

Calix[4]arene-Functionalized Naphthalene and Perylene Imide Dyes

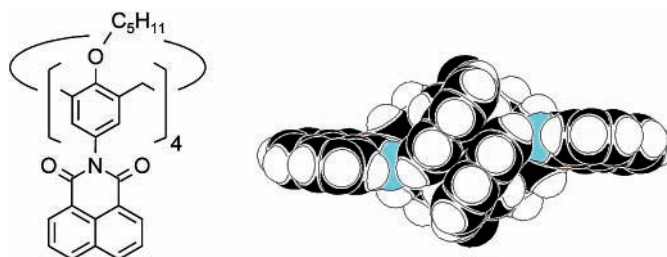
Myroslav O. Vysotsky,[†] Volker Böhmer,^{*,†} Frank Würthner,^{*,‡} Chang-Cheng You,[‡] and Kari Rissanen[§]

Fachbereich Chemie und Pharmazie, Abteilung Lehramt Chemie, Johannes Gutenberg-Universität, Duesbergweg 10-14, D-55099 Mainz, Germany, Abteilung Organische Chemie II, Universität Ulm, Albert-Einstein-Allee 11, D-89081 Ulm, Germany, and Department of Chemistry, University of Jyväskylä, P.O. Box 35, FIN-40351, Jyväskylä, Finland

vboehmer@mail.uni-mainz.de

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ABSTRACT



Calix[4]arenes bearing one, two, or four 1,8-naphthyl imide groups at the wide rim and bis-calix[4]arenes connected via perylene-bisimide dye spacers have been synthesized. The low-temperature NMR spectrum of the tetranaphthylimide suggests, in agreement with a crystal structure, a C_2 -symmetrical *pinched cone* conformation stabilized via face-to-face π - π interactions between opposite naphthylimide groups. UV-vis and fluorescence studies have been carried out for the perylene bis-calix[4]arene dyes.

Calixarenes are easily available in larger quantities by simple one-pot procedures¹ and easily modified in various ways by reactions that can be independently carried out at the narrow rim (the phenolic hydroxy groups) and at the wide rim (the aromatic positions para to the phenolic hydroxy groups).² Consequently, they represent an ideal skeleton or scaffold on which to assemble various (eventually different) functional groups. Receptors for cations, anions, and neutral guests³ have been prepared in this way. Calixarenes have been also used as versatile building blocks for the construc-

tion of larger species in which the calixarene subunits are connected by covalent links⁴ or by reversible bonds (e.g., hydrogen bonds⁵ or metal coordination⁶), an approach described by the term “self-assembly” nowadays.⁷

Perylene bisimide dyes are known as fluorescent and redoxactive units that can be introduced into cyclic,⁸ den-

* Email address for F.W.: frank.wuerthner@chemie.uni-ulm.de.

[†] Johannes Gutenberg-Universität, Mainz.

[‡] Universität Ulm.

[§] University of Jyväskylä.

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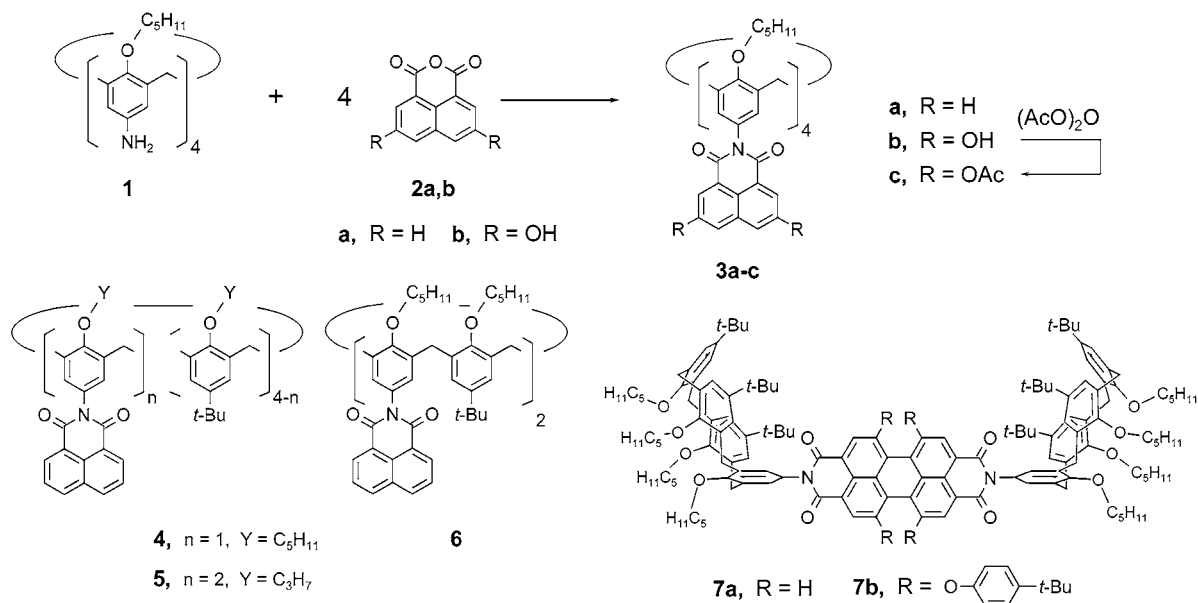
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Scheme 1. Synthesis of Calix[4]arene Imides



dritic,⁹ polymeric,¹⁰ liquid-crystalline,¹¹ and mesoscopic¹² systems via covalent linkage or via self-assembly. From a geometrical point of view, they represent nanosized planar building blocks that can be functionalized (e.g., in form of their dicarboxylic acid anhydrides) and further extended (e.g., terylene) or modified. A covalent linkage of calix[4]arenes with perylene imides or other imide dyes could lead to molecules with an extended cavity, to new chromo- or fluorophoric sensor molecules, and to larger building blocks for self-assembly via π - π interactions of the dye structures.

We describe in the following our first results of the combination of calix[4]arenes with naphthalenes and perylenes via imide linkages at the wide rim.¹³

Tetraamino calix[4]arenes such as **1** are easily available by ipso-nitration of the corresponding tetraethers of *tert*-butylcalix[4]arene followed by hydrogenation of the nitro-groups.¹⁴ First attempts to react **1** with an excess of the 1,8-naphthalic anhydride **2a** in refluxing acetic acid failed

(Scheme 1). A complete conversion was obtained, however, in refluxing quinoline in the presence of Zn-acetate,¹⁵ and the tetraimide **3a** could be easily isolated by column chromatography in 47% yield. In the case of **3b**, the workup was complicated by the higher polarity due to the eight hydroxy groups. Thus, the crude product was acylated to the octaacetate **3c**, which could be (more) easily purified. Mono- (**4**) and bisimides (**5**, **6**) were obtained analogously from the corresponding aminocalixarenes.

The double calix[4]arenes **7a,b** have been synthesized in yields of 50–70% starting from the corresponding bis-anhydrides and a calix[4]arene monoamine.¹⁶

Single crystals of **3a** suitable for an X-ray analysis could be obtained by slow crystallization from chloroform/ethyl acetate at room temperature.¹⁷ The molecule is found in a chiral C_2 -symmetrical pinched cone conformation (Figure 1). The outward-oriented imide residues are nearly perpendicular to their phenolic units ($-76(1)^\circ$), while the inward-oriented ones are twisted by $-61(1)^\circ$ to reach an optimal π - π stacking of the naphthalene systems (distance = 3.415 Å). A single enantiomer packs into a chiral crystal lattice¹⁷

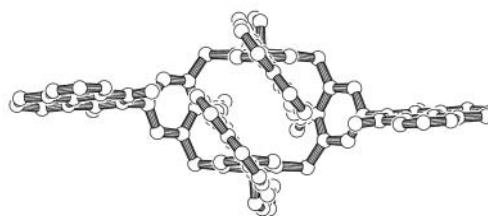


Figure 1. Molecular structure of imide **3a**; H-atoms omitted for clarity.

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with π - π and $\text{ArH}\cdots\text{O}=\text{C}$ interactions between the outer imide residues (Figure 2).¹⁸

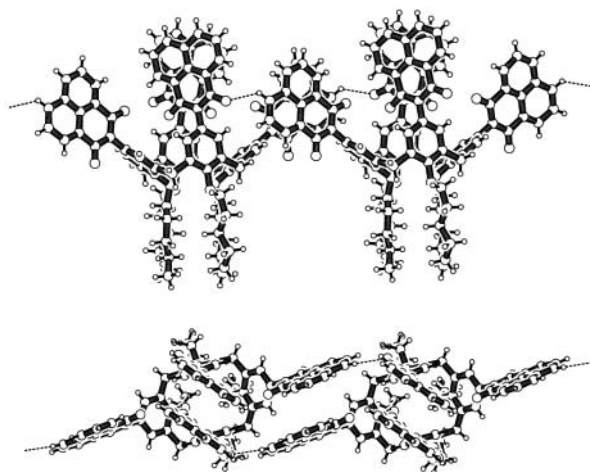


Figure 2. Two perspective views of the packing of the chiral C_2 -symmetrical conformations of **3a** in the crystalline lattice.

The ^1H NMR spectra in CDCl_3 of monoimide **4**, bis-imide **5**, and double-calixarenes **7** are sharp at room temperature and correspond to the symmetry expected for conformationally mobile molecules. For the naphthalene and perylene system(s), there are two doublets and a triplet (*o*-coupling) in **4** and **5**, two *o*-coupled doublets in **7a**, and one singlet in **7b**. The signals for the calixarene are in agreement with a symmetry plane passing through opposite phenolic rings in **4** and **7** (e.g., two pairs of doublets for the methylene bridges and two singlets and a pair of *m*-coupled doublets for the aromatic protons of the calixarene) and through opposite methylene bridges in **5** (three pairs of doublets for $\text{Ar}-\text{CH}_2-\text{Ar}$, ratio = 1:2:1, two pairs of *m*-coupled aromatic protons).¹⁹ In contrast, broad signals are observed for the 1,3-diimide **6** and the tetraimides **3a,c** (with the exception of two sharp doublets for $\text{Ar}-\text{CH}_2-\text{Ar}$).

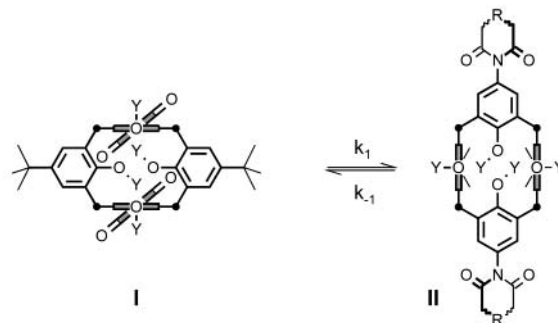
At $-58\text{ }^\circ\text{C}$, the ^1H NMR spectrum of **6** (Figure 1 in Supporting Information) shows two sets of signals (ratio = 1:1.95) that, on the basis of gs-COSY and gs-NOESY experiments, have been assigned to the two possible pinched cone conformations I and II (Scheme 2). Surprisingly conformation I with stacked imide functions is less populated.

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(17) Crystallographic measurement at 173.0(1) K using an Enraf Nonius Kappa-CCD diffractometer, Mo $K\alpha$ radiation. Structure solution by direct methods, full matrix least-squares refinement on F^2 , no absorption correction. $\text{C}_{48.5}\text{H}_{42.5}\text{O}_6\text{N}_2\text{Cl}_{1.5}$, $M = 802.52$, crystal size $0.20 \times 0.25 \times 0.20$ mm, hexagonal, space group $P6$ (No. 171), $a = 15.245(5)$ Å, $c = 33.558(5)$ Å, $V = 6754(3)$ Å³, $Z = 6$, $D_c = 1.184$ g/cm³, $\mu = 0.163$ mm⁻¹, 17 560 reflections, 7058 independent, $R_{\text{int}} = 0.0761$, $R_1 = 0.1121$, $wR_2 = 0.2822$ for $I > 4\sigma I$, 555 parameters, $S = 1.034$. Absolute structure parameter = 0.1(3), largest difference peak and hole were 0.726 and -0.283 e/Å⁻³, respectively.

(18) For other examples of “crystallization-induced asymmetric transformation” of racemates, see: *Stereochemistry of Organic Compounds*; Eliel, E. L., Wilen, S. H., Eds.; Wiley & Sons: New York, 1994; pp 316–317.

Scheme 2. Kinetic Scheme of the Dynamic Processes in **6**



For the two-side exchange, an energy barrier of $\Delta G^\ddagger = 43\text{--}47$ kJ/mol ($T_c = 243$ K) could be roughly estimated from the coalescence temperature of the OCH_2 signals belonging to the same phenolic units in different conformations. The aromatic part of the low-temperature spectrum of **3a** is shown in Figure 3. As confirmed by the gs-COSY spectrum, the

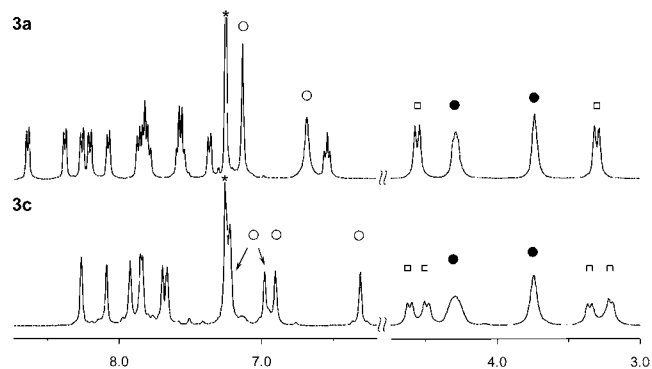


Figure 3. ^1H NMR spectra of **3a,c** at $-58\text{ }^\circ\text{C}$ (CDCl_3 , 400 MHz). Signals of calixarene aromatic protons (O), $\text{OCH}_2\text{C}_4\text{H}_9$ (●), and ArCH_2Ar protons (□) are indicated.

signals of the naphthalene protons belong to four spin systems (four times two doublets and a triplet). Eight signals (*m*-coupling) correspond to these groups in the case of **3c**. This pattern deviates from a “usual” C_{2v} -symmetrical pinched cone conformation and would agree to a conformation with C_2 -symmetry (as found in the X-ray structure, see above). This C_2 -symmetry is additionally expressed for **3c**, by the signals for the methylene groups (two pairs of doublets) and the aromatic protons (two pairs of *m*-coupled doublets). Consequently, the exchange processes are more complex here and a complete analysis will be published later.

The bis-calixarene derivatives **7** have UV/vis spectra (Figure 4) that are typical for the corresponding perylene bisimide chromophores with absorption maxima at 524, 488, and 457 nm (**7a**) and 574, 535, and 447 nm (**7b**). Notably, solutions of **7a** exhibit no fluorescence, while **7b** shows an intense fluorescence (quantum yield $\Phi_F = 0.63$) (Figure 4) with the maximum at 609 nm in CH_2Cl_2 .²⁰

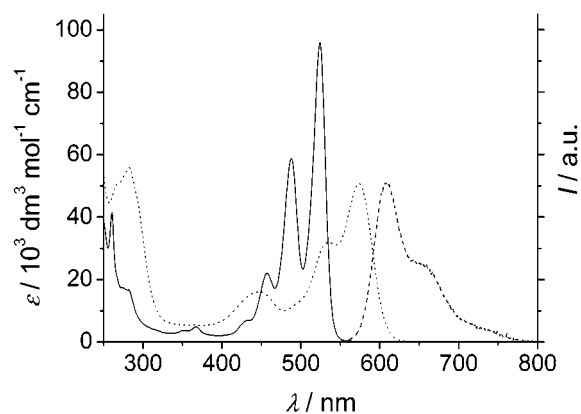


Figure 4. UV/vis absorption spectra of **7a** (solid line, at 1.3×10^{-5} M) and **7b** (dotted line, at 1.8×10^{-5} M) and fluorescence spectrum of **7b** (dashed line, at 6.7×10^{-7} M, $\lambda_{\text{ex}} = 545$ nm) in CH_2Cl_2 .

Without calixarene substituents, both native perylene bisimide dyes belong to the most efficient fluorophores with fluorescence quantum yields of about unity.^{20,21} Accordingly,

(19) ^1H NMR (CDCl_3 , 400 MHz, 25 °C) spectra. **4**: 8.60 (d, $J = 7.4$ Hz, 2H), 8.24 (d, $J = 8.2$ Hz, 2H), 7.82 (t, $J = 7.8$ Hz, 2H), 7.05 (s, 2H), 6.99 (s, 2H), 6.57 (s, 4H), 4.46 and 3.14 (AB two d, $J = 12.9$ Hz, 4H), 4.43 and 3.13 (AB two d, $J = 12.9$ Hz, 4H), 4.13 (t, $J = 8.6$ Hz, 2H), 4.01 (t, $J = 8.2$ Hz, 2H), 3.71 (t, $J = 7.4$ Hz, 4H), 2.14 (m, 4H), 1.92 (m, 4H), 1.50–1.20 (m, 16H), 1.29 (s, 9H), 0.95 (t, $J = 7.0$ Hz, 12H), 0.93 (s, 18H). **5**: 8.44 (d, $J = 7.2$ Hz, 4H), 8.15 (d, $J = 8.1$ Hz, 4H), 7.68 (t, $J = 7.6$ Hz, 4H), 6.90 and 6.80 (AB two d, $J = 2.0$ Hz, 4H), 6.88 and 6.73 (AB two d, $J = 2.4$ Hz, 4H), 4.54 and 3.25 (AB two d, $J = 13.3$ Hz, 2H), 4.52 and 3.21 (AB two d, $J = 12.7$ Hz, 2H), 4.51 and 3.21 (AB two d, $J = 12.7$ Hz, 4H), 3.96 (m, 4H), 3.88 (m, 4H), 2.15–1.95 (m, 8H), 1.21 (s, 18H), 1.04 (t, $J = 7.2$ Hz, 6H), 1.02 (t, $J = 7.3$ Hz, 6H). **6**: 8.70–6.30 (br s, 12H), 6.82 (s, 4H), 6.78 (s, 4H), 4.51 and 3.19 (AB two d, $J = 12.8$ Hz, 8H), 4.01 (t, $J = 7.3$ Hz, 4H), 3.89 (t, $J = 7.3$ Hz, 4H), 2.25–1.85 (m, 8H), 1.50–1.30 (m, 16H), 1.09 (s, 18H), 0.99 (t, $J = 7.0$ Hz, 6H), 0.94 (t, $J = 7.0$ Hz, 6H).

in **7a,b**, the electron-rich calixarene acts as a fluorescence quencher, most probably via photoinduced electron transfer.¹¹ This quenching, however, is far less pronounced for the more electron-rich tetraphenoxy-substituted perylene bisimide **7b**, which is still highly fluorescent. On the other hand, it is exactly this sensitivity to the local environment of perylene bisimides that makes them attractive for calixarene-based fluorescence sensors.

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Supporting Information Available: Experimental procedures for synthesis of **3–7**, variable-temperature ^1H NMR spectra of the bis-imide **6** and crystal structure data for **3a** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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7a: 8.72 and 8.67 (AB two d, 8H, $J = 8.0$ Hz), 7.05 (s, 4H), 7.02 (s, 4H), 6.60 (s, 8H), 4.49 and 3.17 (AB two d, $J = 12.7$ Hz, 8H), 4.45 and 3.15 (AB two d, $J = 12.5$ Hz, 8H), 4.15 (t, $J = 8.2$ Hz, 4H), 4.01 (t, $J = 8.3$ Hz, 4H), 3.74 (t, $J = 6.8$ Hz, 8H), 2.15 (q, $J = 7.8$ Hz, 4H), 2.13 (q, $J = 7.8$ Hz, 4H), 1.94 (q, $J = 7.3$ Hz, 8H), 1.45–1.20 (m, 32H), 1.29 (s, 18H), 0.99 (t, $J = 7.0$ Hz, 24H), 0.96 (s, 36H). **7b**: 8.14 (s, 4H), 7.23 and 6.85 (AB two d, $J = 8.7$ Hz, 16H), 6.86 (s, 4H), 6.79 (s, 4H), 6.65 and 6.60 (AB two d, $J = 1.7$ Hz, 8H), 4.43 and 3.11 (AB two d, $J = 12.4$ Hz, 8H), 4.40 and 3.11 (AB two d, $J = 12.4$ Hz, 8H), 4.00 (t, $J = 7.8$ Hz, 4H), 3.91 (t, $J = 8.2$ Hz, 4H), 3.77 (m, 8H), 2.04 (m, 8H), 1.95 (m, 8H), 1.45–1.35 (m, 32H), 1.27 (s, 36H), 1.08 (s, 18H), 0.96 (t, $J = 7.0$ Hz, 24H), 0.93 (s, 36H).

(20) Measured under dilute condition with *N,N'*-(2,6-diisopropylphenyl)-1,6,7,12-tetraphenoxyperylene-3,4:9,10-tetracarboxylic acid bisimide ($\Phi_{\text{F}} = 0.96$ in CHCl_3) as a reference; see: Gvishi, R.; Reisfeld, R.; Burshtein, Z. *Chem. Phys. Lett.* **1993**, *213*, 338–344.

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