Tetrahedron Letters 50 (2009) 1113–1116

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

# An efficient method for the synthesis of C–C connected phthalocyanine–porphyrin oligomers

Hasrat Ali, Johan E. van Lier *

*Department of Nuclear Medicine and Radiobiology, Faculty of Medicine and Health Sciences, Université de Sherbrooke, Sherbrooke (QC), Canada J1H 5N4*

ARTICLE INFO

*Article history:*
Received 17 November 2008
Revised 10 December 2008
Accepted 11 December 2008
Available online 24 December 2008

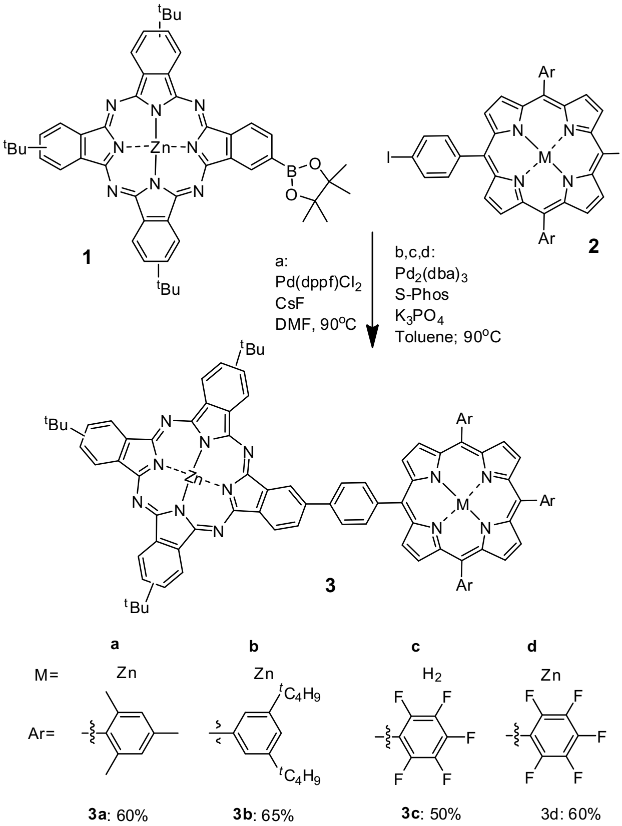
ABSTRACT

An efficient one-step method for the synthesis of covalently linked phthalocyanine–porphyrin (Pc–Por) hetero-dyads and Pc–Por–Pc hetero-triads, connected directly through C–C bonds, is presented. The procedure utilizes a Pd-mediated Suzuki cross-coupling reaction of a Pc–boronate synthon and a halogenated porphyrin. The two chromophores are directly linked, without spacer, through the β-pyrrolic-, meso-, and para-position of the meso-phenyl group of the porphyrins. The electronic absorption spectrum of the Pc–Por–Pc triad shows red-shifted, split Q-bands reflecting energy transfer.

Porphyrins (Por) and phthalocyanines (Pc) are structurally related macrocyclic compounds with highly π-conjugated systems exhibiting intense absorption in the visible region with strong Soret and Q-bands, respectively.[1] The absorption spectrum of the Por–Pc hetero-array covers a broad range of the solar spectrum. The sub-units interact through photoinduced electron and/or energy transfer from Por to Pc rendering them of prime interest for light harvesting arrays, which is of importance for effective use in photovoltaic and molecular photonics.[2]

A number of multi-component systems containing mixed Por–Pc systems connected via covalent and non-covalent bonds have been reported. Among these are non-conjugated Por–Pc hetero-dyad systems in which the macrocycle units are joined by various spacers such as oxygen-[3] or N-linkages.[4] Efficient photoinduced energy transfer from the Por to Pc unit depends strongly on the relative orientations and distances between the chromophores. The metal-mediated cross-coupling methodology of alkynes (connected by ethynyl or butadiynyl bridges) is a highly efficient method to prepare covalently linked conjugated Por–Pc hetero-dyads.[2b,5] The availability of such conjugates permitted detailed studies on electronic- and photonic-based cooperation between individual sub-units of the dyads.

A few reports for the synthesis of Pc–Por dyads attached directly through C–C bonds have appeared.[6] However, these earlier reported pathways require multi-step procedures. Recently, we reported[7] a method for the synthesis of a Suzuki Pc–boronate synthon and showed its successful application for the preparation of Pc–Pc hetero-dyads and Pc–$(Pc)_2$ homo-triad using a Pd-mediated Suzuki-coupling reaction. Here, we report the use of this Pc–boronate synthon to prepare Pc–Por dyads and Pc–Por–Pc triads in a single step.



**Scheme 1.** Phthalocyanine-*p*-phenyl porphyrin dyads.

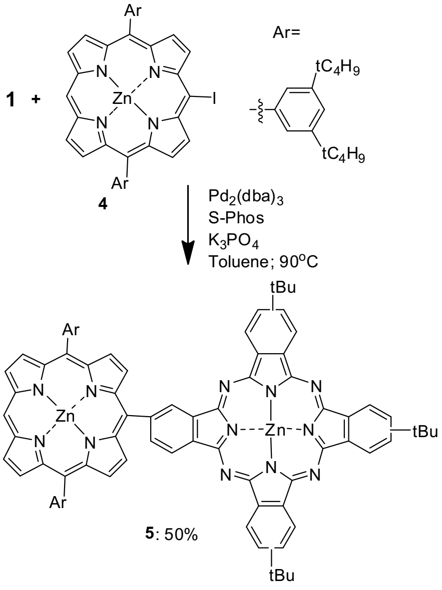
---

* Corresponding author. Tel.: +1 819 564 5409; fax: +1 819 564 5442.
*E-mail address:* johan.e.vanlier@usherbrooke.ca (J.E.v. Lier).

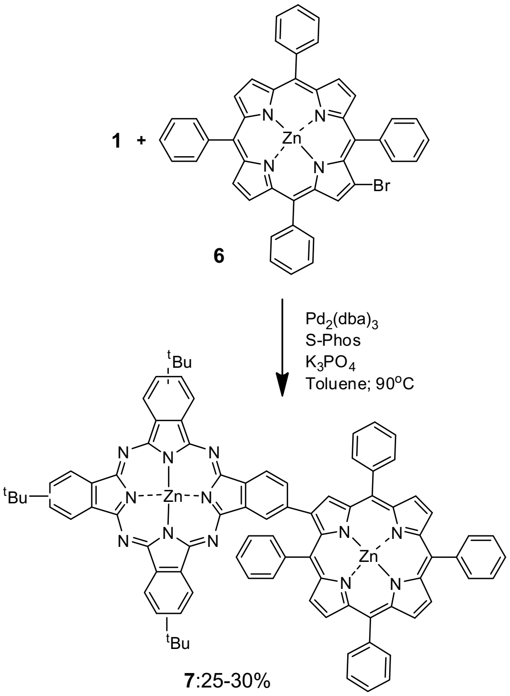
0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.12.059

In our first approach, we prepared the dyad containing the Por and ZnPc chromophores with the Pc directly linked at the *para*-position of the *meso*-phenyl group of the porphyrins using the Suzuki cross-coupling reaction (Scheme 1). A mixture of Pc–boronate (**1**) (8.7 mg, 10 μmol) and 5-(*p*-iodophenyl)-5,10,15,trimesityl-20(*p*-iodophenyl) Zn porphyrin[8] (**2a**) (9.4 mg, 11 μmol), [1,1-bis(diphenylphosphino)-ferrocene]dichloro Pd(II)-dichloromethane complex (1:1) [Pd(dppf)Cl$_2$] (catalyst) (5 mg), and CsF (base) (10 mg), in DMF (5 mL) (under N$_2$), was heated at 90 °C for 3 h. After purification, **3a** was obtained in about 60% yield. This method was used to incorporate a number of substituted porphyrin derivatives. Treatment of Pc–boronate (**1**) (8.7 mg, 10 μmol) with 5-(*p*-iodophenyl)-10,15,20-tris(*m*-di-*tert*-butylphenyl) Zn porphyrin (**2b)**[9] (12.6 mg, 11 μmol) using tris(dibenzylideneacetone) dipalladium (Pd$_2$dba$_3$) (7 mg) as catalyst, 2-(2,6-dimethoxybiphenyl)-dicyclohexyl phosphine (S-phos, ligand) (8 mg), and K$_3$PO$_4$ (10 mg), in toluene (5 mL) (under N$_2$), for 3 h at 90 °C gave **3b** in 60% yield (after purification over a silica gel column). An analytical sample was obtained after HPLC on a reversed-phase C-18 column in THF–H$_2$O. In a similar manner, treatment of **1** with 5-(*p*-iodophenyl)-10,15,20-tris (pentafluorophenyl) porphyrin (**2c)** and Zn derivative[10] **2d** in toluene under N$_2$ using the same catalyst and ligand at 90 °C for 2–3 h afforded the corresponding dyads **3c** and **3d** in 50–65% yield. [12] The metal-free **3c** can be used to prepare dimetallic Pc–Por conjugates.

Next, we prepared a dyad where the Pc moiety is directly bonded to a *meso*-position of the tetraphenylporphyrin (Scheme 2). The Pc–boronate synthon **1** (10 μmol) and 5-bromo-10,20-bis(3,5-bis-*tert*-butylphenyl) Zn porphinato[11] (**4**) (9 mg, 11 μmol), catalyst Pd$_2$dba$_3$ (6 mg), ligand S-phos (10 mg), and K$_3$PO$_4$ (base) (10 mg) were dissolved in toluene (8 mL) under N$_2$, and the mixture was heated at 90 °C for 24 h. Two products corresponding to the reduced porphyrin analog and Pc–Por dyad **5** (50%) were isolated. In the third group of dyads, the Pc moiety is directly bonded to a β-pyrrolic position of a *meso*-tetraphenylporphyrin. To Pc–borane complex **1** (13 mg, 15 μmol) and β-bromo-5,10,15,20-tetraphenyl Zn porphyrin (**6**) (13 mg, 16 μmol), Pd$_2$dba$_3$ (7 mg) (catalyst), S-Phos (ligand) (9 mg), and K$_3$PO$_4$ (10 mg) (base) was added toluene (8 mL) (under N$_2$), and the mixture was heated at 90 °C for 24 h. Purification on a silica gel column, followed by HPLC gave **7** in about 25–30% yield (Scheme 3). As expected, the reactivity of the bromoporphyrin is less than that of the iodo analog. The coupling product **7** gave the expected HRMS and UV–vis spectra in THF corresponding to the dyad with a broad absorption Soret band at 349 nm and Q-band at 676 nm characteristic of Pc and a 418 nm porphyrin Soret band. The spectra were similar to those of the corresponding monomers and were in close agreement with those reported by Torres et al.,[6b] who obtained the same compound through a multi-step procedure in 30% yield.



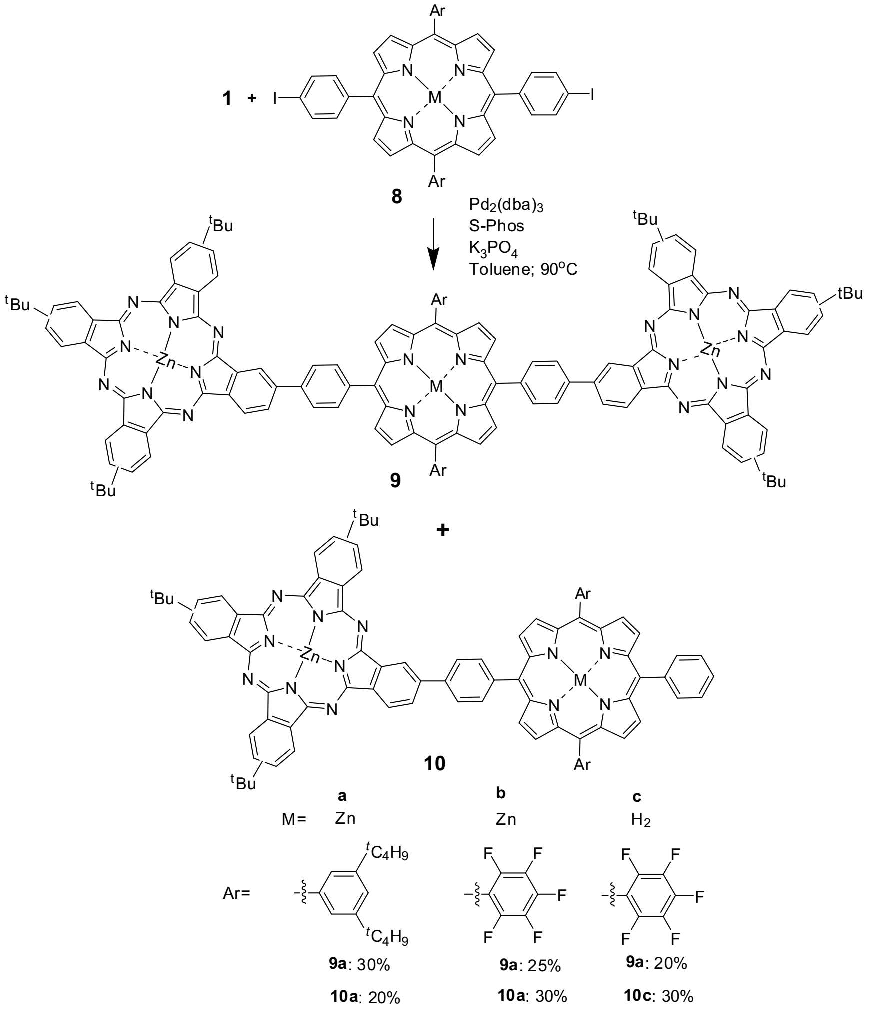
**Scheme 2.** Phthalocyanine–*meso*-porphyrin dyad.



**Scheme 3.** Phthalocyanine β-pyrrolic porphyrin dyad.

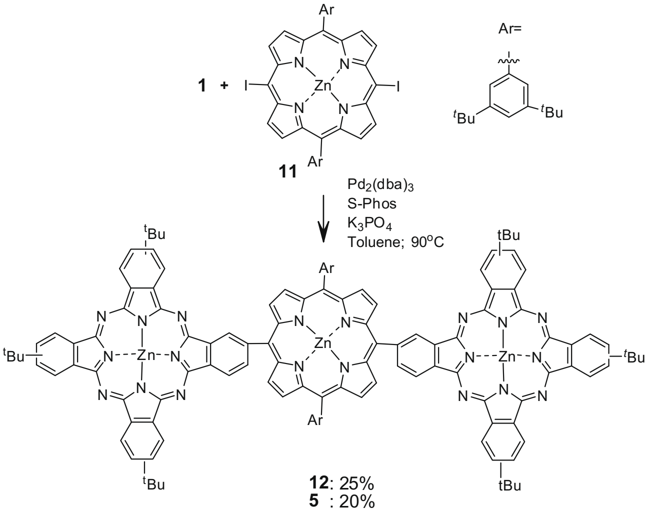
Dihalo porphyrin derivatives were also investigated for the synthesis of Pc–Por–Pc triad using the above procedure. Two types of triads were prepared in which the Pc was connected at either the *p*-phenyl-or *meso*-position of the porphyrins. Pc–borane **1** (26 mg, 30 μmol) and 5,15-bis(3,5di-*tert*-butylphenyl)-10,20-bis(*p*-iodophenyl) Zn(II) porphyrin (**8a**) (12 mg, 10 μmol), Pd$_2$dba$_3$ (10 mg) (catalyst), S-Phos (12 mg) (ligand), and K$_3$PO$_4$ (10 mg) were dissolved in toluene (10 mL) and reacted for 4 h at 90 °C. After purification by silica gel column chromatography, HPLC analysis showed the presence of a number of peaks. Two main components were characterized as the triad **9a** (30%) and a dyad in which one of the halo groups is reduced, that is, **10a** (25%). Compounds **8b** and **8c** were treated with **1** in the same manner as described for **8a** to yield the corresponding trimers **9b** and **9c** together with the reduced dyads **10b** and **10c** as secondary products (Scheme 4). No attempts were made to optimize the reaction conditions to improve the yield of the triad. In an analogous manner, Pc–Por–Pc triads substituted at the two *meso*-positions of the porphyrin were also prepared. Treatment of **11** with a 3 M excess of **1** gave Pc–Por dimer **5** (20%) and a trimer **12** (25%) (Scheme 5) along with some other products. When the above reaction was conducted in THF using tetrakis (triphenylphosphine) Pd(0) (catalyst) and K$_3$PO$_4$ (base), a dyad containing a bromo group was also obtained. The latter product could serve as a substrate for further modifications. The metal-free derivatives can be used to prepare different heterodimetallic oligomers.

The spectral features of the **3**, **7,** and **9** dyad arrays are very similar to those of the monomers. Compounds **3a** and **b** exhibit a strong Soret band at 425 nm, and **3c** at 421 nm and **3d** at 414 nm show weak Soret bands at about 350 nm along with weak



**Scheme 4.** Phthalocyanine-*p*-phenyl porphyrin-phthalocyanine triads.

Q-bands for the porphyrins and a strong Q-band at 676 nm for the Pc. Similarly, the spectral features of triad arrays containing two Pc units and one Por unit, that is, **9a**, **9b,** and **9c,** exhibit strong Soret bands at 425, 423, and 417 nm, respectively, and a strong Q-band at 676 nm along with other weak absorption peaks. However, the ratio between the intensities of the Soret band of the Por and Q-band of the Pc decreases confirming the presence of two Por units per molecule. The absorption spectra of the arrays are approximately imposable on the absorption spectra of the Por and Pc monomers. These results indicate that the added torsional constraints do not significantly alter the overall structure of the array or result in discernible changes in the electronic coupling between the constituents, which conform with weak electronic coupling.



**Scheme 5.** Phthalocyanine–*meso*-porphyrin–phthalocyanine triads.

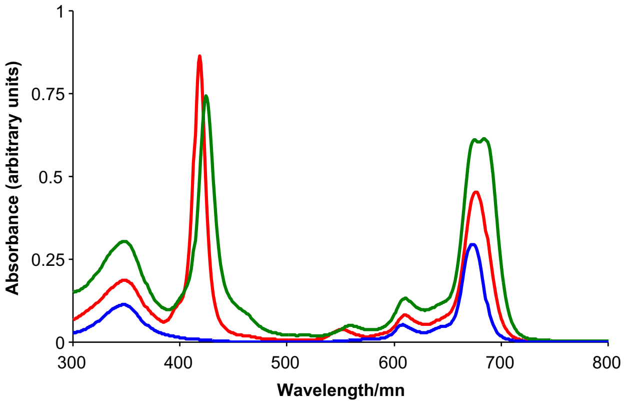


**Figure 1.** Electronic spectra of ZnPc(*t*-bu)-4-borane **1** (blue), the Por–Pc dimer **5** (red), and Pc–Por–Pc triad **12** (green).

The absorption spectrum of compound **5** exhibits an intense Soret band at 418 nm and weaker Q-band at 554 nm attributed to the porphyrin moiety; the additional Soret band at 354 nm and intense Q-band at 677 nm reflect the presence of the Pc moiety. The absorption spectrum of compound **12** exhibits an intense Soret band at 424 nm and weaker Q-bands of the porphyrin moiety at 563 nm. The Soret band of the Pc moiety lies near 350 nm with a relatively strong split Q-band at 676 nm and 685 nm (Fig. 1). The Pc Q-bands are red-shifted 11 nm relative to those of the Pc–borane synthon. This red shift is attributed to extension of the conjugated π-system involving the two linkers from the attached porphyrins.

In summary, we report the synthesis of covalently C–C linked Pc–Por hetero-dimers and Pc–Por–Pc hetero-triads using a Pd-catalyst Suzuki cross-coupling reaction and Pc–boronate synthon. Photophysical data reveal π-conjugation between the sub-units that correlate to the degree of planarity of the molecules.

## Acknowledgment

The Jeanne and J.-Louis Lévesque Chair in Radiobiology supported this research.

## References and notes

1. (a)*The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2003; Vols. 15 and 16, (b) Gouterman, M.. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, NY, 1978; Vol. 3.
2. (a)*The Porphyrin Handbook*; Kadish, K. M., Smith, K. M., Guilard, R., Eds.; Academic Press: San Diego, CA, 2003; Vol. 18, (b) Miller, M. A.; Lammi, R. K.; Prathapan, S.; Holten, D.; Lindsey, J. S. *J. Org. Chem.* **2000**, *10*, 6634–6649; (c) Ito, F.; Ishobashi, Y.; Khan, S. R.; Miyasaka, H.; Kameyama, K.; Morisue, M.; Satake, A.; Ogawa, K.; Kobuke, Y. *J. Phys. Chem. A* **2006**, *110*, 12734–12742; (d) Tannerst, S.; Ermilov, E. A.; Vogel, J. O.; Choi, T. M.; Ng, D. K. P.; Roder, B. *J. Phys. Chem. B* **2007**, *111*, 8053–8062.
3. (a) Gaspard, S.; Giannotti, C.; Millard, P.; Schaeffer, C.; Tran-Thi, T.-H. *J. Chem. Soc., Chem. Commun.* **1986**, 1239; (b) Tian, H.-J.; Zhou, Q.-F.; Shen, S.-Y.; Xu, H. J. *Chin. Chem. Lett.* **1992**, *3*, 873–876; (c) Tian, H. J.; Zhou, Q.-F.; Shen, S.-Y.; Xu, H.-J. *Photochem. Photobiol. A: Chem.* **1993**, *72*, 163–168; (d) Li, L.; Shen, S.; Yu, Q.; Zhou, Q.; Xu, H. J. *J. Chem. Soc., Chem. Commun.* **1991**, 619–620; (e) Zhao, Z.; Nyokong, T.; Maree, M. D. *Dalton Trans.* **2005**, 3732–3737; (f) Bian, Y.; Chen, X.; Wang, D.; Choi, C.-F.; Zhou, Y.; Zhu, P.; Ng, D. K. P.; Jiang, J.; Weng, Y.; Li, X. *Chem. Eur.* **2007**, *13*, 4169–4177; (f) Zhao, Z.; Maree, D. M.; Ogunsipe, A. O.; Nyokong, T. *J. Porphrins Phthalocyanines* **2005**, *9*, 186–197; (g) Lyubimtsev, A,; Iqbal, Z.; Hanack, M. *Australian J. Chem.* **2008**, *61*, 273–278.; (h) Lo, P.-C.; Leng, X.; Ng, D. K. P. *Coord. Chem. Rev.* **2007**, *251*, 2334–2353.
4. Soares, A. R. M.; Martinez-diaz, M. V.; Bruckner, A.; Pereira, A. M. V. M.; Tome, J. P. A.; Alonso, C. M. A.; Faustino, M. A. F.; Neves, M. G. P. M. S.; Tome, A. C.; Silva, A. M. S.; Cavaleiro, J. A. S.; Torres, T.; Guldi, D. M. *Org. Lett.* **2007**, *19*, 1557–1560.
5. (a) Ik Yang, S.; Li, J.; Chao, H. S.; Kim, D.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *J. Mater. Chem.* **2000**, *10*, 283–296; (b) Ambroise, A.; Wagner, R. W.; Rao, P. D.; Riggs, J. A.; Hascoat, P.; Diers, J. R.; Seth, J.; Lammi, R. K.; Bocian, D. F.; Holten, D.; Lindsey, J. S. *Chem. Mater.* **2001**, *13*, 1023–1034; (c) Sutton, J. M.; Boyle, R. W. *Chem. Commun.* **2001**, 2012–2013.
6. (a) Kameyama, K.; Satake, A.; Kobuke, Y. *Tetrahedron Lett.* **2004**, *45*, 7617–7620; (b) Tome, J. P. C.; Pereira, A. M. V. M.; Alonso, C. M. A.; Neves, M. G. P. M. S.; Tomes, A. C.; Silva, A. M. S.; Cavaleiro, J. A. S.; Martinez-diaz, M. V.; Torres, T.; Rahman, G. M. A.; Ramey, J.; Guldi, D. M. *Eur. J. Org. Chem.* **2006**, 257–267.
7. Ali, H.; van Lier, J. E. *Tetrahedron Lett.* **2009**, *50*, 337–339.
8. Lindsey, J. S.; Prathapan, S.; Johnson, T. E.; Wagner, R. W. *Tetrahedron* **1994**, *50*, 8941–8968.
9. Adapted from the procedure of Tong, L. H.; Pascu, S. I.; Jarrosson, T.; Sanders, K. M. *Chem. Commun.* **2006**, 1085–1087.
10. Strachan, J.-P.; Gentermann, S.; Seth, J.; Kalsbeck, A.; Lindsey, J. L.; Holten, D.; Bocian, D. F. *J. Am. Chem. Soc.* **1997**, *119*, 11191–11201.
11. Plater, M.; Aiken, S.; Bourhill, G. *Tetrahedron* **2002**, *58*, 2405–2413.
12. *MS analysis*: MS (MALDI-TOF) *m/z*: Compound **3a**: calcd for $C_{97}H_{84}N_{12}Zn_2$: 1548.6 found 1548.6; **3b**: calcd for $C_{112}H_{114}N_{12}Zn_2$: 1759; found 1759.1412; **3c**: calcd for $C_{88}H_{53}F_{15}N_{12}Zn$ 1626.36; found 1625.9; **3d**: calcd for $C_{88}H_{51}F_{15}N_{12}Zn_2$ 1688.27; found 1689.2; **5**: calcd for $C_{92}H_{90}N_{12}Zn_2$ 1494.57; found 1494.97; **7**: calcd for $C_{98}H_{66}N_{12}Zn_2$ 1418.41; found 1418.4046; **9a**: calcd for $C_{148}H_{136}N_{20}Zn_2$ 2391.03; found 2391.065; **9b**: calcd for $C_{132}H_{94}F_{10}N_{20}Zn_3$ 2346.51.36; found 2346.8; **9c**: calcd for $C_{132}H_{96}F_{10}N_{20}Zn_3$ 2278.66; found 2278.6; **10a**: calcd for $C_{104}H_{98}N_{12}Zn_2$ 1642.66; found 1444.2; **10b**: calcd for $C_{88}H_{56}F_{13}N_{12}Zn_2$ 1598.32.36; found 1598.2; **10c**: calcd for $C_{88}H_{56}F_{10}N_{12}Zn$ 1536.40; found 1535.7; **12**: calcd for $C_{136}H_{128}N_{20}Zn_3$ 2232.85; found 2232.9.