Tetrahedron Letters 51 (2010) 2423–2426

Contents lists available at ScienceDirect

Tetrahedron Letters

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

An oxacalix[2]arene[2]pyrimidine-bis(Zn-porphyrin) tweezer as a selective receptor towards fullerene C_{70}

Wim Van Rossom [a], Ondrej Kundrát [b], Thien Huynh Ngo [a], Pavel Lhoták [b,*], Wim Dehaen [a,*], Wouter Maes [a,c]

[a] Molecular Design and Synthesis, Department of Chemistry, Katholieke Universiteit Leuven, Celestijnenlaan 200F, B-3001 Leuven, Belgium
[b] Department of Organic Chemistry, Prague Institute of Chemical Technology, Technická 5, 166 28 Prague 6, Czech Republic
[c] Institute for Materials Research (IMO), Research Group Organic and (Bio)Polymeric Chemistry, Hasselt University, Universitaire Campus, Agoralaan Building D, B-3590 Diepenbeek, Belgium

ARTICLE INFO

Article history:
Received 30 January 2010
Revised 18 February 2010
Accepted 22 February 2010
Available online 1 March 2010

Keywords:
Oxacalixarenes
Porphyrinoids
Fullerenes
Supramolecular receptors

ABSTRACT

An oxacalix[2]arene[2]pyrimidine-bis(Zn^{II}-porphyrin) conjugate was readily prepared via nucleophilic aromatic substitution of a phenolic AB_3-Zn-porphyrin on the upper rim of a (*1,3-alternate*) 5,17-bis(methylsulfonyl)oxacalix[4]arene precursor. Efficient 1:1 complex formation between the 'jaws' bisporphyrin tweezer and fullerene C_{70} was evidenced by ^{1}H NMR titrations ($K = 3.0 \times 10^4\ M^{-1}$), while no detectable complexation could be observed with C_{60}. On the other hand, an analogous oxacalix[4]arene-bis(Cu-corrole) conjugate did not show any measurable (C_{60} or C_{70}) fullerene binding.

Traditional methylene-bridged calixarenes and thiacalixarenes are well-known, generally applied building blocks and scaffolds within supramolecular chemistry.[1,2] These macrocycles are relatively easy to prepare and functionalize, and show particular conformational preferences. The N- and O-bridged counterparts (aza- and oxacalixarenes, respectively) are less familiar members of the heteracalixarene subclass.[3–6] Oxacalixarene chemistry has been rejuvenated in recent years,[4–6] but supramolecular applications have only scarcely been explored. A particular advantage of oxacalixarenes in respect to most other members of the calixarene family is the *1,3-alternate* conformation of the smallest and most rigid oxacalix[4]arene, as generally observed in solid-state X-ray structures.[4–7] This conformation appears to be (most) promising to generate preorganized supramolecular receptors, for example, for cations, anions or fullerenes.

Recently, the Leuven group has developed versatile and selective synthetic protocols towards both oxacalix[2]arene[2]pyrimidines,[8] applying a convenient one-pot procedure, and enlarged calixarene macrocycles (oxacalix[6]- and oxacalix[8]arenes),[9] using efficient fragment-coupling approaches. The most appealing aspect of oxacalix[*m*]arene[*m*]pyrimidines is the ease and wide scope of derivatization of the outer perimeter, for example, via nucleophilic aromatic substitution (S_NAr) reactions.[10] Alongside the assumed preorganization in a *1,3-alternate* conformation,[7] this prompted us to investigate supramolecular host–guest complexation by introducing receptor motifs on the oxacalixarene framework.

Designing effective host molecules capable of (size-) selective complexation of fullerenes is highly important to reduce costs due to laborious fullerene purification and isolation procedures, and facilitate their application in (bio)chemistry and (photoactive) material sciences.[11] The geometrical complementarity of concave calixarene cavities and spherical fullerenes has evidently aroused the interest of calixarene chemists. As indicated in seminal work by the Atwood and Shinkai groups, particular calixarene derivatives indeed show high affinity for fullerenes.[12] The (classical) *p-tert*-butylcalix[8]arene binds to the fullerene surface through van der Waals concave–convex π–π interactions and is selective for [60]fullerene (C_{60}). Inspired by this early observation, many other research groups have studied fullerene complexation properties with various other calixarenes and derivatives thereof. Noteworthy for the presented results are the fullerene affinities reported for hetero-atom bridged calix(hetero)aromatics. Azacalix([*m*]arene)[*n*]pyridines and N,O-bridged calix[1]arene[4]pyridines exhibit rather high association constants (up to $K = 1.4 \times 10^5\ M^{-1}$) for C_{60} and/or C_{70}, as revealed by UV–vis and fluorescence quenching titration experiments,[13] while very modest binding constants were observed for homooxacalix[3]arenes.[14]

The spontaneous attraction of fullerenes to the centre of a (metallo)porphyrin is an intriguing supramolecular recognition

* Corresponding authors. Tel.: +420 220 445 055; fax: +420 220 444 288 (P.L.); tel.: +32 16 327390; fax: +32 16 327990 (W.D.).
E-mail addresses: pavel.lhotak@vscht.cz (P. Lhoták), wim.dehaen@chem.kuleuven.be (W. Dehaen).

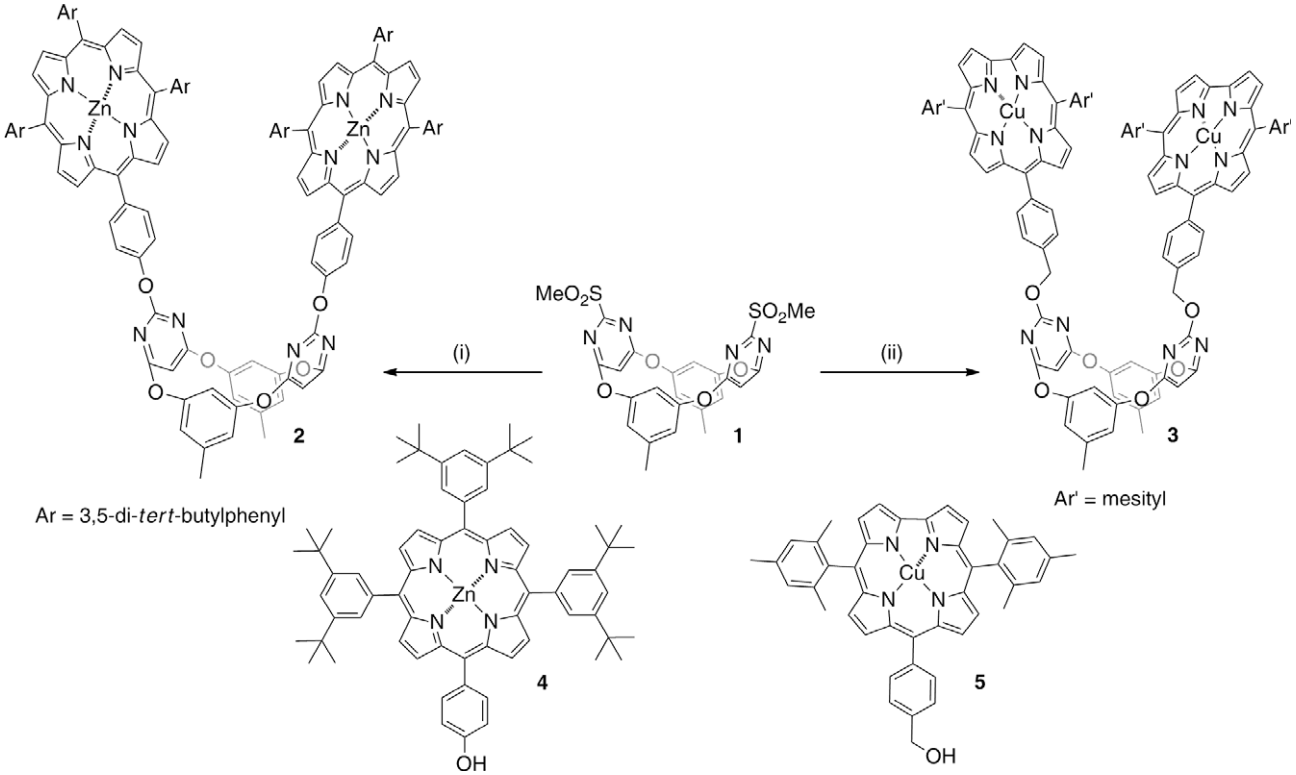
0040-4039/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2010.02.137

element that can also be applied to produce discrete host-guest systems. To obtain strong interaction of the curved π-surface of the fullerene sphere with the electropositive centre of the planar porphyrin π-surface (in addition to the regular π–π attraction and differential solvation effects), a suitable arrangement of the porphyrin units with respect to one another appears to be crucial.[15] The use of (thia)calixarene scaffolds (among others[11]) has shown to position porphyrins at an appropriate mutual distance of 12 Å (diameter C_{60}/C_{70} ~10 Å), affording calixarene-porphyrin tweezers, often referred to as 'jaws' porphyrins, with strong fullerene binding properties.[16] Besides the (centre of the) flat porphyrin π-system, the cavity of the calixarene itself can possibly also contribute to the inclusion properties.

To determine the fullerene binding strength of the oxacalixarene framework, several oxacalix[*n*]arenes were selected from the small library available to us from previous work. 5,17-Diphenyloxacalix[2]arene[2]pyrimidine and the analogous oxacalix[8]arene, enlarging the cavity's π-surface and approaching the shape of a molecular tweezer, were initially selected.[17] A larger π-surface could also be achieved via oxacalix[2]arene[2]quinazolines.[18] Both a *syn*- and *anti*-oxacalix[2]arene[2]quinazoline as well as expanded *syn*- and *anti*-oxacalix[2]naphthalene[2]quinazolines were studied.[17] Unfortunately, ^{1}H NMR titrations indicated that none of these oxacalixarenes shows any detectable binding with either fullerene C_{60} or C_{70}. This was not completely unexpected considering the (too) small calix[4]arene cavity, the supposed *1,3-alternate* conformation and the more electron-deficient structure compared to azacalix[*n*]arenes. Although the contribution to actual fullerene binding might be negligible, the oxacalixarene framework can still serve as a versatile scaffold enabling appropriate arrangement of porphyrinoid units with recognition potential for fullerenes.

Hence, a strategy for the construction of tweezer-type bisporphyrinoid receptors has been explored. The synthetic protocol towards oxacalix[4]arene-porphyrinoid conjugates **2** and **3** is depicted in Scheme 1.[19] Inspired by the post-macrocyclization procedures previously optimized for bis(methylsulfonyl)oxacalix[2]arene[2]pyrimidine **1**,[10] more sophisticated functional units such as porphyrins and corroles could be introduced to obtain preorganized tweezer-type host molecules. Since *tert*-butyl substituents were previously shown to enhance the fullerene binding properties (by π–CH_3 interactions),[16c,20] 5,10,15-tris(3,5-di-*tert*-butylphenyl)-20-(4-hydroxyphenyl)porphyrinato zinc (**4**) was selected as the nucleophilic porphyrin. The porphyrin moiety, synthesized according to a reported method,[21] was coupled to the upper rim of oxacalix[4]arene **1** via a S_NAr reaction employing K_2CO_3 as a base in DMF at 70 °C to afford oxacalix[2]arene[2]pyrimidine-bis(Zn^{II}-porphyrin) receptor **2** in 73% yield (Scheme 1).[22] Previous activities of the Leuven group in the corrole field ignited our interest to study analogous corrole derivatives.[23] To our knowledge, supramolecular complexation of fullerenes with corrole derivatives has not been demonstrated so far. Since Cu-metallated corroles usually show an improved (oxidative) stability over their free-base counterparts, nucleophilic Cu-corrole precursor **5** was selected, available to us from ongoing corrole research,[24] and a similar S_NAr approach was then used to obtain the first 'jaws' biscorrole receptor. Treatment of oxacalix[4]arene substrate **1** with a small excess (2.2 equiv) of Cu-corrole **5** in the presence of NaH base in acetonitrile at 70 °C resulted in the formation of oxacalix[2]arene[2]pyrimidine-bis(Cu-corrole) receptor **3**, which could be isolated in 80% yield (Scheme 1).[25]

The complexation abilities of the novel conjugates **2** and **3** towards fullerenes C_{60}/C_{70} were studied by ^{1}H NMR titrations in benzene-d_6. Upon addition of an excess of C_{70} to a solution of receptor **2**, the signals corresponding to the β-pyrrolic protons of the porphyrin moieties shifted upfield (complexation-induced chemical shifts (CIS) >50 Hz after the addition of 5 equiv C_{70}), while the signals of the oxacalixarene skeleton remained almost unchanged. These changes in chemical shifts clearly point to direct interactions



Scheme 1. Reagents and conditions: (i) K_2CO_3, 18-crown-6, DMF, 70 °C, 24 h (73%); (ii) NaH, MeCN, 70 °C, 15 min (80%).

between the porphyrin and fullerene entities. The complexation-induced chemical shifts were used for the construction of a titration curve (Fig. 1), which was analyzed by a nonlinear least-squares method assuming 1:1 stoichiometry.[26] The rather high complexation constant $K = 30000 \pm 4600\ M^{-1}$ indicates that cooperation of both porphyrin units likely occurs during the binding process.[27] The 1:1 stoichiometry of the C_{70}-bisporphyrin **2** complex was also established by an independent Job plot analysis (Fig. 2). By contrast, upon the addition of C_{60}, the porphyrin aromatic resonances for compound **2** showed only negligible CIS (<5 Hz), which did not allow the construction of the corresponding titration curve.[28] Higher K_{ass} for C_{70} compared to C_{60} have previously been attributed to a maximization of ovoid-shaped C_{70}–porphyrin interactions.[29]

Unfortunately, in the case of biscorrole receptor **3** no salient ^{1}H NMR CIS were observed in the presence of either C_{60} or C_{70}, which might be attributed to the additional conformational flexibility introduced by the methylene linker or to sterical effects imposed by the *meso*-mesityl moieties.[30] As both systems (porphyrin **2** vs corrole **3**) are not fully structurally comparable, one of the fundamental questions—whether corroles can be used instead of porphyrins for the construction of efficient fullerene receptors—remains partly unanswered at this stage. To achieve efficient binding with 'jaws' corroles, more work should be devoted to optimize the subtle balance between optimal receptor properties and corrole stability, for which electron-deficient and sterically bulky *ortho*,*ortho*′-substituted *meso*-aryl units are often favourable.

In conclusion, novel tweezer-type bisporphyrinoid receptors were easily obtained via straightforward and high-yielding synthetic S_NAr procedures based on a preorganized *1,3-alternate* oxacalix[2]arene[2]pyrimidine platform and a nucleophilic porphyrin or corrole reaction partner. Solution-phase binding studies with fullerenes C_{60} and C_{70} were conducted by ^{1}H NMR titration experiments, which revealed pronounced selectivity for the egg-shaped C_{70} employing oxacalixarene-linked bisporphyrin **2**, with a significant binding constant ($K = 3.0 \times 10^4\ M^{-1}$). Although the contribution of the oxacalix[4]arene part to fullerene binding seems small, the oxacalixarene skeleton is a versatile building block towards efficient tweezer-type supramolecular receptors. Further studies will be directed towards exploration of the binding capacity of 'jaws' corrole hosts and fullerene receptors based on larger oxacalix[*n*]arene scaffolds ($n = 6$, 8) with additional complexing porphyrinoid units.

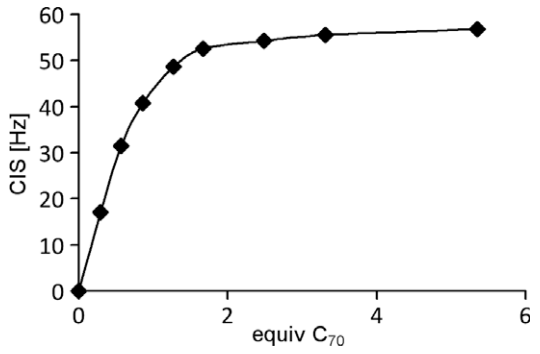


Figure 1. ^{1}H NMR titration of receptor **2** with C_{70} (C_6D_6, 300 MHz, 298 K).

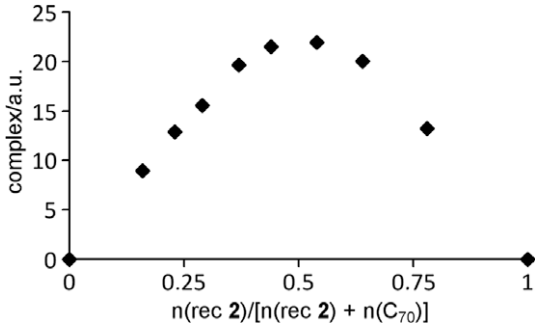


Figure 2. Job plot for the **2** + C_{70} system (^{1}H NMR, C_6D_6, 300 MHz, 298 K; $[2] + [C_{70}] = 5 \times 10^{-3}$ M).

Acknowledgements

We thank the FWO (Fund for Scientific Research—Flanders) for financial support and a postdoctoral fellowship to W. Maes, and the K. U. Leuven and the Ministerie voor Wetenschapsbeleid for continuing financial support. T. H. Ngo is grateful to the IWT (Institute for the Promotion of Innovation through Science and Technology in Flanders) for a doctoral fellowship. P.L. and O.K. thank the Czech Science Foundation (Grant 203/09/0691).

Supplementary data

Supplementary data (experimental procedures and characterization data for all porphyrin/corrole precursors, and ^{1}H NMR spectra of receptors **2** and **3**) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.02.137.

References and notes

1. (a) Gutsche, C. D. *Calixarenes Revisited*; Royal Society of Chemistry: Cambridge, 1998; (b)*Calixarenes 2001*; Asfari, Z., Böhmer, V., Harrowfield, J., Vicens, J., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2001.
2. For recent reviews on thiacalixarenes, see: (a) Lhoták, P. *Eur. J. Org. Chem.* **2004**, 1675–1692; (b) Morohashi, N.; Narumi, F.; Iki, N.; Harroti, T.; Miyano, S. *Chem. Rev.* **2006**, *106*, 5291–5316.
3. For a recent review on azacalixarenes, see: Tsue, H.; Ishibashi, K.; Tamura, R. In *Heterocyclic Supramolecules I*; Matsumoto, K., Ed.; Topics in Heterocyclic Chemistry; Springer: Heidelberg, 2008; Vol. 17, pp 73–96.
4. Oxacalixarenes: (a) Wang, M.-X.; Yang, H.-B. *J. Am. Chem. Soc.* **2004**, *126*, 15412–15422; (b) Katz, J. L.; Feldman, M. B.; Conry, R. R. *Org. Lett.* **2005**, *7*, 91–94; (c) Hao, E.; Fronczek, F. R.; Vicente, M. G. H. *J. Org. Chem.* **2006**, *71*, 1233–1236; (d) Konishi, H.; Tanaka, K.; Teshima, Y.; Mita, T.; Morikawa, O.; Kobayashi, K. *Tetrahedron Lett.* **2006**, *47*, 4041–4044; (e) Jiao, L.; Hao, E.; Fronczek, F. R.; Smith, K. M.; Vicente, M. G. H. *Tetrahedron* **2007**, *63*, 4011–4017; (f) Katz, J. L.; Geller, B. J.; Foster, P. D. *Chem. Commun.* **2007**, 1026–1028; (g) Sobransingh, D.; Dewal, M. B.; Hiller, J.; Smith, M. D.; Shimizu, L. S. *New J. Chem.* **2008**, *32*, 24–27; (h) Wang, D.-X.; Zheng, Q.-Y.; Wang, Q.-Q.; Wang, M.-X. *Angew. Chem., Int. Ed.* **2008**, *47*, 7485–7488; (i) Wu, L.; Jiao, L.; Lu, Q.; Hao, E.; Zhou, Y. *Spectrochim. Acta, Part A* **2009**, *73*, 353–357; (j) Ma, M.-L.; Li, X.-Y.; Wen, K. *J. Am. Chem. Soc.* **2009**, *131*, 8338–8339.
5. For a recent review on oxacalixarenes, see: Maes, W.; Dehaen, W. *Chem. Soc. Rev.* **2008**, *37*, 2393–2402.
6. For a recent review on both aza- and oxacalixarenes from the Wang group: Wang, M.-X. *Chem. Commun.* **2008**, 4541–4551.
7. The conformational behaviour of oxacalix[4]arenes in solution has been investigated by VT NMR experiments, indicating either a single conformation or a very rapid interconversion on the NMR time scale. Based on the upfield shifts for the interior protons on the electrophilic components, attributed to (partial) orientation in the anisotropic shielding cone of the adjacent aromatic rings, it has been presumed that the preferred conformation in solution resembles the solid-state *1,3-alternate* conformation (Ref. 5).
8. Maes, W.; Van Rossom, W.; Van Hecke, K.; Van Meervelt, L.; Dehaen, W. *Org. Lett.* **2006**, *8*, 4161–4164.
9. Van Rossom, W.; Ovaere, M.; Van Meervelt, L.; Dehaen, W.; Maes, W. *Org. Lett.* **2009**, *11*, 1681–1684.
10. Van Rossom, W.; Maes, W.; Kishore, L.; Ovaere, M.; Van Meervelt, L.; Dehaen, W. *Org. Lett.* **2008**, *10*, 585–588.
11. (a) Kawase, T.; Kurata, H. *Chem. Rev.* **2006**, *106*, 5250–5273; (b) Martin, N., Nierengarten, J.-F., Eds.; For a special issue devoted to 'Supramolecular Chemistry of Fullerenes', see: *Tetrahedron* **2006**, *62*, 1905–2132.
12. (a) Atwood, J. L.; Koutsantonis, G. A.; Ratson, C. L. *Nature* **1994**, *368*, 229–231; (b) Suzuki, T.; Nakashima, K.; Shinkai, S. *Chem. Lett.* **1994**, 699–702.
13. (a) Wang, M.-X.; Zhang, X.-H.; Zheng, Q.-Y. *Angew. Chem., Int. Ed.* **2004**, *43*, 838–842; (b) Liu, S.-Q.; Wang, D.-X.; Zheng, Q.-Y.; Wang, M.-X. *Chem. Commun.* **2007**, 3856–3858; (c) Zhang, E.-X.; Wang, D.-X.; Zheng, Q.-Y.; Wang, M.-X. *Org. Lett.* **2008**, *10*, 2565–2568; (d) Wu, J.-C.; Wang, D.-X.; Huang, Z.-T.; Wang, M.-X. *Tetrahedron Lett.* **2009**, *50*, 7209–7212.
14. (a) Ikeda, A.; Suzuki, Y.; Yoshimura, M.; Shinkai, S. *Tetrahedron* **1998**, *54*, 2497–2508; (b) Tsubaki, K.; Tanaka, K.; Kinoshita, T.; Fuji, K. *Chem. Commun.* **1998**, 895–896; (c) Komatsu, N. *Org. Biomol. Chem.* **2003**, *1*, 204–209.

15. For a review on fullerene-porphyrin constructs, see: Boyd, P. D. W.; Reed, C. A. *Acc. Chem. Res.* **2005**, *38*, 235–242.
16. (a) Arimura, T.; Nishioka, T.; Suga, Y.; Murata, S.; Tachiya, M. *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A* **2002**, *379*, 413–418; (b) Dudič, M.; Lhoták, P.; Stibor, I.; Petříčková, H.; Lang, K. *New J. Chem.* **2004**, *28*, 85–90; (c) Hosseini, A.; Taylor, S.; Accorsi, G.; Armaroli, N.; Reed, C. A.; Boyd, P. D. W. *J. Am. Chem. Soc.* **2006**, *128*, 15903–15913; (d) Káš, M.; Lang, K.; Stibor, I.; Lhoták, P. *Tetrahedron Lett.* **2007**, *48*, 477–481; (e) Kundrát, O.; Káš, M.; Tkadlecová, M.; Lang, K.; Cvačka, J.; Stibor, I.; Lhoták, P. *Tetrahedron Lett.* **2007**, *48*, 6620–6623.
17. Structural representations of these oxacalix[*n*]arenes can be found in the Supplementary data file.
18. Van Rossom, W.; Kishore, L.; Robeyns, K.; Van Meervelt, L.; Dehaen, W.; Maes, W., submitted for publication.
19. A few related oxacalixarene-porphyrin conjugates have recently been prepared by other research groups (Refs. 4c,e,i).
20. Georghiou, P. E.; Tran, A. H.; Stroud, S. S.; Thompson, D. W. *Tetrahedron* **2006**, *62*, 2036–2044.
21. Maes, W.; Vanderhaeghen, J.; Smeets, S.; Asokan, C. V.; Van Renterghem, L. M.; Du Prez, F. E.; Smet, M.; Dehaen, W. *J. Org. Chem.* **2006**, *71*, 2987–2994.
22. *Preparation of oxacalix[2]arene[2]pyrimidine-bis(Zn-porphyrin) conjugate* **2**: 5,17-bis(methylsulfonyl)oxacalix[4]arene **1** (30 mg, 0.05 mmol), AB_3-porphyrin **4** (117 mg, 0.11 mmol, 2.2 equiv), K_2CO_3 (22 mg, 0.15 mmol) and 18-crown-6 (5 mg, 0.02 mmol) were dissolved in DMF (2 mL) and the mixture was heated at 70 °C for 24 h (under Ar). DMF was removed under vacuum, and the residue was redissolved in ethyl acetate (50 mL) and washed with water (3 × 25 mL). The organic fraction was dried over $MgSO_4$, filtered and the solvent was removed under vacuum. After column chromatographic purification (silica, eluent heptane/ethyl acetate 9:1), oxacalix[4]arene-bisporphyrin conjugate **2** (96 mg, 73%) was isolated in pure form as a pink-purple solid. mp >350 °C; MS (ESI+) *m/z* 2457.0 $[M+H]^+$; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.07–9.01 (m, 16H; H_β-pyr), 8.31 (d, ^3J = 8.2 Hz, 4H; Ph-O), 8.10–8.08 (m, 12H; *t*-Bu-Ph), 7.79 (s, 6H; *t*-Bu-Ph), 6.67 (d, ^3J = 8.2 Hz, 4H; Ph-O), 7.02 (s, 4H; 4,6-orc), 6.84 (s, 2H; 2-orc), 5.27 (s, 2H; 5-pyr), 2.45 (s, 6H; CH_3-orc), 1.53 (s, 108H; *t*-Bu); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6 (C; 4,6-pyr), 166.3 (C; 2-pyr), 159.9, 153.0 (C; 1,3-orc), 152.3 (C), 150.6 (C), 150.3 (C), 148.7 (C; C_i-*t*-Bu), 144.0 (C; 5-orc), 142.0 (C), 140.6 (C), 135.6 (CH), 132.6/132.5/132.4/132.0 (CH_β), 129.9 (CH), 129.8 (CH), 122.9 (C), 122.7 (C), 120.9 (CH), 119.8 (CH; 4,6-orc), 112.1 (CH; 2-orc), 82.6 (CH; 5-pyr), 35.2 (C; *t*-Bu), 32.0 (CH_3; *t*-Bu), 21.8 (CH_3; orc); UV–vis (CH_2Cl_2) λ_{max} (log ε) 402sh (4.992), 422 (6.073), 549 (4.679), 588 (4.134).
23. (a) Maes, W.; Ngo, T. H.; Vanderhaeghen, J.; Dehaen, W. *Org. Lett.* **2007**, *9*, 3165–3168; (b) Ngo, T. H.; Van Rossom, W.; Dehaen, W.; Maes, W. *Org. Biomol. Chem.* **2009**, *7*, 439–443.
24. The synthetic procedure towards this metallocorrole can be found in the Supplementary data file.
25. *Preparation of oxacalix[2]arene[2]pyrimidine-bis(Cu-corrole) conjugate* **3**: 5,17-bis(methylsulfonyl)oxacalix[4]arene **1** (30 mg, 0.05 mmol), Cu-corrole **5** (77 mg, 0.11 mmol, 2.2 equiv) and NaH (60% dispersion, 7 mg, 0.15 mmol) were dissolved in CH_3CN (2 mL) and the resulting mixture was heated at 70 °C for 15 min (under Ar). Subsequently, ethyl acetate (50 mL) was added and the mixture was washed with water (3 × 25 mL), dried over $MgSO_4$, filtered and the solvents were removed under vacuum. After column chromatographic purification (silica, eluent heptane/ethyl acetate 7:3), oxacalix[4]arene-biscorrole conjugate **3** (78 mg, 80%) was isolated in pure form as a red-brown solid. mp >350 °C; MS (ESI+) *m/z* 1798.6 $[M+H]^+$, 899.9 $[M+2H]^{2+}$; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s_{br}, 4H; H_β-pyr), 7.64–7.59 (m, 8H; H_β-pyr), 7.35 (s_{br}, 4H; H_β-pyr), 7.20–7.15 (m, 8H), 7.02 (s, 8H; Mes), 6.90 (s, 4H; 4,6-orc), 6.67 (s, 2H; 2-orc), 5.59 (s, 4H; CH_2), 5.06 (s, 2H; 5-pyr), 2.39 (s, 12H; CH_3-Mes), 2.37 (s, 6H; CH_3-orc), 2.06 (s, 24H; CH_3-Mes); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1 (C; 4,6-pyr), 166.1 (C; 2-pyr), 152.9 (C; 1,3-orc), 148.9 (C), 144.3 (C), 143.8 (C; 5-orc), 138.5 (br; CH_β), 137.7 (C; Mes), 136.4 (C), 132.6 (br, CH_β), 131.4 (CH), 128.2 (CH; Mes), 127.8 (CH), 121.0 (CH), 120.6 (CH; 4,6-orc), 111.9 (CH; 2-orc), 81.5 (CH; 5-pyr), 69.6 (CH_2), 21.6 (CH_3; orc), 21.4 (CH_3; Mes), 19.9 (CH_3; Mes); UV–vis (CH_2Cl_2) λ_{max} (log ε) 256 (4.856), 403 (5.123), 538 (4.175).
26. The binding constants were calculated using the computer program OPIUM freely available at http://www.natur.cuni.cz/~kyvala/opium.html.
27. This binding constant is comparable to those observed for a thiacalixarene-based tweezer employing the same porphyrin entity (Ref. 16e) and a related traditional calixarene-based bisporphyrin (Ref. 16b).
28. Since the CIS were too small (in the range of the accuracy of the NMR measurements) to allow quantitative determination of the binding constants, one can state that there is virtually no measurable binding under the applied conditions and method (although in principle, strong binding can occur even with very small CIS).
29. Zheng, J. Y.; Tashiro, K.; Hirabayashi, Y.; Kinbara, K.; Saigo, K.; Aida, T.; Sakamoto, S.; Yamaguchi, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 1858–1861.
30. Another factor to consider is the role of corrole metallation (somewhat variable trends are observed for metalloporphyrins). For Cu-corroles, inherent saddling of the corrolato ligand and the partial radical character might have an influence as well. Electronic effects—corroles are in general more electron rich than porphyrins—cannot be excluded either.