Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron Letters
Tetrahedron Letters 48 (2007) 477–481

Novel fullerene receptors based on calixarene–porphyrin conjugates

Martin Káš,[a] Kamil Lang,[b] Ivan Stibor[a] and Pavel Lhoták[a,*]

[a]*Department of Organic Chemistry, Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic*
[b]*Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež, Czech Republic*

Received 7 September 2006; revised 31 October 2006; accepted 8 November 2006
Available online 30 November 2006

Abstract—Several different synthetic approaches enabling a direct covalent connection between the *meso*-position of porphyrin and the upper rim of calix[4]arene have been studied. The best results were obtained via condensation of an excess of pyrrole and *p*-methylbenzaldehyde with calix[4]arene-5,17-dialdehyde under $BF_3{\cdot}Et_2O$ catalysis in $CHCl_3$. Subsequent oxidation of the intermediate porphyrinogen gave the corresponding bis-porphyrin–calixarene conjugate in 15% overall yield. The ^1H NMR complexation study revealed the pronounced selectivity of the bis-porphyrin derivative towards C_{70} fullerene.

Calix[4]arenes and their relatives[1] are frequently used as molecular scaffolds in the design of elaborate supramolecular systems, including a variety of functional receptors. Among various hosts for fullerene recognition, calix[*n*]arenes have played an important role since the pioneering work of Shinkai's and Atwood's groups.[2] There are numerous examples[3] demonstrating that spherical fullerenes are attracted by a shape-complementary cavity of calixarenes to form complexes both in solution and in the solid state. Recent studies have shown that the curved π surfaces of C_{60} or C_{70} fullerenes can interact with the (metallo)porphyrin moieties by attractive π–π interactions.[4] Consequently, various multiporphyrin systems and extensive studies of porphyrin/fullerene interactions have been reported.[5]

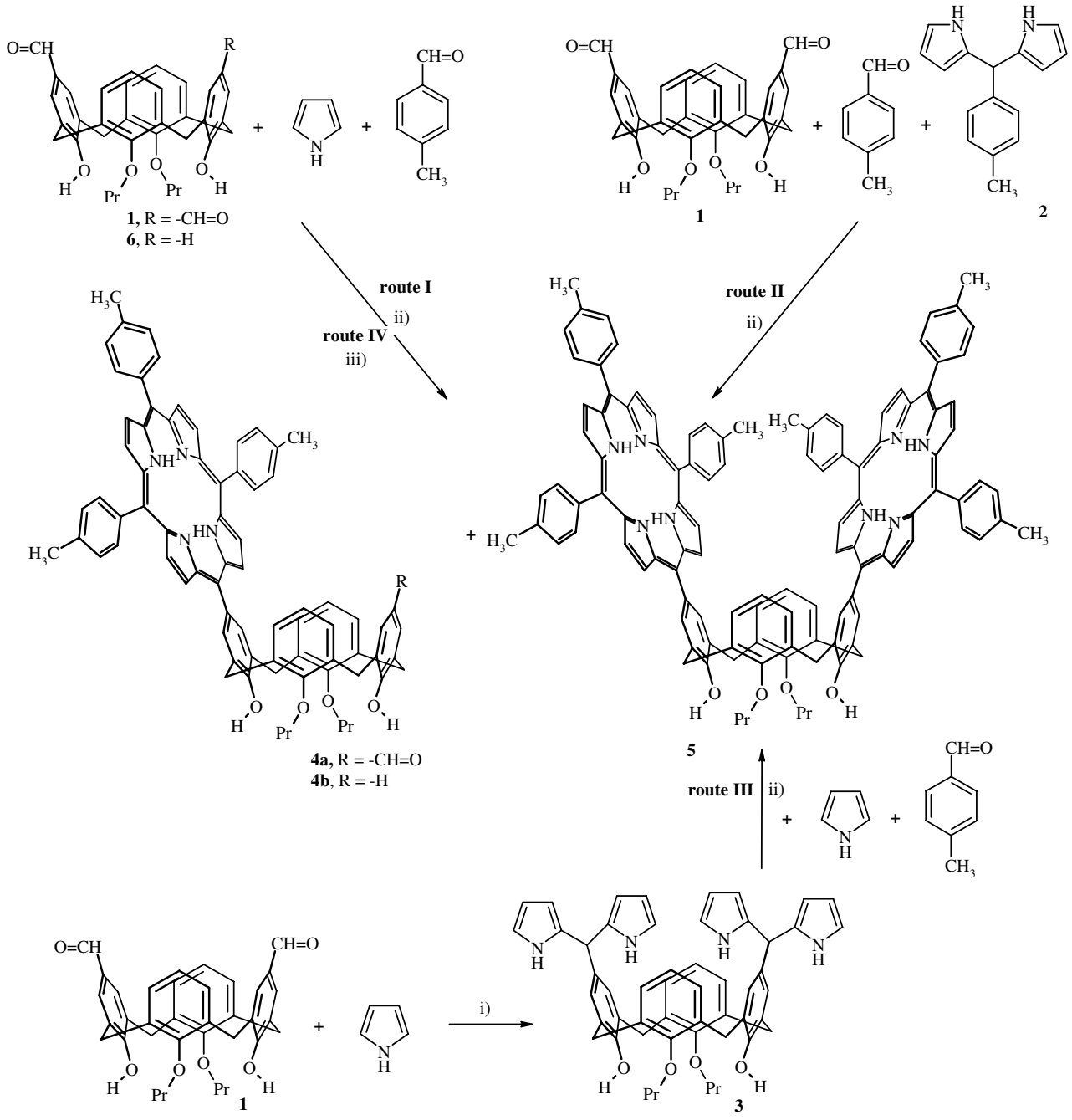
In our previous study we showed that the combination of porphyrin and calixarene motifs within one molecule leads to novel receptors with many interesting complexation properties.[6] As we have reported recently, calix[4]arene or thiacalix[4]arene–porphyrin conjugates with porphyrin units preorganised in the distal positions, behave as molecular tweezers[7] that can pick up fullerenes in solution. Despite the fact that the connection between the porphyrin and calixarene units was constructed via relatively mobile spacers, the receptors exhibited pronounced selectivity towards fullerene C_{70}. In this context, we expected that mounting the tetraarylporphyrin moiety directly to the upper rim of calix[4]arene would lead to more preorganised structures, and hence, to higher selectivity of fullerene complexation. In this letter we report on the synthesis and binding properties of such compounds—calix[4]arenes bearing porphyrins directly connected via the *meso*-positions.

Calix[4]arenes with porphyrin moieties directly connected via the *meso* position to the upper rim are not easily accessible and only a few examples of these types of structures can be found in the literature.[6a,8] The synthesis of the target compound **5** is depicted in Scheme 1. The starting dialdehyde **1** was obtained via formylation of 25,27-dipropoxycalix[4]arene with dichloromethyl methyl ether[9] in a high yield, which was then used for the mixed aldehyde condensation[10] with *p*-tolualdehyde and pyrrole (route I). The stoichiometric ratio of the reactants (**1**:*p*-tolualdehyde:pyrrole = 1:6:8) under $BF_3{\cdot}Et_2O$ catalysis gave the target bis-porphyrin derivative **5** in a very low yield (0.4%). Surprisingly, under these conditions the mono-substituted calixarene **4a** bearing one unreacted formyl group was isolated (in addition to tetra-*p*-tolylporphyrin) as the main product (14%).[11]

As the use of excess pyrrole did not lead to good results, we turned our attention to the application of more preorganised starting compounds. Thus, *p*-tolualdehyde was transformed into the corresponding dipyrromethane **2** and used for the condensation (route II). Although the number of molecules needed for condensation is much lower than that in route I (7 vs 15), this

* Corresponding author. Tel.: +420 220 445 055; fax: +420 220 444 288; e-mail: lhotakp@vscht.cz

0040-4039/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2006.11.044



Scheme 1. Reagents and conditions: (i) Excess pyrrole, rt/3 h (85%); (ii) (a) $CHCl_3$, cat. $BF_3{\cdot}Et_2O$, rt/7 h, (b) DDQ, rt (0.4–15%); (iii) CH_3CH_2COOH, reflux (0.1%).

strategy gave only a slightly better result—compound **5** was isolated in 1% yield. In route III, calix[4]arene dialdehyde **1** was reacted with excess pyrrole to give the bis-dipyrromethane derivative **3** in 85% yield.[12,13] Unfortunately, condensation of **3** with pyrrole and *p*-tolualdehyde and subsequent oxidation of the intermediate porphyrinogen with DDQ gave the target compound **5** in only 3% yield. The next method used for porphyrin synthesis involved route IV, where a mixture of **1**, pyrrole and *p*-tolualdehyde was stirred under reflux in propionic acid in the presence of air. This procedure led to a complicated reaction mixture from which derivative **5** was isolated in a very low yield (0.1%) via repeated preparative TLC. As all attempts to obtain compound **5** in an acceptable yield failed, we decided to return to route I and further optimise the reaction conditions. After many trials and errors, we found that the condensation of dialdehyde **1**, pyrrole and *p*-tolualdehyde in a ratio of 1:86:88 ($CHCl_3/BF_3{\cdot}Et_2O$ catalysis) gave bis-porphyrin **5** in 15% yield.[14] To gain a deeper insight into the mechanism of fullerene complexation, a model compound **4b** having only one porphyrin unit on the upper rim was prepared. Compound **4b** was obtained via route IV from the corresponding monoaldehyde **6** in 10% yield.[15]

The UV–vis absorption spectra of **5**, shown in Figure 1, are similar to those obtained for 5,10,15,20-tetraphenylporphyrin (**TPP**). In our opinion, a small red

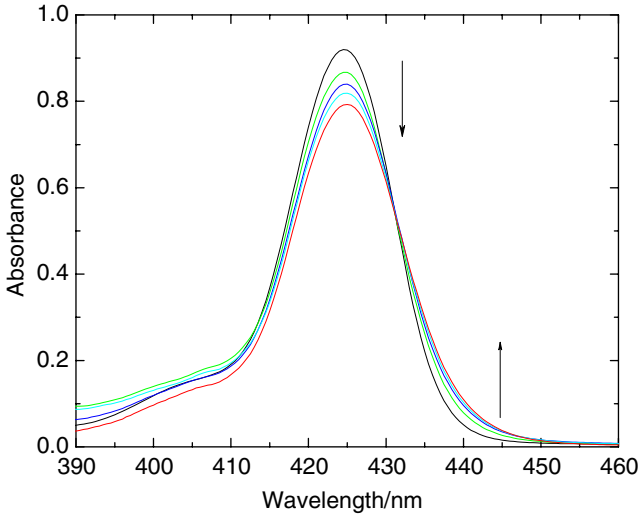


Figure 1. Spectral changes induced by the addition of C_{60} to **5** ($c_0 = 14\ \mu M$) in toluene. Arrows indicate the absorbance changes induced by C_{60} with concentration varied from 0 (black line) to 3.1×10^{-3} M (1 mm cell, 298 K).

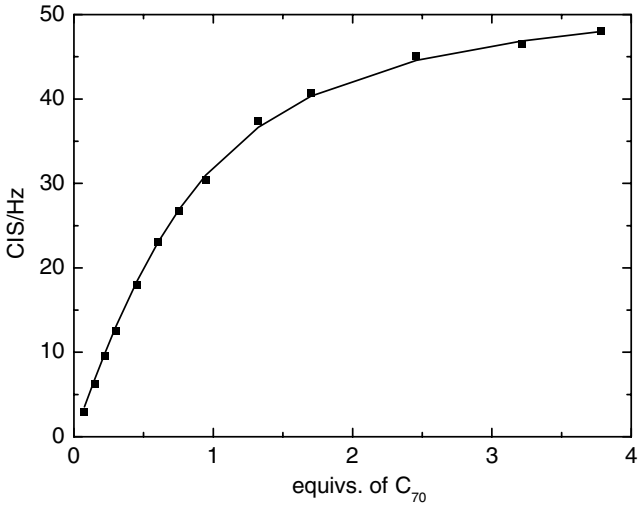


Figure 2. ^{1}H NMR titration of **5** with C_{70} (porphyrin NH protons, C_6D_6, 300 MHz, 298 K). The solid line is the theoretical isotherm obtained by the least-squares fit to the experimental data.

shift of the Soret band of **TPP** from 419 nm to 423 nm and 425 nm in **4b** and **5**, respectively, is an indication of weak interactions between the porphyrin and calixarene moieties. The two transition dipoles B_x and B_y of the porphyrin moiety in compound **5** are degenerate and show one strong Soret band. This indicates that intramolecular dipole–dipole exciton coupling between the directly attached porphyrin units in **5** is very weak. In contrast, the porphyrin-substituted lower rim in structurally similar bisporphyrin receptors leads to a closer contact of the porphyrin units as documented by a broadening and splitting of the Soret bands due to exciton coupling.[7] In this case the B_x and B_y transition dipoles become nondegenerate.

The addition of C_{60} or C_{70} to a toluene solution of **5** leads to hypochromicity of the original Soret band and the appearance of a well-defined isosbestic point (Fig. 1), which indicates noncovalent interaction between fullerene and the porphyrin units. Unfortunately, the spectral changes are weak (especially with C_{60}) and the solubilities of C_{60} and C_{70} are poor such that the precise values of the binding constants could not be evaluated. It was estimated that compound **5** binds C_{60} with K below 140 M^{-1} (Fig. 1). Very small spectral changes of the single arm compound **4b** or **TPP** also confirmed their weak interaction with fullerenes. Especially in the case of TPP, the hypochromicity was very small (~1% after addition of 5×10^{-4} M C_{60}) and could only be observed at high concentrations of the components. This fact is responsible for the lack of detectable interactions in our previous paper.[7]

An improved insight into the binding ability of calixarene–porphyrin conjugates was gained using ^{1}H NMR titrations. Upon the addition of C_{70} to a solution of **5** in benzene-d_6 or toluene-d_8, the proton resonances of the porphyrin pyrrole NHs moved upfield (ca 0.2 ppm in the **5** + C_{70} system) (Fig. 2). Similar behaviour, albeit not so pronounced, was observed for the aromatic protons of the porphyrin moieties, while the signals of the calixarene skeleton remained almost unchanged. The complexation-induced chemical shifts (CIS) indicate interaction between the porphyrin and fullerene moieties. Moreover, a Job plot constructed with the help of ^{1}H NMR spectroscopy (Fig. 3) confirmed the formation of a 1:1 complex.

Assuming 1:1 stoichiometry, the binding isotherms were analysed by a nonlinear least-squares method.[16] The corresponding binding constants K are summarised in Table 1. While the binding constants of **4b** and **5** for C_{70} were almost identical in toluene, the corresponding constants in benzene were rather distinct. The much higher constant for compound **5** ($K = 4500 \pm 600\ M^{-1}$) compared with **4b** ($K = 1100 \pm 200\ M^{-1}$) indicates a cooperative binding of fullerene by both porphyrin units. More efficient complexation of

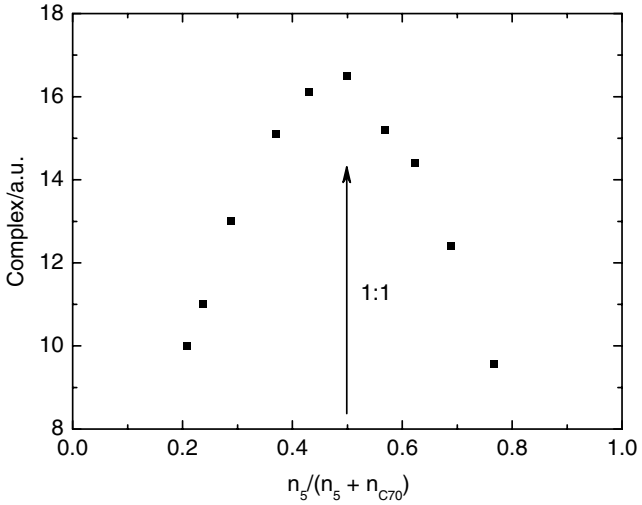


Figure 3. Job plot for the **5** + C_{70} system (^{1}H NMR, C_6D_6, 300 MHz, 298 K).

Table 1. Binding constants K of **4b** and **5** towards fullerene C_{70} (^{1}H NMR, 25 °C, 300 MHz)

	K [mol^{-1} l][a]	
	Toluene-d_8	Benzene-d_6
4b	1300 ± 500	1100 ± 200
5	1000 ± 200	4500 ± 600

[a] CIS for C_{60} were too small (<10 Hz).

C_{70} by **5** in benzene (compared with toluene) could be related to different solvation effects and/or competitive interactions of toluene with the receptor. Nevertheless, direct competitive binding of toluene into the calixarene cavity (NMR titration experiments in $CDCl_3$) was not observed. Interestingly, C_{60} induces only very minor changes in the ^{1}H NMR spectra suggesting very weak binding of fullerene C_{60}. In all cases the CIS values were too small (CIS <10 Hz) to allow quantitative determination of the binding constants.

In conclusion, we have shown that calix[4]arenes bearing porphyrin units directly connected to the upper rim at the *meso*-position represent good preorganised molecular clefts with C_{70}/C_{60} binding selectivity. Synthetic procedures leading to similar derivatives are currently under investigation.

Acknowledgements

This research was partially supported by the Ministry of Education, Youth and Sports of the Czech Republic (Research Centre LC06070).

References and notes

1. For books on calixarenes, see: (a) *Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Eds.; Kluwer Academic: Dordrecht, 2001; (b) Mandolini, L.; Ungaro, R. *Calixarenes in Action*; Imperial College Press: London, 2000; (c) Gutsche, C. D. Calixarenes Revisited. In *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; The Royal Society of Chemistry: Cambridge, 1998; Vol. 6; (d) *Calixarenes 50th Anniversary: Commemorative Issue*; Vicens, J., Asfari, Z., Harrowfield, J. M., Eds.; Kluwer Academic: Dordrecht, 1994.
2. (a) Suzuki, T.; Nakashima, K.; Shinkai, S. *Chem. Lett.* **1994**, 699–702; (b) Atwood, J. L.; Koutsantonis, G. A.; Raston, C. L. *Nature* **1994**, *368*, 229–231.
3. For selected papers, see: (a) Zhang, S.; Eschegoyen, L. *J. Org. Chem.* **2005**, *70*, 9874–9881; (b) Makha, M.; Raston, C. L.; Sobolev, A. N.; Turner, P. *Cryst. Growth Des.* **2005**, *6*, 224–228; (c) Kunsagi-Mate, S.; Szabo, K.; Bitter, I.; Nagy, G.; Kollar, L. *Tetrahedron Lett.* **2004**, *45*, 1387–1390; (d) Atwood, J. L.; Barbour, L. J.; Heaven, M. W.; Raston, C. L. *Angew. Chem., Int. Ed.* **2003**, *42*, 3254–3257; (e) Atwood, J. L.; Barbour, L. J.; Heaven, M. W.; Raston, C. L. *Chem. Commun.* **2003**, 2270–2271; (f) Mizyed, S.; Ashram, M.; Miller, D. O.; Georghiou, P. E. *J. Chem. Soc., Perkin Trans. 2* **2001**, 1916–1919; (g) Buvári-Barcza, A.; Rohonczy, J.; Rozlosnik, N.; Gilányi, T.; Szabo, B.; Lovas, G.; Braun, T.; Samu, J.; Barcza, L. *J. Chem. Soc., Perkin Trans. 2* **2001**, 191–196; (h) Haino, T.; Araki, H.; Yamanaka, Y.; Fukazawa, Y. *Tetrahedron Lett.* **2001**, *42*, 3203–3206; (i) Yanase, M.; Matsuoka, M.; Tatsumi, Y.; Suzuki, M.; Iwamoto, H.; Haino, T.; Fukazawa, Y. *Tetrahedron Lett.* **2001**, *42*, 493–497; (j) Wang, J.; Bodige, S. G.; Watson, W. H.; Gutsche, C. D. *J. Org. Chem.* **2000**, *65*, 8260–8263; (k) Hardie, M. J.; Raston, C. L. *Chem. Commun.* **1999**, 1153–1163; (l) Yanase, M.; Haino, T.; Fukazawa, Y. *Tetrahedron Lett.* **1999**, *40*, 2781–2784; (m) Atwood, J. L.; Barbour, L. J.; Raston, C. L.; Sudria, I. B. N. *Angew. Chem., Int. Ed.* **1998**, *37*, 981–983.
4. For a review on fullerene–porphyrin interactions, see: Boyd, P. D. W.; Reed, C. A. *Acc. Chem. Res.* **2005**, *38*, 235–242.
5. For some recent examples, see: (a) Wu, Z. Q.; Shao, X. B.; Li, C.; Hou, J. L.; Wang, K.; Jiang, X. K.; Li, Z. T. *J. Am. Chem. Soc.* **2005**, *127*, 17460–17468; (b) Yamaguchi, T.; Ishii, N.; Tashiro, K.; Aida, T. *J. Am. Chem. Soc.* **2003**, *125*, 13934–13935; (c) Sun, D.; Tham, F. S.; Reed, C. A.; Chaker, L.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2002**, *124*, 6604–6612; (d) Ayabe, M.; Ikeda, A.; Shinkai, S.; Sakamoto, S.; Yamaguchi, K. *Chem. Commun.* **2002**, 1032–1033; (e) Konarev, D. V.; Kovalevsky, A. Y.; Li, X.; Neretin, I. S.; Litvinov, A. L.; Drichko, N. V.; Slovokhotov, Y. L.; Coppens, P.; Lyubovskaya, R. N. *Inorg. Chem.* **2002**, *41*, 3638–3646; (f) Guldi, D. M.; Da Ros, T.; Braiuca, P.; Prato, M.; Alessio, E. *J. Mater. Chem.* **2002**, *12*, 2001–2008; (g) Sun, D.; Tham, F. S.; Reed, C. A.; Chaker, L.; Burgess, M.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2000**, *122*, 10704–10705; (h) Boyd, P. D. W.; Hodgson, M. C.; Rickard, C. E. F.; Oliver, A. G.; Chaker, L.; Brothers, P. J.; Bolskar, R. D.; Tham, F. S.; Reed, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 10487–10495.
6. (a) Dudič, M.; Lhoták, P.; Král, V.; Lang, K.; Stibor, I. *Tetrahedron Lett.* **1999**, *40*, 5949–5952; (b) Dudič, M.; Lhoták, P.; Stibor, I.; Dvořáková, H.; Lang, K. *Tetrahedron* **2002**, *58*, 5475–5482; (c) Dudič, M.; Lhoták, P.; Stibor, I.; Lang, K.; Prošková, P. *Org. Lett.* **2003**, *5*, 149–152; (d) Dudič, M.; Lhoták, P.; Petříčková, H.; Stibor, I.; Lang, K.; Sýkora, J. *Tetrahedron* **2003**, *59*, 2409–2415.
7. Dudič, M.; Lhoták, P.; Stibor, I.; Petříčková, H.; Lang, K. *New J. Chem.* **2004**, *28*, 85–90.
8. (a) Arimura, T.; Ide, S.; Sugihara, H.; Murata, S.; Sessler, J. L. *New J. Chem.* **1999**, *23*, 977; (b) Arimura, T.; Nishioka, T.; Ide, S.; Sugihara, H.; Murata, S.; Tachiya, J. *J. Chem. Res.* **2002**, 333–335; (c) Khoury, R. G.; Jaquinod, L.; Aoyagi, K.; Olmstead, M. M.; Fisher, A. J.; Smith, K. M. *Angew. Chem., Int. Ed.* **1997**, *36*, 2497–2500.
9. Arduini, A.; Fabbi, M.; Mantovani, M.; Mirone, L.; Pochini, A.; Secchi, A.; Ungaro, R. *J. Org. Chem.* **1995**, *60*, 1454–1457.
10. Lee, C. H.; Lindsey, J. S. *Tetrahedron* **1994**, *39*, 11427–11440.
11. *Preparation of derivative* **4a** (*route I*): A mixture of dialdehyde **1** (0.2 g, 0.35 mmol), *p*-tolualdehyde (0.25 ml, 2.10 mmol) and pyrrole (0.196 ml, 2.83 mmol) was dissolved over 10 min in 250 ml of dry chloroform under an N_2 atmosphere. Five drops of boron trifluoride diethyl etherate were added (the reaction vessel was shielded from light) and the reaction mixture was stirred at room temperature for 7 h. Then, 2 g of DDQ was added at once in powder form and the resulting dark solution was stirred for a further 2 h. The reaction mixture was extracted with aqueous sodium carbonate, dried over magnesium sulfate and evaporated with 5 g of silica gel to dryness. Column chromatography (silica gel, CH_2Cl_2:petroleum ether:Et_3N 250:250:1, then $CHCl_3$:Et_3N 100:1) gave 2 mg of **5** (0.4%), 55 mg of **4a** (14%) and 5,10,15,20-tetrakis(*p*-tolyl)-porphyrin as an undesired by-product.

Derivative **4a**: purple powder, mp: >300 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.85 (s, 1H, *OH*), 9.59 (s, 1H, *CHO*), 8.93–8.8 (m, 8H, Ar–*H*), 8.74 (s, 1H, *OH*), 8.08–8.05 (m, 6H, Ar–*H*), 7.92 (s, 2H, Ar–*H*), 7.7 (s, 2H, Ar–*H*), 7.58–7.53 (m, 6H, Ar–*H*), 7.14 (d, 2H, $J = 7.3$ Hz, Ar–*H*), 7.07 (d, 2H, $J = 7.7$ Hz, Ar–*H*), 6.91 (dd, 2H, $J_1 = 7.7$ Hz, $J_2 = 7.3$ Hz, Ar–*H*), 4.6 (d, 2H, $J = 12.8$ Hz, Ar–CH_2–Ar), 4.43 (d, 2H, $J = 13.2$ Hz, Ar–CH_2–Ar), 4.13–4.05 (m, 4H, –O–CH_2–CH_2–CH_3), 3.63 (d, 2H, $J = 12.83$ Hz, Ar–CH_2–Ar), 3.58 (d, 2H, $J = 13.2$ Hz, Ar–CH_2–Ar), 2.72 (s, 3H, Ar–CH_3), 2.71 (s, 6H, Ar–CH_3), 2.25–2.16 (m, 4H, –O–CH_2–CH_2–CH_3), 1.46 (t, 6H, $J = 7.3$ Hz, –O–CH_2–CH_2–CH_3), −2.75 (s, 2H, *NH*). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 190.94, 160.12, 152.96, 151.95, 146.22, 140.06, 139.39, 139.31, 139.29, 138.81, 137.25, 135.27, 134.48, 134.38, 133.87, 133.05, 132.45, 132.34, 131.06, 130.88, 129.67, 129.11, 128.72, 128.56, 127.38, 126.22, 125.73, 120.56, 119.95, 119.78, 78.60, 31.58, 31.49, 23.61, 21.53, 11.09. IR (KBr): 3318, 3023, 2960, 1809, 1725, 1687, 1595 cm^{-1}. EA calcd for $C_{76}H_{66}N_4O_5$: C, 81.84; H, 5.96. Found: C, 81.68; H, 5.81%. MS TOF ESI + *m*/*z* 1115.47 $[M+H]^+$ (100%), 1137.49 $[M+Na]^+$ (20%).

12. This compound was recently prepared by a different method: Seigle-Ferrand, P.; Sdira, S. B.; Felix, C.; Lamartine, R.; Bavoux, C.; Fenet, B.; Bayard, F.; Vocanson, F. *Mater. Sci. Eng.* **2006**, *C26*, 181–185.
13. *Preparation of derivative* **3**: Dialdehyde **1** (0.5 g, 0.855 mmol), was dissolved in hot pyrrole (6.1 ml, 88 mmol) under an N_2 atmosphere. Five drops of boron trifluoride diethyl etherate were added and the solution was stirred at room temperature for 3 h. The reaction mixture was then poured into 150 ml of aqueous sodium hydroxide (5%) and extracted with chloroform (6 × 40 ml). The combined organic layers were washed with water and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by column chromatography (silica gel, $CHCl_3$:MeOH = 10:1) to give 0.60 g of bis(dipyrromethane) derivative **3** (85%) as a yellowish solid. Mp: >190 °C (decomp.). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.52 (s, 2H, *OH*), 7.87 (br s, 4H, *NH*), 6.89–6.87 (m, 4H, Ar–*H*), 6.85 (s, 4H, Ar–*H*), 6.78–6.76 (m, 2H, Ar–*H*), 6.68–6.67 (m, 4H, Ar–*H*), 6.18–6.15 (m, 4H, Ar–*H*), 5.95–5.94 (m, 4H, Ar–*H*), 5.35 (s, 2H, Ar–*CH*Ar_2), 4.28 (d, 4H, $J = 12.7$, Ar–CH_2–Ar), 3.95 (t, 4H, $J = 6$ Hz, –O–CH_2–CH_2–CH_3), 4.28 (d, 4H, $J = 12.7$ Hz, Ar–CH_2–Ar), 2.06 (m, 4H, –O–CH_2–CH_2–CH_3), 1.32 (t, 6H, $J = 7.4$ Hz, –O–CH_2–CH_2–CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz) δ (ppm) 152.55, 152.13, 133.79, 133.33, 132.41, 129.14, 128.73, 128.50, 125.72, 117.10, 108.50, 107.12, 78.63, 43.34, 31.71, 23.71, 11.21. IR (KBr): 3425, 2965, 2935, 1707, 1635 cm^{-1}. EA calcd for $C_{52}H_{52}N_4O_4$: C, 78.36; H, 6.58; N, 7.08. Found: C, 78.08; H, 6.51; N, 6.91. MS TOF ESI + *m*/*z* 819.4 $[M+Na^+]$ (100%).
14. *Preparation of bis-porphyrin* **5**, (*route I-optimised procedure*): A mixture of dialdehyde **1** (85 mg, 0.15 mmol), *p*-tolualdehyde (1.53 ml, 13 mmol) and pyrrole (0.90 ml, 13.3 mmol) was dissolved over 10 min in 1000 ml of dry chloroform under N_2. Five drops of boron trifluoride diethyl etherate were added and the reaction mixture was stirred in the dark at room temperature for 7 h. Then 5 g of DDQ were added in one portion and the resulting dark solution was stirred for an additional 2 h. The reaction mixture was extracted with aqueous sodium carbonate, dried over magnesium sulfate and evaporated with 10 g of silica gel to dryness. Subsequent column chromatography using silica gel (eluent:CH_2Cl_2:petroleum ether:Et_3N = 250:250:1, then $CHCl_3$:Et_3N 100:1) gave 36 mg of derivative **5** (15%) and 5,10,15,20-tetrakis(*p*-tolyl)-porphyrin as a by-product.
Derivative **5**: purple powder, mp: >300 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 9.03–8.87 (m, 18H, 16 Ar–*H* + 2-*OH*), 8.15–8.11 (m, 12H, Ar–*H*), 8.05 (s, 4H, Ar–*H*), 7.60–7.55 (m, 12H, Ar–*H*), 7.22 (d, 4H, $J = 7.33$ Hz, Ar–*H*), 7.00 (t, 2H, $J = 7.3$ Hz, Ar–*H*), 4.76 (d, 4H, $J = 12.83$ Hz, Ar–CH_2–Ar), 4.19 (t, 4H, $J = 6.2$ Hz, –O–CH_2–CH_2–CH_3), 3.72 (d, 4H, $J = 12.83$ Hz, Ar–CH_2–Ar), 2.74 (s, 6H, Ar–CH_3), 2.73 (s, 6H, Ar–CH_3), 2.72 (s, 6H, Ar–CH_3), 2.32–2.26 (m, 4H, –O–CH_2–CH_2–CH_3), 1.55 (t, 6H, $J = 7.3$ Hz, –O–CH_2–CH_2–CH_3), −2.7 (s, 4H, *NH*). ^{13}C NMR (C_6D_6, 75 MHz) δ (ppm): 154.42, 152.49, 140.24, 140.20, 140.09, 137.23, 137.17, 137.13, 136.57, 134.96, 134.89, 133.41, 133.18, 129.77, 128.21, 128.15, 128.08, 127.83, 127.76, 127.39, 127.09, 121.77, 120.70, 120.67, 120.43, 30.14, 23.91, 21.46, 21.42, 21.39, 11.25. EA calcd for $C_{116}H_{96}N_8O_4$: C, 83.63; H, 5.81; N, 6.73. Found: C, 83.28; H, 5.71; N, 6.54. MS TOF ESI + *m*/*z* 1666.69 $[M+H^+]$ (100%). UV–vis (toluene) λ_{max} (nm), ε (M^{-1} cm^{-1}) in parentheses: 425 (6.4×10^5), 518 (2.4×10^4), 553 (2.2×10^4), 594 (9.1×10^3), 651 (6.5×10^3).
15. *Preparation of derivative* **4b** (*route IV*): A mixture of aldehyde **6** (0.200 g), *p*-tolualdehyde (0.133 ml) and pyrrole (0.133 ml) was dissolved in 200 ml of propionic acid and the resulting mixture was stirred under reflux for 6 h in the presence of air. Propionic acid was removed under reduced pressure and the residue was purified by column chromatography on silica gel (petroleum ether:CH_2Cl_2 1:1 containing 0.25% of TEA) to obtain 40 mg (10%) of compound **4b** as a purple powder. Mp: 279–281 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm): 8.95–8.83 (m, 8H, Ar–*H*), 8.78 (s, 1H, *OH*), 8.58 (s, 1H, *OH*), 8.12–8.07 (m, 6H, Ar–*H*), 7.92 (s, 2H, Ar–*H*), 7.57–7.53 (m, 6H, Ar–*H*), 7.15 (d, 2H, $J = 7.7$ Hz, Ar–*H*), 7.1 (d, 2H, $J = 7.3$ Hz, Ar–*H*), 7.05 (d, 2H, $J = 7.7$ Hz, Ar–*H*), 6.89 (dd, 2H, $J_1 = 7.7$ Hz, $J_2 = 7.3$ Hz, Ar–*H*), 6.72 (t, 1H, $J = 7.7$, Ar–*H*), 4.63 (d, 2H, $J = 12.8$ Hz, Ar–CH_2–Ar), 4.44 (d, 2H, $J = 12.8$ Hz, Ar–CH_2–Ar), 4.08 (t, 4H, $J = 6.1$ Hz, –O–CH_2–CH_2–CH_3), 3.61 (d, 2H, $J = 12.8$, Ar–CH_2–Ar), 3.48 (d, 2H, $J = 12.8$ Hz, Ar–CH_2–Ar), 2.71 (s, 3H, Ar–CH_3), 2.7 (s, 6H, Ar–CH_3), 2.22–2.16 (m, 4H, –O–CH_2–CH_2–CH_3), 1.44 (t, 6H, $J = 7.3$ Hz, –O–CH_2–CH_2–CH_3), −2.75 (s, 2H, *NH*). ^{13}C ($CDCl_3$, 75 MHz) δ (ppm): 153.94, 153.33, 152.27, 139.71, 139.65, 137.50, 137.48, 135.55, 134.76, 134.70, 134.01, 133.77, 133.20, 129.37, 128.83, 128.31, 127.65, 126.80, 125.88, 124.73, 124.26, 121.05, 120.22, 120.19, 119.99, 119.34, 119.27, 78.71, 31.84, 30.41, 23.88, 21.78, 11.36. EA calcd for $C_{75}H_{66}N_4O_4$: C, 82.84; H, 6.12. Found: C, 82.68; H, 6.11. MS TOF ESI + *m*/*z* 1087.75 $[M+H^+]$ (100%). UV–vis (toluene) λ_{max} (nm), ε (M^{-1} cm^{-1}) in parentheses: 423 (4.1×10^5), 518 (1.6×10^4), 554 (1.1×10^4), 595 (5.2×10^3), 651 (4.8×10^3).
16. The binding constants were calculated using the computer program OPIUM (Kyvala, M.) freely available at: http://www.natur.cuni.cz/~kyvala/opium.html.