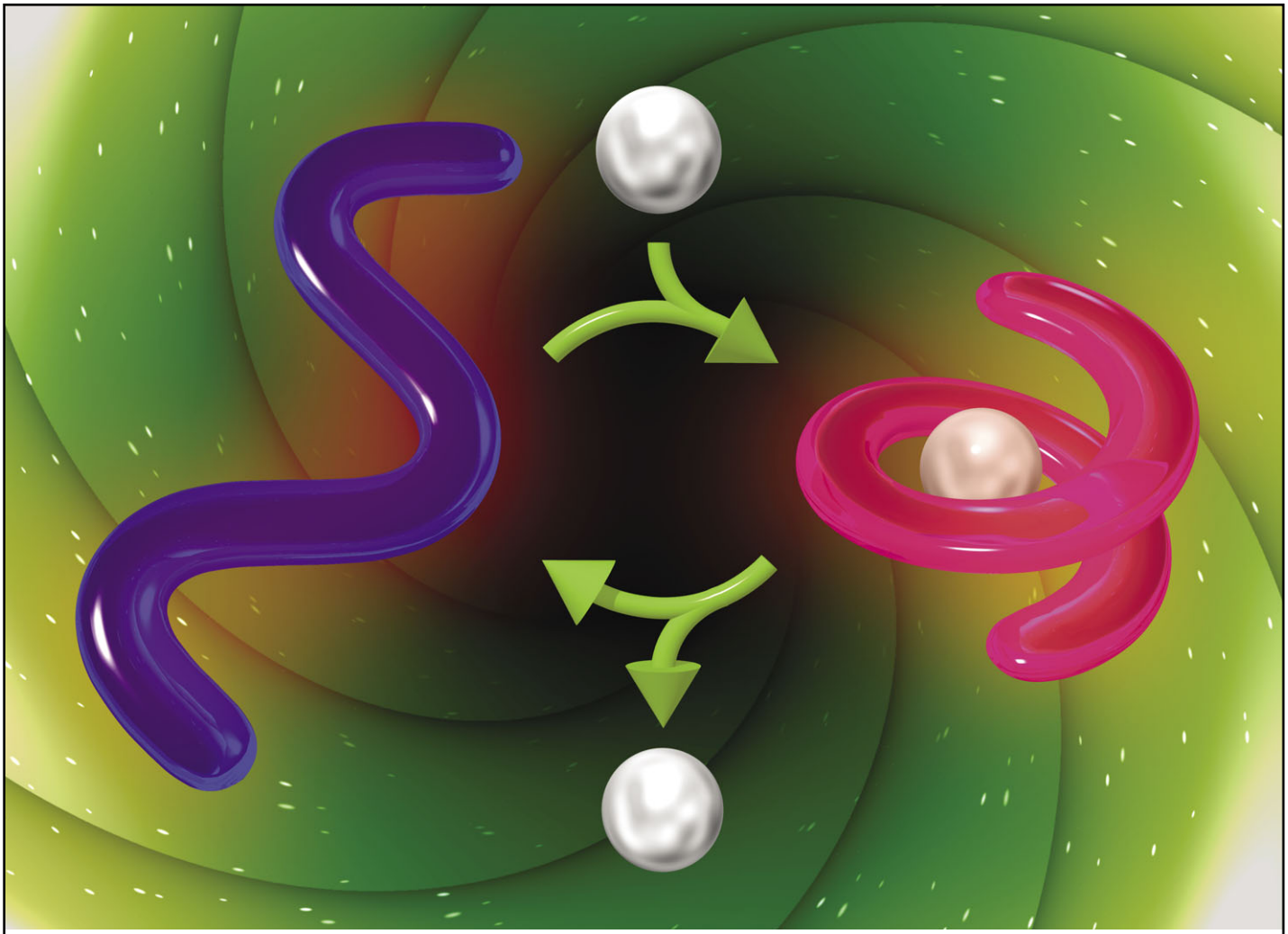

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COMMUNICATION

α-Bridged BODIPY oligomers with switchable near-IR photoproperties by external-stimuli-induced foldamer formation and disruption†

Naoya Sakamoto,[a] Chusaku Ikeda,[a] Masaki Yamamura[ab] and Tatsuya Nabeshima*[ab]

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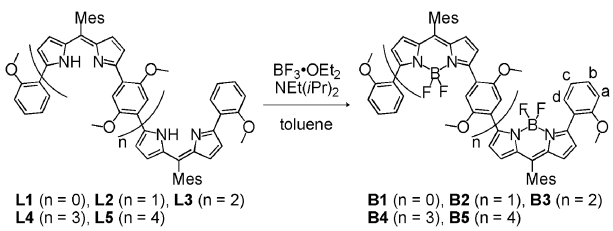
We designed and synthesized a series of new α-bridged linear BODIPY oligomers, which exhibited strong absorption and high fluorescence efficiency in the near infrared region. The oligomers can be reversibly converted to the first NIR emissive BODIPY foldamers upon selective complexation with Cs^+.

Boron-dipyrrins (BODIPYs) are of broad and considerable use in various research fields such as electrogenerated chemiluminescence materials,[1] laser dyes,[2] and molecular probes for biomolecules[3] because of their intense absorption and fluorescence properties and excellent photostability.[4] Thus, tuning of their photophysical properties was intensively studied by introducing a substituent. Recently, in particular, BODIPYs bearing an extended π-conjugated skeleton[5] or conjugated BODIPY oligomers and polymers[6] have been synthesized to absorb and emit light in the near infrared (NIR) region, because the NIR photoproperties are often claimed for practical applications such as in solar cells, laser dyes, *in vivo* probes, *etc*.[7]

Switching of the BODIPY photoproperties is another important current topic because BODIPYs are most utilized for logic gates,[8] photodynamic therapy,[9] and chemosensors,[10] *etc*. The conformational change in a long π-conjugated system of oligo-BODIPYs seemed to very efficiently control both the wavelengths and intensities of the NIR absorption and fluorescence. However, no switchable BODIPY oligomers based on the *conjugation-control* strategy described have been reported, although many simple on–off or off–on BODIPY fluorophores are known. We were convinced that the interconversion of the unfolded and folded structures of the oligomers[11] should be one of the most effective ways to significantly change their photoproperties due to the expected drastic conformational change in their π-conjugated systems. If the conformation of the BODIPY oligomers can be reversibly controlled by the foldamer formation, they can be very useful as an NIR dye with possible applications in data storage, optical device, and molecular sensing. Nevertheless, no NIR fluorescent switchable π-conjugated foldamers, even excluding the BODIPY foldamers, have been reported to date. However, we envisaged that oligomeric BODIPYs connected to each other at the α-positions of the pyrrole moieties may have NIR photophysical properties due to their elongated π-system and should be flexible enough to give the corresponding foldamers with different photoproperties upon receiving a metal ion as an external stimulus by electrostatic interactions of a BF_2 unit with cations. We designed the α-bridged flexible BODIPY oligomers, **B1–B5**, bearing a mesityl group at the *meso*-position to increase emission efficiency[12] and 2,5-dimethoxyphenylene linkers at the α-positions of the pyrrole units, because (1) the steric hindrance between the BF_2 moieties and methoxy groups should make an unfolded structure more favorable than a folded one, (2) the rotatable bonds between a pyrrole and a linker phenyl group should enable cation binding as a stimulus-induced event by using unique multiple B–F···M^+ interactions[13] to form the folded structure.



Scheme 1 Synthetic route to **B1–B5**.

Linear dipyrrin oligomers **L2–L5** have been synthesized *via* the acid-catalyzed condensation of 1,4-bis(pyrrol-2-yl)-2,5-dimethoxybenzene‡ and 2,4,6-trimethylbenzaldehyde in the presence of 2-(2-methoxyphenyl)pyrrole followed by oxidation using DDQ.[14] Column chromatography and subsequent gel permeation chromatography produced the dipyrrin monomer **L1** (54%), linear dipyrrin dimer **L2** (14%), trimer **L3** (11%), tetramer **L4** (5.5%), and pentamer **L5** (3.7%). The boron complexes **B1–B5** were synthesized from the corresponding dipyrrins by the reaction with boron trifluoride etherate in the presence of *N*,*N*-diisopropylethylamine (Scheme 1).[14]

These oligomeric compounds showed ^{1}H NMR spectral patterns similar to that of the monomer **B1**. In particular, the resonances of H_a, H_b, H_c, and H_d (aromatic protons of the terminal methoxyphenyl moieties) of **B1–B5** appeared around 6.9, 7.3, 7.0, and 7.8 ppm, respectively. This spectral similarity

[a] *Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan. E-mail: nabesima@chem.tsukuba.ac.jp; Fax: +81-29-853-4507; Tel: +81-29-853-4507*
[b] *Tsukuba Research Center for Interdisciplinary Materials Science (TIMS), University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan*

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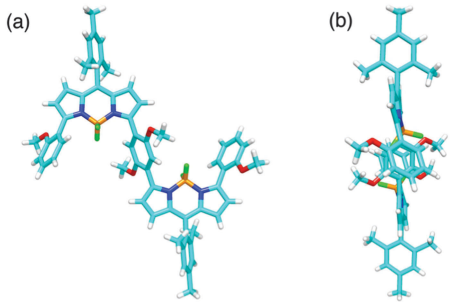

Fig. 1 Crystal structure of **B2**: (a) top view; (b) side view. Color: C, sky blue; H, white; B, orange; F, green; N, blue; O, red.

between the monomer **B1** and oligomers **B2–B5** strongly suggests that the oligomers adopt an unfolded conformation instead of a folded or intramolecularly stacked structure, which should lead to a chemical shift change due to the anisotropic effect of the aromatic moieties, *etc.*

An X-ray crystallographic analysis of **B2** revealed its zig-zag structure in which the two BODIPY moieties are nearly coplanar with the maximum mean plane deviation of 0.393 Å (Fig. 1).[15] The dihedral angle between the BODIPY unit and *p*-phenylene linker is 58.2°. In spite of the tilted conformation, the DFT calculation of **B2** based on the crystal structure gave the HOMO and LUMO delocalized over the entire molecule, indicating that the π-conjugation is extended along the two BODIPY moieties and phenylene linker (Fig. S12, ESI†).

B1–B5 showed a red shift of an absorption band at the longer wavelength, gradually increasing from **B1** to **B5** (Table 1 and Fig. S13 (ESI†)). The fluorescence maxima of **B2–B5** also shifted and reached the NIR region (715–770 nm). These spectra again suggest that the π-conjugation of the BODIPY oligomers is effectively elongated along the linear oligomer backbones. **B2–B5** show larger Stokes shifts (*ca.* 100 nm) than the monomer **B1**, probably reflecting their flexible structures. These shifts are striking because the BODIPY derivatives usually exhibit a relatively small Stokes shift, which would be unfavorable for various photofunctions. An additional advantage of **B2–B5** is their high fluorescence efficiencies. Noteworthy is that even **B5** showed a high quantum yield (0.49) at 770 nm because the quantum yield of luminescence at the longer wavelengths tends to get smaller due to an energy gap rule.

The addition of caesium tetrakis(3,5-bis(trifluoromethyl)-phenyl)borate (Cs^+TFPB^-) to **B2** and **B3** in $CHCl_3$–CH_3OH (10 : 1) decreased the absorbance at 615 and 645 nm along with a concomitant increase in the absorption bands at 511 and 510 nm (Fig. 2b), suggesting a decrease in the effective conjugation length of the oligomers due to the folded structure formation (Fig. 2a). A blue solution of **B3** turned pink upon the addition of Cs^+ (Fig. 2d). The UV-vis titration isotherms of **B3** with Cs^+ showed clear isosbestic points, indicative of a

Table 1 Optical properties of **B1–B5** in $CHCl_3$

	λ_{abs}/nm	ε/M^{-1} cm^{-1}	λ_{flu}/nm	Φ_F
B1	551	4.8×10^4	600	0.88
B2	621	6.1×10^4	715	0.65
B3	650	8.6×10^4	750	0.48
B4	660	8.8×10^4	760	0.47
B5	668	9.5×10^4	770	0.49

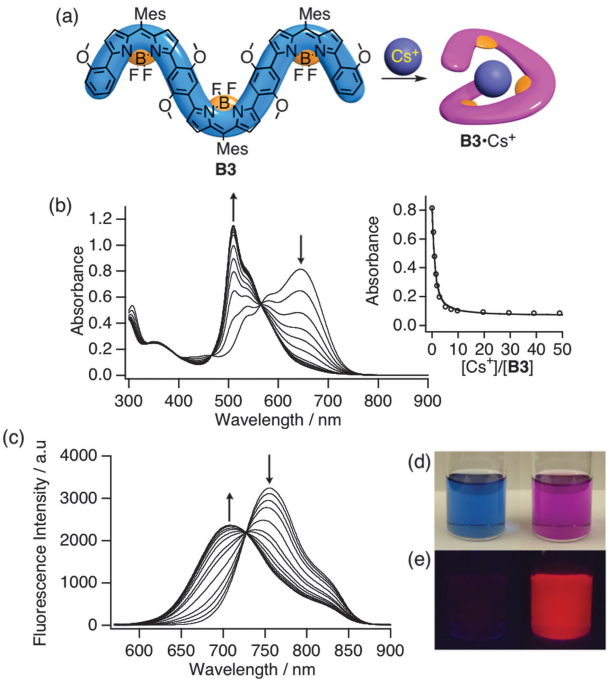

Fig. 2 (a) Schematic representation of Cs^+-induced folding of **B3**. (b) UV-vis spectral changes of **B3** upon the addition of CsTFPB. Inset shows the binding isotherm recorded at 645 nm with the calculated 1 : 1 binding curve: [**B3**] = 10.0 μM, $0 \leq [Cs^+]/[\mathbf{B3}] \leq 50$, $CHCl_3$–CH_3OH (10 : 1). (c) Fluorescence spectral changes of **B3** upon the addition of CsTFPB: [**B3**] = 1.0 μM, $0 \leq [Cs^+]/[\mathbf{B3}] \leq 100$, $CHCl_3$–CH_3OH (10 : 1), λ_{ex} = 565 nm. Photographs of **B3** (left) and **B3**·Cs^+ (right) were taken under (d) ambient light and (e) UV light (365 nm).

1 : 1 complexation. **B2** and **B3** exhibited size-selective binding to alkali metal ions. The K_a values of **B3** are higher than those of **B2**. The highest K_a values among the alkali metal ions were observed for Cs^+ ($\log K_a$ (M^{-1}): 3.83 ± 0.04 in **B2**, 5.28 ± 0.04 in **B3**, Table 2) probably because the binding cavity generated by the fluorine atoms of the two or three BF_2 moieties fits the Cs^+ ionic diameter as suggested by the Cs^+ binding geometry of the macrocyclic BODIPY trimer.[13] In sharp contrast, the monomeric compound **B1** showed a very small spectral change even in the presence of excess Cs^+. The low Cs^+ affinity was determined to be 67 M^{-1} by ^1H NMR titration in $CDCl_3$–CD_3OD (10 : 1). The facts, (1) the low affinity of **B1** and (2) the K_a enhancement as the oligomer length increased, indicated that the simultaneous interactions of the BF_2 units in the folded structure play an essential role in the strong binding. An increase in the methanol content ($CHCl_3$–CH_3OH (1 : 1)) decreased $\log K_a$ (M^{-1}) to 3.06 ± 0.01 in **B3**. This result again suggests that the B–F···M^+ is a kind of an electrostatic interaction.

Table 2 $\log K_a$ (M^{-1}) values of **B2** and **B3**

	Na^+	K^+	Rb^+	Cs^+
B2	—[a]	2.65 ± 0.03	3.34 ± 0.01	3.83 ± 0.04
B3	—[a]	3.56 ± 0.01	4.56 ± 0.01	5.28 ± 0.04

K_a values were determined by UV-vis spectral changes in $CHCl_3$–CH_3OH (10 : 1), assuming a 1 : 1 stoichiometry. [a] Too small to be determined.

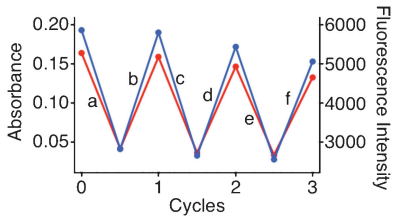

Fig. 3 Changes of absorbance at 645 nm (red line) and fluorescence intensity at 755 nm (blue line) for three cycles of the folding–unfolding process: (a) Cs^+ (10 eq.); (b) 18C6 (20 eq.); (c) Cs^+ (20 eq.); (d) 18C6 (20 eq.); (e) Cs^+ (20 eq.); (f) 18C6 (20 eq.), [**B3**] = 2.0 μM.

A decrease in the fluorescence at 755 nm and a concomitant increase in the fluorescence at 708 nm were observed in **B3** by the addition of Cs^+ (Fig. 2c). These blue shifts also suggested the decrease of the effective π-conjugation length between the BODIPY moieties upon cation binding. The fluorescence quantum yield slightly decreased upon the addition of Cs^+ (0.47 to 0.41). We can realize the guest binding by the naked eye based on not only the absorption change, but also the fluorescence change (Fig. 2e). On the other hand, monomeric compound **B1** showed a negligibly small spectral change even in the presence of excess Cs^+. Thus, this also supported the fact that the Cs^+ binding of **B2** and **B3** was caused by the simultaneous chelation of at least two BODIPY units, indicative of the formation of foldamers. This structural change was also supported by ^1H NMR and theoretical examinations (*vide infra*).

The Hartree–Fock calculation of the **B3**·Cs^+ supported a folded structure, in which the three BF_2 moieties contact a Cs^+ ion. The ^{19}F NMR spectral titration of **B3** with Cs^+ showed downfield shifts ($\Delta\delta$: *ca.* 3 ppm), suggesting the B–F···Cs^+ interactions.[13] In addition, the ROESY spectrum confirmed the cation-induced folding. The correlation peaks between the aromatic proton H_b of the terminal phenyl group and methoxy protons of the dimethoxyphenylene linker were observed, while no correlation existed for the free **B3** (see ESI†).

Finally, we successfully switched the NIR photophysical properties of the oligomers by utilizing a reversible interconversion between the folded and unfolded structures. The Cs^+ binding caused a color change in the **B3** solution from blue to pink. In contrast, upon the addition of 18-crown-6 (18C6) the pink solution immediately changed to blue due to the removal of Cs^+ from the complex. The electronic absorption and fluorescence spectra above 400 nm indicated that these two processes proceeded almost quantitatively and repeatedly (Fig. 3).

We have synthesized a series of new α-bridged linear BODIPY oligomers, which exhibited NIR photophysical properties such as a strong absorption and high fluorescence efficiency. The oligomers can be converted to the novel NIR emissive foldamers upon selective complexation with Cs^+ as an external stimulus. Reversible switching between the folded and unfolded structures was achieved by the addition and removal of Cs^+ in order to regulate the NIR photophysical properties. These frameworks based on the switchable NIR fluorescent BODIPY oligomers would lead to controllable NIR photodevices including NIR photoswitches, highly sensitive biosensors, *etc*.

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Notes and references

‡ The methoxy groups significantly improve solubility of 1,4-bis(1*H*-pyrrol-2-yl)-2,5-dimethoxybenzene as a synthetic intermediate (see ESI†) to organic solvents.

1 (*a*) R. Y. Lai and A. J. Bard, *J. Phys. Chem. B*, 2003, **107**, 5036; (*b*) A. B. Nepomnyashchii, M. Bröring, J. Ahrens and A. J. Bard, *J. Am. Chem. Soc.*, 2011, **133**, 8633.
2 (*a*) T. G. Pavlopoulos, M. Shah and J. H. Boyer, *Appl. Opt.*, 1988, **27**, 4998; (*b*) J. H. Boyer, A. Haag, M.-L. Soong, K. Thangaraj and T. G. Pavlopoulos, *Appl. Opt.*, 1991, **30**, 3788.
3 *The Molecular Probes® Handbook: A Guide to Fluorescent Probes and Labeling Technologies*, ed. I. Johnson and M. T. Z. Spence, Invitrogen Corp., Carsbad, 11th edn, 2010.
4 (*a*) A. Loudet and K. Burgess, *Chem. Rev.*, 2007, **107**, 4891; (*b*) G. Ulrich, R. Ziessel and A. Harriman, *Angew. Chem., Int. Ed.*, 2008, **47**, 1184.
5 (*a*) K. Umezawa, A. Matsui, Y. Nakamura, D. Citterio and K. Suzuki, *Chem.–Eur. J.*, 2009, **15**, 1096; (*b*) O. Buyukcakir, O. A. Bozdemir, S. Kolemen, S. Erbas and E. U. Akkaya, *Org. Lett.*, 2009, **11**, 4644; (*c*) C. Jiao, K.-W. Huang and J. Wu, *Org. Lett.*, 2011, **13**, 632.
6 (*a*) V. R. Donuru, G. K. Vegesna, S. Velayudham, G. Meng and H. Liu, *J. Polym. Sci., Part A: Polym. Chem.*, 2009, **47**, 5354; (*b*) V. R. Donuru, G. K. Vegesna, S. Velayudham, S. Green and H. Liu, *Chem. Mater.*, 2009, **21**, 2130; (*c*) A. Nagai and Y. Chujo, *Macromolecules*, 2010, **43**, 193.
7 G. Qian and Z. Y. Wang, *Chem.–Asian J.*, 2010, **5**, 1006.
8 (*a*) M. Yuan, W. Zhou, X. Liu, M. Zhu, J. Li, X. Yin, H. Zheng, Z. Zuo, C. Ouyang, H. Liu, Y. Li and D. Zhu, *J. Org. Chem.*, 2008, **73**, 5008; (*b*) O. A. Bozdemir, R. Guliyev, O. Buyukcakir, S. Selcuk, S. Kolemen, G. Gulseren, T. Nalbantoglu, H. Boyaci and E. U. Akkaya, *J. Am. Chem. Soc.*, 2010, **132**, 8029; (*c*) F. Puntoriero, F. Nastasi, T. Bura, R. Ziessel, S. Campagna and A. Giannetto, *New J. Chem.*, 2011, **35**, 948.
9 S. Ozlem and E. U. Akkaya, *J. Am. Chem. Soc.*, 2009, **131**, 48.
10 (*a*) K. Rurack, M. Kollmannsberger and J. Daub, *New J. Chem.*, 2001, **25**, 289; (*b*) X. Peng, J. Du, J. Fan, J. Wang, Y. Wu, J. Zhao, S. Sun and T. Xu, *J. Am. Chem. Soc.*, 2007, **129**, 1500.
11 (*a*) D. J. Hill, M. J. Mio, R. B. Prince, T. S. Hughes and J. S. Moore, *Chem. Rev.*, 2001, **101**, 3893; (*b*) V. Dehm, M. Büchner, J. Seibt, V. Engel and F. Würthner, *Chem. Sci.*, 2011, **2**, 2094; (*c*) M. Barboiu, L. Prodi, M. Montalti, N. Zaccheroni, N. Kyritsakas and J.-M. Lehn, *Chem.–Eur. J.*, 2004, **10**, 2953; (*d*) R. B. Prince, T. Okada and J. S. Moore, *Angew. Chem., Int. Ed.*, 1999, **38**, 233; (*e*) C. Dolain, V. Maurizot and I. Huc, *Angew. Chem., Int. Ed.*, 2003, **42**, 2738; (*f*) K.-J. Chang, B.-N. Kang, M.-H. Lee and K.-S. Jeong, *J. Am. Chem. Soc.*, 2005, **127**, 12214; (*g*) H. Juwarker, J. M. Lenhardt, D. M. Pham and S. L. Craig, *Angew. Chem., Int. Ed.*, 2008, **47**, 3740; (*h*) Y. Hua and A. H. Flood, *J. Am. Chem. Soc.*, 2010, **132**, 12838; (*i*) Z. Yu and S. Hecht, *Angew. Chem., Int. Ed.*, 2011, **50**, 1640.
12 (*a*) K. Yamada, T. Toyota, K. Takakura, M. Ishimaru and T. Sugawara, *New J. Chem.*, 2001, **25**, 667; (*b*) I. V. Sazanovich, C. Kirmaier, E. Hindin, L. Yu, D. F. Bocian, J. S. Lindsey and D. Holten, *J. Am. Chem. Soc.*, 2004, **126**, 2664.
13 N. Sakamoto, C. Ikeda and T. Nabeshima, *Chem. Commun.*, 2010, **46**, 6732.
14 (*a*) A. Treibs and F.-H. Kreuzer, *Justus Liebigs Ann. Chem.*, 1968, **718**, 208; (*b*) R. W. Wagner and J. S. Lindsey, *Pure Appl. Chem.*, 1996, **68**, 1373; (*c*) C. Brückner, V. Karunaratne, S. J. Rettig and D. Dolphin, *Can. J. Chem.*, 1996, **74**, 2182.
15 G. M. Sheldrick, *Acta Crystallogr., Sect. A.*, 2008, **64**, 112.