac.kr
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^[a] Toluene was used as solvent. ^[b] 2 equiv, 0 °C, 4 h.

Scheme 1. Synthesis of subporphyrins bearing an axial B–C bond by the reaction of **1** with Grignard reagents

These reaction conditions gave B-aryl subporphyrins 2-5 from both electron-rich and electron-deficient arylmagnesium bromides, B-thienyl subporphyrin 6 from 2-thienylmagnesium bromide, B-ferrocenyl subporphyrin 7 from ferrocenylmagnesium bromide, and B-polycyclic aryl subporphyrins 8-10 from the corresponding Grignard reagents including sterically demanding 1-naphthylmagneisum bromide and 1pyrenylmagnesium bromide. B-styryl subporphyrin 11 and B-phenylethynyl subporphyrin 12 were also synthesized from styrylmagnesium bromide and phenylethynylmagnesium bromide, respectively. In all cases, B-arylated, B-styrylated, and B-ethynylated subporphyrins are stable during usual aqueous workup and separation by silica gel chromatography. In the case of ethylmagnesium bromide, only two equivalents of the reagent were required to complete the reaction, efficiently yielding 13 even at 0°C. However, subporphyrin 13 was hydrolytically unstable and was readily con-

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verted to B(hydroxo)subporphyrin. Hence, in the synthesis of **13**, the reaction mixture was simply passed through a short pad of silica gel as opposed to aqueous workup, and subsequent quick purification using a short silica gel column allowed isolation of **13**. All these reactions were run in a reproducible manner with isolated yields indicated in Scheme 1. Therefore, subporphyrins possessing B–C(sp³), B–C(sp²), and B–C(sp) bonds were all prepared by this simple synthetic methodology. We also found that subporphyrin **2** was quantitatively hydrolyzed to B-(hydroxo)subporphyrin upon treatment with trifluoroacetic acid in CH₂Cl₂ at room temperature followed by aqueous workup.

X-ray quality crystals have been obtained for 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, and 13, and their structures have been determined.^[12,13] A subset of structures are shown in Figure 1. The axial B–C bonds of B-aryl subporphyrins 2–10 are in the range of 1.60–1.64 Å, being longer than that of the axial B–O bond of 1 (1.44 Å; see the Supporting Information). The elongated B–C bond lengths (1.63–1.64 Å) observed in 8–10 may reflect the steric congestion around the axial ligand. The bowl-depths, which are defined as the vertical





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height from the central boron atom to the mean plane of the six peripheral β -carbon atoms, are in a range of 1.34– 1.46 Å for **2–13**, which are larger than **1** (1.29 Å),^[1b] and the B–N bonds are slightly longer than those of **1** (1.49, 1,50, and 1.51 Å). These structural features arise from the increased electron donation from the axial carbon ligands. The structure of B-phenylethynyl subporphyrin **12** exhibits a B–C bond length of 1.59 Å, a bowl-depth of 1.37 Å, and a B–N bond length of 1.50, 1.50, and 1.50 Å. The structure of B-ethyl subporphyrin **13** indicates a B–C bond length of 1.61 Å, a bowl-depth of 1.41 Å, and a B–N bond length of 1.50, 1.51, and 1.52 Å, respectively. Therefore, it may be concluded that the change of B–C(sp²) to B–C(sp) or B–C-(sp³) causes only slight structural changes.

The diatropic ring current arising from the 14π -electron circuit is preserved for these subporphyrins, which is clearly highlighted by the high-field shifts corresponding to the protons of the B-axial group. Typically, the 4-methoxyphenyl group protons of **4** are observed as a pair of doublets at $\delta = 4.60$ and 5.90 ppm (J=8.7 Hz), the 2-thienyl protons of **6** are observed as a set of signals at $\delta = 6.46$, 6.10, and 4.58 ppm. The vinyl protons of **11** are observed at $\delta = 3.72$ and 3.13 ppm as a pair of doublets (J=17.9 Hz), and the ethyl protons of **13** are observed as a triplet at $\delta = -1.36$ ppm and a quartet at $\delta = -3.05$ ppm. Subporphyrins **2–10**, **12**, and **13** show considerably broad ¹¹B NMR peaks around $\delta = -15.9$ ppm, whereas that of **11** exhibits a sharp and largely high-field shifted peak at $\delta = -21.3$ ppm similarly to **1**.

The oxidation and reduction potentials of the B-subporphyrins were measured by cyclic voltammetry in CH_2Cl_2 containing $0.10 \text{ M} \text{ Bu}_4\text{NPF}_6$ as a supporting electrolyte (see Table 1 and Figure S6 in the Supporting Information). Subporphyrin 1 has reversible reduction and oxidation potentials at -1.84 and 0.82 V, respectively. Subporphyrins 2–13 show oxidation and reduction potentials at higher potentials as compared with 1, findings attributed to the axially coordinated electron-donating groups. Since the oxidation and reduction potentials are both elevated by the same extent, the electrochemical HOMO–LUMO gaps are kept similar, lying in the range of 2.57–2.66 eV, with the exception of 5 and 7.

Table 1. Oxidation and reduction potentials of $1\!\!-\!\!13$ [V vs. Fc/Fc+ ion pair].

Cmpd	$E_{\rm ox3}$	$E_{\rm ox2}$	$E_{\rm ox1}$	$E_{\rm red1}$	$E_{\rm red2}$	$E_{\rm ox1} - E_{\rm red1}^{\rm [b]}$
1			0.82	-1.84		2.66
2			0.58	-2.01		2.59
3			0.67	-1.96		2.63
4			0.62	-1.97	-2.38	2.59
5	0.82	0.68	0.32 ^[a]	-2.04		2.36
6			0.67	-1.97		2.64
7		0.80	-0.17	-2.01		1.84
8		0.94	0.68	-1.97		2.65
9			0.61	-1.96		2.57
10		0.85	$0.64^{[a]}$	-1.93		2.57
11			0.59	-2.00		2.59
12			0.67	-1.97		2.64
13		0.90	$0.52^{[a]}$	-2.14		2.66

[a] Irreversible. [b] Electrochemical HOMO-LUMO gap [eV]

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(b)

(c)

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In the cyclic voltammogram of **5**, the irreversible wave at 0.32 V corresponds to the oxidation of the 4-dimethylaminophenyl moiety, as referring to the relevant data.^[14] Thus, the electrochemical HOMO–LUMO gap of **5** is 2.36 eV. Similarly, the first oxidation potential of **7** was observed at -0.17 V, which is ascribed to the oxidation of the ferrocene moiety. The electrochemical HOMO–LUMO gap of **7** is much smaller, being 1.84 eV.

Table 2 summarizes the optical properties of subporphyrins 1-13. Subporphyrins 2-11 show Soret-like bands in the range of 382-385 nm and Q-like bands in the range of 501-508 nm. Soret-like bands of 12 and 13 are observed at 379 and 389 nm, which are slightly blue- and red-shifted, respectively, as compared with those of 2-11. These data suggests that the effects of the axial carbon ligands on the absorption spectra of the subporphyrins is negligible, as seen for the subphthalocyanine bearing a B-C bond.^[10e] On the other hand, the fluorescence quantum yields of subporphyrins bearing a B-C bond are variable. While many of the B-fabricated subporphyrins exhibit fluorescence quantum yields $(\Phi_{\rm F})$ in the range of 0.10–0.16, which are comparable to that of 1, subporphyrins 5 and 7 bearing a strongly electron-donating axial group exhibit very small Φ_F values and subporphyrin 10 shows a slightly small Φ_F value. The fluorescence decays measured by time-correlated single photon counting techniques in toluene obey a single exponential function in most cases with the following time constants; 2.44 ns for 2, 2.31 ns for **3**. 2.45 ns for **4**. 1.99 ns for **6**. 1.74 ns for **8**. 2.45 ns for 9, 1.53 ns for 10, 2.51 ns for 11, and 2.01 ns for 12, respectively (see Figure S8 in the Supporting Information). The fluorescence decay of 5 was analysed by a bi-exponen-

Table 2. Optical properties of subporphyrins 1-13.[a]

Cmpd	$\lambda_{abs} [nm]$	$(\varepsilon [10^5 \mathrm{m}^{-1} \mathrm{cm}^{-1})$	λ_{em} [nm]	${oldsymbol{\varPhi}_{ extsf{F}}^{[b]}}$	
1	372	460	485	517	0.13
	(1.66)	(0.12)	(0.09)		
2	385	478	507	541	0.16
	(1.36)	(0.09)	(0.13)		
3	384	478	506	544	0.15
	(1.40)	(0.09)	(0.13)		
4	385	480	507	546	0.14
	(1.31)	(0.09)	(0.13)		
5	385	481	508	546	< 0.01
	(1.43)	(0.09)	(0.14)		
6	382	474	502	538	0.12
	(1.36)	(0.09)	(0.12)		
7	383		505	542	< 0.01
	(1.22)		(0.09)		
8	383	473	501	534	0.10
	(1.37)	(0.10)	(0.12)		
9	385	479	507	545	0.14
	(1.35)	(0.09)	(0.13)		
10	385	473	501	541	0.087
	(1.12)	(0.08)	(0.10)		
11	382	480	502	546	0.15
	(1.44)	(0.09)	(0.12)		
12	379	471	497	528	0.12
	(1.56)	(0.10)	(0.12)		
13	389		514	-	< 0.01
	(1.40)		(0.10)		

[a] Measured in CH_2Cl_2 . [b] Absolute fluorescence quantum yield

tial function with a time constant of 1.54 ns and a very short time constant ($\tau < 30$ ps), suggesting the presence of an additional decay channel from their S₁-excited states. The absence of a measureable fluorescence of 7 provides further support for existence of efficient nonradiative decay channel. While preliminary experiments indicated a non-fluorescent nature of subporphyrin 13, its facile hydrolytic reactivity hampered detailed studies of its fluorescence, since hydrolysis produced fluorescent B(hydroxo)subporphyrin. The efficient fluorescence quenching observed for 5 and 7 may be attributed to intramolecular electron transfer from the axial group to the subporphyrin S₁-state. Relevant driving force values of the electron transfer have been estimated to be -0.51 and -0.99 eV for 5 and 7, respectively.^[15] These large negative driving forces support the fact that the intramolecular electron transfer processes are responsible for the fluorescence quenching.^[16]

To understand the electrochemical and optical properties, MO calculations were performed at the B3LYP/6-311G(d) level using the Gaussian 09 package^[17] (see Figure S7 in the Supporting Information). Subporphyrin **1** has a_{2u} -like HOMO, a_{1u} -like HOMO-1, and a couple of degenerate e_g -like LUMO and LUMO+1 levels. Subporphyrins **2-13** show essentially the same orbital features, except the cases of **5**, **7**, and **10**, in which HOMOs are localized at the axial groups, reflecting their electron-donating properties. These data are consistent with the electrochemical measurements, and support the fact that the fluorescence quenching is ascribed to the intramolecular electron transfer from the axial group to the S₁-state of the subporphyrins.

Finally, it is worth noting that the optical properties of 5 contrast with those of meso-(4-dibenzylaminophenyl) subporphyrin $14^{[5a]}$ and *meso-*(4-dimethylaminophenyl)ethynyl subporphyrin 15,^[18] both of which exhibit split Soret-like bands and red-shifted and enhanced fluorescence. In subporphyrins 14 and 15, conjugative interactions of the electrondonating meso-substituents are responsible for the perturbed absorption spectra and fluorescence spectra. In other words, the electronic interactions of 4-dibenzylaminophenyl and (4dimethylaminophenyl)ethynyl substituents with the subporphyrin core are strong enough to create an expanded chromophoric conjugation by including meso-substituents. In contrast, the axial 4-dimethylaminophenyl group in 5 is entirely non-conjugated with the subporphyrin core due to the nodal character of the central B atom and the orthogonal orientation. This situation is favorable for state-to-state dynamics such as intramolecular electron transfer.

In summary, a convenient methodology for efficient axial fabrication of subporphyrins has been developed by reaction of B-(methoxo)triphenylsubporphyrin with Grignard re-



agents such as aryl-, polycyclic aryl-, heteroaryl-, ferrocenyl-, phenylethynyl-, β -styryl-, and ethylmagnesium bromides. The axial groups introduced are electronically de-coupled from the subporphyrin core. This situation allows the effective fluorescence quenching of subporphyrins **5** and **7** that bear strongly electron-donating axial groups. The synthetic protocol described here is simple and convenient, allowing the creation of various functional subporphyrins.

Experimental Section

A THF solution of phenylmagnesium bromide (2.0 mL, 2.0 mmol) was added to a solution of methoxo(triphenylsubporphyrinato)boron (1, 46.4 mg, 92.6 μ mol) in dioxane (4.5 mL) and the resulting solution was refluxed for 1 h under nitrogen atmosphere. After the reaction mixture was quenched by passing through a short pad of silica gel with CH₂Cl₂ and the solvent was evaporated, the product was separated by using a GPC column (6×40 cm, THF). Recrystallization from CH₂Cl₂/hexane furnished pure **2** as an orange solid (45.3 mg, 89%).

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Keywords: boron–carbon bond • electron transfer • Grignard reaction • porphyrinoids • subporphyrins

- a) Y. Inokuma, J. H. Kwon, T. K. Ahn, M.-C. Yoo, D. Kim, A. Osuka, Angew. Chem. 2006, 118, 975; Angew. Chem. Int. Ed. 2006, 45, 961; b) Y. Inokuma, Z. S. Yoon, D. Kim, A. Osuka, J. Am. Chem. Soc. 2007, 129, 4747.
- [2] a) N. Kobayashi, Y. Takeuchi, A. Matsuda, Angew. Chem. 2007, 119, 772; Angew. Chem. Int. Ed. 2007, 46, 758; b) Y. Takeuchi, A. Matsuda, N. Kobayashi, J. Am. Chem. Soc. 2007, 129, 8271.
- [3] a) T. Torres, Angew. Chem. 2006, 118, 2900; Angew. Chem. Int. Ed.
 2006, 45, 2834; b) R. Myśliborski, L. Latos-Grażyński, L. Sztrenberg,
 T. Lis, Angew. Chem. 2006, 118, 3752; Angew. Chem. Int. Ed. 2006, 45, 3670.
- [4] a) Y. Inokuma, A. Osuka, *Dalton Trans.* 2008, 2517; b) A. Osuka, E. Tsurumaki, T. Tanaka, *Bull. Chem. Soc. Jpn.* 2011, 84, 679.
- [5] a) Y. Inokuma, S. Easwaramoorthi, S. Y. Jang, K. S. Kim, D. Kim, A. Osuka, Angew. Chem. 2008, 120, 4918; Angew. Chem. Int. Ed. 2008, 47, 4840; b) Y. Inokuma, S. Easwaramoorthi, Z. S. Yoon, D. Kim, A. Osuka, J. Am. Chem. Soc. 2008, 130, 12234; c) Y. Inokuma, A. Osuka, Org. Lett. 2009, 38, 206; e) Y. Inokuma, S. Hayashi, A. Osuka, Chem. Lett. 2009, 38, 206; e) Y. Inokama, A. Osuka, Chem. Lett. 2009, 38, 206; e) Y. Inokama, A. Osuka, Chem. Lett. 2009, 38, 206; e) Y. Inokama, A. Osuka, Chem. Eur. J. 2009, 15, 6863; f) S. Hayashi, Y. Inokuma, S. Easwaramoorthi, K. S. Kim, D. Kim, A. Osuka, Angew. Chem. 2010, 122, 331; Angew. Chem. Int. Ed. 2010, 49, 321; g) S. Hayashi, J. Sung, M. Sung, Y. Inokuma, D. Kim, A. Osuka, Angew. Chem. 2011, 123, 3311; Angew. Chem. Int. Ed. 2011, 50, 3253.
- [6] a) E. Tsurumaki, Y. Inokuma, S. Easwaramoorthi, J. M. Lim, D. Kim, A. Osuka, *Chem. Eur. J.* 2009, 15, 237.
- [7] Y. Inokuma, A. Osuka, Chem. Commun. 2007, 2938.

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- [8] a) E. Tsurumaki, S. Saito, K. S. Kim, J. M. Lim, Y. Inokuma, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2008**, *130*, 438; b) S. Hayashi, E. Tsurumaki, Y. Inokuma, P. Kim, Y. M. Sung, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2011**, *133*, 4254.
- [9] C. G. Classens, D. González-Rodríguez, T. Torres, *Chem. Rev.* 2002, 102, 835.
- [10] a) J. Rauschnabel, M. Hanack, *Tetrahedron Lett.* 1995, *36*, 1629;
 b) M. Geyer, F. Plenzig, J. Rauschnabel, M. Hanack, B. del Rey, A. Sastre, T. Torres, *Synthesis* 1996, 1139; c) C. G. Claessens, D. González-Rodríguez, B. del Rey, T. Torres, G. Mark, H.-P. Schuchmann, C. von Sonntag, J. G. MacDonald, R. S. Nohr, *Eur. J. Org. Chem.* 2003, 2547; d) F. Camerel, G. Ulrich, P. Retailleau, R. Ziessel, *Angew. Chem.* 2008, *120*, 9008; *Angew. Chem. Int. Ed.* 2008, *47*, 8876; e) Y. Yamasaki, T. Mori, *Chem. Lett.* 2010, *39*, 1108; f) N. Shibata, B. Das, E. Tokunaga, M. Shiro, N. Kobayashi, *Chem. Eur. J.* 2010, *16*, 7554; g) J. Guilleme, D. González-Rodríguez, T. Torres, *Angew. Chem.* 2011, *123*, 3568; *Angew. Chem. Int. Ed.* 2011, *50*, 3506.
- [11] E. Tsurumaki, S. Hayashi, F. Tham, C. A. Reed, A. Osuka, J. Am. Chem. Soc. 2011, 133, 11956.
- [12] Crystallographic data for 6: $C_{37}H_{24}B_1N_3S_1$, M = 553.46, triclinic, space group $P\bar{1}$ (no. 2), a=8.08600(10), b=13.4361(3), c=14.1566(4) Å, $\alpha = 117.93438(8)$, $\beta = 91.6645(10)$, $\gamma = 92.5536(14)^{\circ}$, $V = 1355.19(5) \text{ Å}^3, T = 93 \text{ K}, \rho_{\text{calcd}} = 1.356 \text{ g cm}^{-3}, Z = 2, R_1 = 0.0689$ $(I > 2\sigma(I))$, $R_w = 0.1937$ (all data), GOF = 1.025. Crystallographic data for **11**: $C_{82}H_{28}B_2N_6$, M=1146.95, triclinic, space group $P\bar{1}$ (no. 2), a = 12.6432(2), b = 15.6313(4), c = 17.6443(3) Å, a = 85.9715(11), $\beta = 69.3300(16), \quad \gamma = 67.5029(11)^{\circ}, \quad V = 3005.80(10) \text{ Å}^3, \quad T = 93 \text{ K},$ $\rho_{\text{calcd}} = 1.267 \text{ g cm}^{-3}, Z = 2, R_1 = 0.0533 (I > 2\sigma(I)), R_w = 0.1139 \text{ (all}$ GOF = 1.016. Crystallographic 12: data), data for $C_{41}H_{26}B_1N_3$ ·CH₂Cl₂, M = 656.38, monoclinic, space group $P2_1/n$ (no. $a = 13.7682(3), \quad b = 15.2869(3), \quad c = 16.1548(4) \text{ Å},$ 106.9498(11)°, V = 3252.45(11) Å³, T = 93 K, $\rho_{calcd} = 1.340$ g cm⁻³, Z = 4, $R_{c} = 0.0500$ ($L_{c} > 2.5(D)$). $P_{c} = 0.0500$ ($L_{c} > 2.5(D)$). 4, $R_1 = 0.0590 \ (I > 2 \sigma(I))$, $R_w = 0.1659$ (all data), GOF = 1.068. Crystallographic data for 13: C35H26B1N3·CH2Cl2, M=584.32, triclinic, space group $P\bar{1}$ (no. 2), a=9.7488(2), b=11.4142(2), c=13.9488(3) Å, $\alpha = 103.7224(14)$, $\beta = 103.2730(14)$, $\gamma = 94.3542(14)^{\circ}$, V = 1453.55(5) Å³, T = 93 K, $\rho_{calcd} = 1.335$ g cm⁻³, Z = 2, $R_1 = 0.0517$ $(I > 2\sigma(I)), R_w = 0.1351$ (all data), GOF = 1.049. CCDC-941348(6), CCDC-941343(11), CCDC-941344(12), and CCDC-942781(13) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif
- [13] The structure of **2** was reported previously (ref. [11]).
- [14] A. Ito, Y. Kang, S. Saito, E. Sakuda, N. Kitamura, *Inorg. Chem.* 2012, 51, 7722.
- [15] The driving force values ($\Delta G_{\rm ET}$) were estimated from the following equation

$$\Delta G_{\rm ET} = -E(S_1) + E_{\rm ox} - E_{\rm red} - \frac{1}{4\pi\varepsilon_0} \cdot \frac{e}{\varepsilon_{\rm s} r}$$

where ε_s is static dielectric constant and r is the center to center distance between subporphyrin and the dimethylaminophenyl moiety (3.06 Å for 5) and between subporphyrin and the ferrocene moiety (3.54 Å for 7). E_{ox} and E_{red} were given in Table 1. $E(S_1)$ was calculated from the mid-point of the S₁-state energies of absorption and fluorescence spectra to be 2.36 eV for 5 and 2.37 eV for 7.

- [16] H. Sugimoto, T. Tanaka, A. Osuka, Chem. Lett. 2011, 40, 629.
- [17] Gaussian 09 (Revision A.2), Gaussian, Inc., Wallingford, CT, 2009. For full citation, see Supporting Information.
- [18] M. Kitano, S. Hayashi, T. Tanaka, H. Yorimitsu, N. Aratani, A. Osuka, *Angew. Chem.* **2012**, *124*, 5691; *Angew. Chem. Int. Ed.* **2012**, *51*, 5593.

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