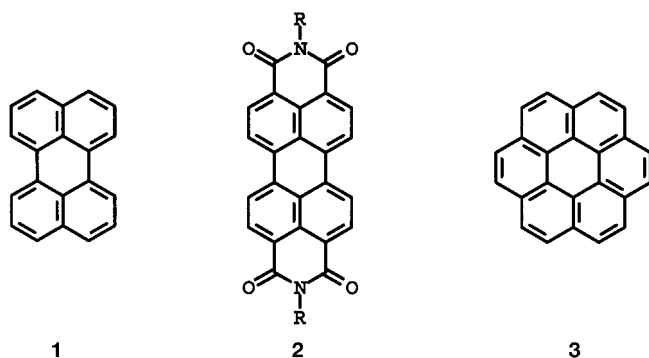


Liquid Crystalline Coronene Derivatives with Extraordinary Fluorescence Properties**

Ulrike Rohr, Peter Schlichting, Arno Böhm, Markus Gross, Klaus Meerholz, Christoph Bräuchle, and Klaus Müllen*

Dedicated to Professor Emanuel Vogel on the occasion of his 70th birthday

Perylene (1) and perylene-3,4:9,10-bis(dicarboximide)s 2 are among the most intensively investigated chromophores in dye chemistry.^[1] Coronene (3), which is similar to perylene,



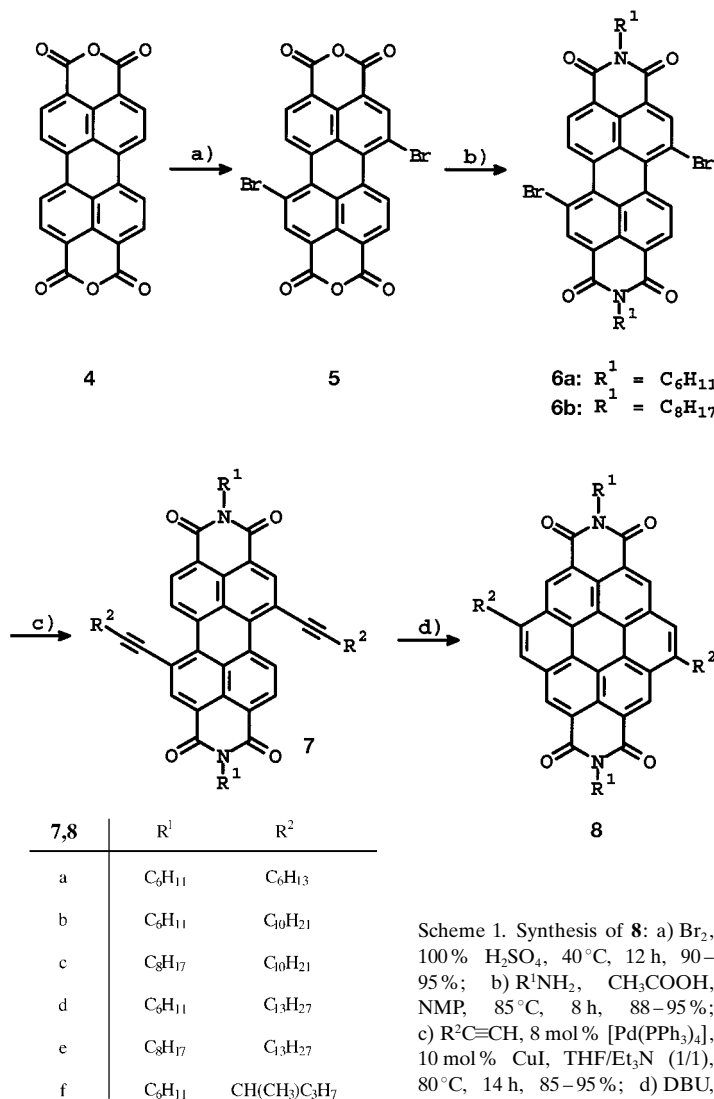
constitutes a classical aromatic hydrocarbon; however, owing to its limited preparative accessibility, there have been only few attempts to modify it chemically.^[2] We present here the coronene-3,4:9,10-bis(dicarboximide)s 8, which as a combination of 2 and 3 represent a novel type of dye.

The photostable yellow title compounds 8

- are obtained by a surprisingly simple procedure from readily available derivatives of 2, and provide access to additional chromophores.
- are active in an interesting wavelength range between that of 1 and 2 in both absorption and emission spectra,
- form, when they contain suitable alkyl substituents R¹ and R², discotic mesophases and combine the properties of both dyes and liquid crystals,^[3] and
- form aggregates in a solid matrix whose photoluminescence wavelength varies depending on the respective tempering process. Therefore, 8 is a promising compound for the preparation of multicolored displays on the basis of organic luminescent diodes.

The functionalization and alkylation of perylene (1) was achieved by coupling 3,9(10)-dibromoperylene with various

terminal alkynes and subsequent catalytic hydrogenation of the triple bonds.^[4] It appeared logical to apply this aryl-ethynyl coupling to the functionalization of the *N,N'*-dialkyl-1,7-dibromo-3,4:9,10-bis(dicarboximide)s 6. However, a very surprising reaction sequence was observed which led to the novel compounds 8 (Scheme 1). The derivatives 6a and 6b



Scheme 1. Synthesis of 8: a) Br₂, 100% H₂SO₄, 40 °C, 12 h, 90–95%; b) R¹NH₂, CH₃COOH, NMP, 85 °C, 8 h, 88–95%; c) R²C≡CH, 8 mol% [Pd(PPh₃)₄], 10 mol% CuI, THF/Et₃N (1/1), 80 °C, 14 h, 85–95%; d) DBU, toluene, 100 °C, 12 h, 95–100%. NMP = *N*-methylpyrrolidone.

required in the first step of the alkyne coupling can be obtained in a two-step synthesis. The commercially available perylene-3,4:9,10-tetracarboxylic dianhydride (4) is subjected to a twofold bromination with elemental bromine in 100% sulfuric acid to provide 5 (90–95%), which is then converted into 6a and 6b (88–95%) with cyclohexylamine or *n*-octylamine, respectively.^[5] The palladium(0)-catalyzed^[4] reactions of 6 with 1-alkynes in the presence of bases such as triethylamine afforded the expected bis(alkynyl)-substituted perylene-3,4:9,10-bis(dicarboximide)s 7a–e in high yields (85–95%). Treatment of 7 with strong, nonnucleophilic bases such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) triggers a cyclization reaction of unknown mechanism to yield almost

[*] Prof. Dr. K. Müllen, Dipl.-Chem. U. Rohr, Dipl.-Chem. P. Schlichting
Max-Planck-Institut für Polymerforschung
Ackermannweg 10, D-55128 Mainz (Germany)
Fax: (+49) 6131-379-350
E-mail: muellen@mpip-mainz.mpg.de

Dr. A. Böhm
BASF AG, Farbenlaboratorium, Ludwigshafen (Germany)
Dipl.-Chem. M. Gross, Dr. K. Meerholz, Prof. Dr. C. Bräuchle
Institut für Physikalische Chemie
der Universität München (Germany)

[**] This work was supported by BASF AG, the Bundesministerium für Bildung und Forschung, and the Fonds der Chemischen Industrie. We thank Dipl.-Chem. C. Kayser for measuring the X-ray diffractograms.

quantitatively the yellow title compounds **8** with various substituents at the resulting phenyl rings.^[6] The structures of the coronenebis(dicarboximide)s **8** could be verified by ¹H and ¹³C NMR spectroscopy, UV/Vis spectroscopy, and FD mass spectrometry (Table 1). Saponification of the imide functionalities in **8b** under standard conditions (KOH in *tert*-

Table 1. Spectroscopic data of **8b**.

M.p. (DSC): $T_m = 245^\circ\text{C}$ (Col _{ho}); ¹ H NMR (500 MHz, CDCl ₃): $\delta = 9.31$ (s, 2H; ArH), 9.06 (s, 2H; ArH), 8.13 (s, 2H; ArH), 5.37–5.31 (m, 2H; NCH), 3.46–3.42 (t, 4H, ³ J = 7.8 Hz; CH ₂ C≡C), 2.91–2.85 (m, 4H; cHex), 2.18–2.12 (m, 8H; cHex and CH ₂), 2.01–1.90 (m, 6H; cHex), 1.74–1.23 (m, 34H; cHex and CH ₂), 0.89–0.86 (t, 6H, ³ J = 7 Hz; CH ₃); ¹³ C NMR (125 MHz, CDCl ₃ , spin-echo experiment): $\delta = 164.86$ (q; C=O), 164.6 (q; C=O), 140.72 (q; arom. C), 128.97 (arom. CH), 128.43 (q; arom. C), 127.79 (q; arom. C), 127.12 (arom. CH), 125.00 (arom. CH), 121.84 (q; arom. C), 121.35 (q; arom. C), 121.27 (q; arom. C), 121.08 (q; arom. C), 120.59 (q; arom. C), 119.19 (q; arom. C), 54.58 (CHN), 33.70 (CH ₂), 31.78 (CH ₂), 31.37 (CH ₂), 31.22 (CH ₂), 29.64 (CH ₂), 29.53 (CH ₂), 26.85 (CH ₂), 25.71 (CH ₂), 22.74 (CH ₂), 14.10 (CH ₃); UV/Vis (CH ₂ Cl ₂): λ_{max} (ϵ) = 477 (9400), 511 (19700), 428 (62100), 404 (30500), 382 (7900), 338 (73200), 334 nm (72800); FD-MS (8 kV, FD = field desorption): $m/z = 882.5$ (100%) [M^+]
--

butyl alcohol/water) afforded the dianhydride **9** in high yields (85–90 %, Scheme 2).^[7] Reaction of the latter with diamines can be used to build up coronene-based polyimides, analogous to the well-known polyperylenebis(dicarboximide)s.^[8] Compound **9** can be decarboxylated with Cu/Cu₂O^[9] to the previously unknown dialkylcoronene **10**.

The absorption bands of **8** show a hypsochromic shift with respect to those of **2** and a bathochromic shift with respect to those of **3**. Coronenebis(dicarboximide)s **8** fluoresce with an intensive green-yellow color with the maxima at 517 nm (in CHCl₃).^[10] With suitable substituents R¹ and R², compounds **8** form mesophases with transition temperatures between 177 and 266 °C; this could be proven by differential scanning calorimetry (DSC) as well as by polarization microscopy and X-ray diffractometry (for the transition temperatures see Table 2; isotropization could not be observed, and decomposition occurred at approximately 450 °C). A comparison of the transition temperatures for the derivatives prepared to date does not allow a correlation between the melting points and the type of alkyl side chains at the imide groups and the

Table 2. Melting points of **8**.

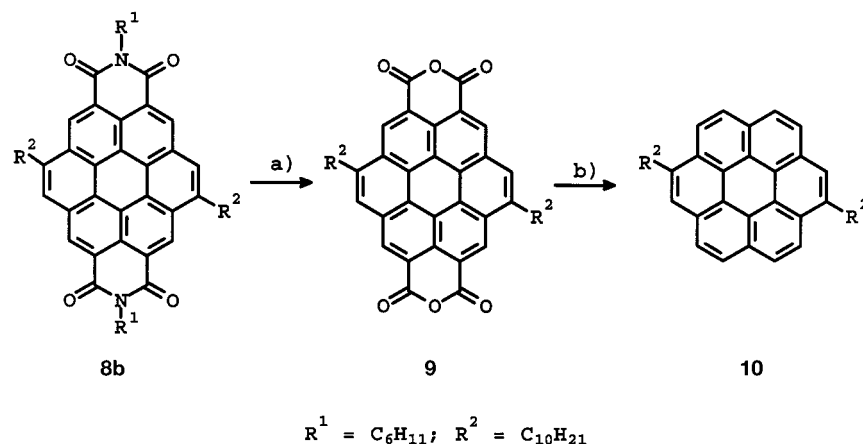
R ²	R ¹ = C ₆ H ₁₁		R ¹ = C ₈ H ₁₇	
	8	T_m [°C]	8	T_m [°C]
C ₆ H ₁₃	a	> 300	–	–
C ₁₀ H ₂₁	b	245 ^[a]	c	192 ^[a]
C ₁₃ H ₂₇	d	266 ^[a]	e	177 ^[a]
CH(CH ₃)C ₃ H ₇	f	> 300	–	–

[a] These derivatives form a mesophase at $T > T_m$.

coronene skeleton. However, hexyl substituents at the aromatic moiety do not suffice to form a mesophase (Table 2: derivative **8a**; R¹ = C₆H₁₁, R² = C₆H₁₃). X-ray diffractometry investigations suggest the presence of a columnar discotic mesophase with a hexagonal superstructure (Col_{ho}) at temperatures above the melting point.^[11] For the use of the coronene derivatives **8** as photoconductors, the order in the mesophase is important for a high charge-carrier mobility;^[12] however, lower transition temperatures are required for application purposes.

The formation of columnar mesophases with stacks of disclike chromophores leads to the question of whether aggregates are formed in solution, in amorphous films of the pure substance, or in mixtures with host polymers, and furthermore to what extent the absorption and emission behavior can be controlled by the type of aggregate formation. UV/Vis spectra of solutions of **8b** in chloroform are concentration-independent in a range from 4×10^{-7} to 1×10^{-3} mol L⁻¹.^[14] At the same concentration (10^{-3} mol L⁻¹ ~ 0.1 mass %) of **8b** in a polystyrene (PS) matrix the absorption spectrum of the film matches that of dissolved **8b**, except for the strong broadening of the band. Only at concentrations above 1–2 mass % does a new absorption band develop in the long-wave range which suggests the formation of an aggregate (Figure 1). PS films doped with 1–40 mass % of **8b** and amorphous layers of the pure compound fluoresce orange, and the spectra exhibit only a slight concentration dependence (Figure 2a).

Entirely different spectra are obtained (Figure 2) when these PS films and the film consisting of pure **8b** are tempered under an atmosphere of inert gas for 5 min at 280 °C (i.e., above the melting point of 245 °C in the mesophase): The broad fluorescence band (590 nm) of films containing small amounts of **8b** (1–2 mass %) is shifted towards blue, whereas the band at 510 nm becomes more intense. The emission spectrum of the tempered film containing 1 % of **8b** exactly matches the existence of isolated coronenebis(dicarboximide) molecules. Whereas tempering films with intermediate concentrations of **8b** (5–10 mass %) has a negligible effect on the fluorescence spectrum, a shift towards red can be observed after tempering films containing more than 20 mass % of **8b**. The transition from PS films containing 40 mass % of **8b** to a film of the pure compound is abrupt, with the band



Scheme 2. Synthesis of **10**: a) KOH, H₂O, *t*BuOH, 100 °C, 4 h, 90%; b) decarboxylation with Cu and Cu₂O in quinoline at 220 °C.

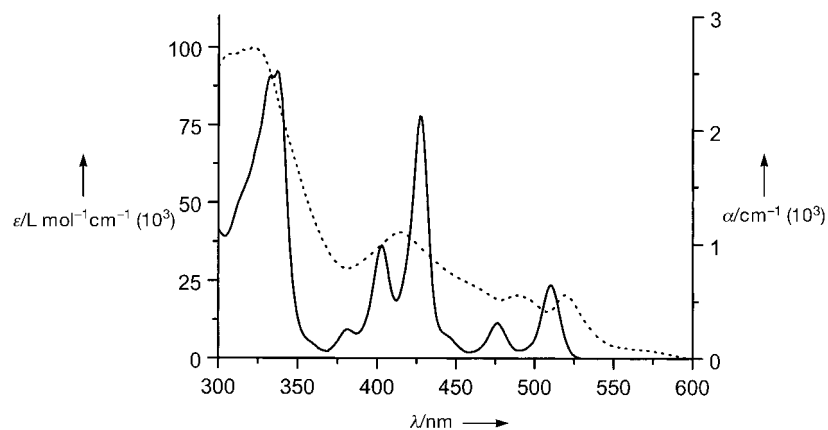


Figure 1. Absorption spectra of **8b** in solution (solid line) and in a PS matrix (10 mass %, dotted line). ϵ = extinction coefficient, α = absorption coefficient.

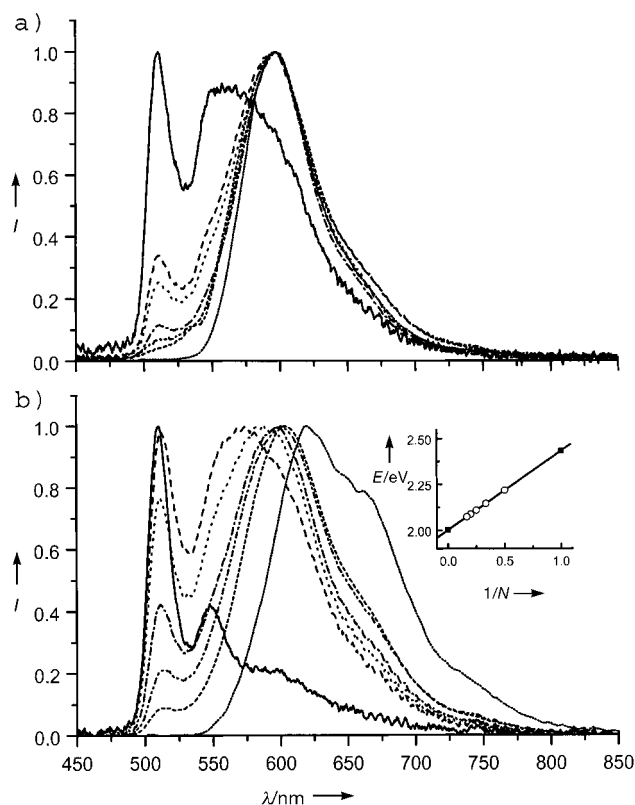


Figure 2. Normalized fluorescence intensities of PS films doped with various concentrations of **8b** [1 % (—), 2 % (---), 5 % (·····), 10 % (-·-·-), 20 % (-----), 40 % (-----), 100 % (·····)]; a) freshly prepared films, b) films tempered at 280 °C. Inset: plot of E_0 versus $1/N$ (N = number of coronenebis(dicarboximide) mesogens in an aggregate). For $N=1$, the energy of the fluorescence band of shortest wavelength of the smallest concentration (0–0 vibrational transition; 510 nm $\equiv$ 2.43 eV) was used, and for $N=\infty$, the transition energy of the pure **8b** films (620 nm $\equiv$ 2.00 eV) was assumed. The following values were calculated from the linear transformation: $N=2$: 560 nm; $N=3$: 578 nm; $N=4$: 588 nm; $N=5$: 594 nm.

being shifted 25 nm towards red (Figure 2b). The film of pure **8b** fluoresces red.

In the case of the films doped with small concentrations of **8b**, similar observations were also made at lower temperatures; however, much longer tempering times are required

(several hours at 120 °C). In contrast, pure **8b** has to be tempered at temperatures above the transition point in order to obtain a color change. Time-dependent experiments show that the process occurring during tempering at 175 °C advances in a few seconds to such a degree that could be utilized for the fabrication of multicolor pixelated displays. Particularly noteworthy in this context is that, in contrast to other known fluorophores that tend to form aggregates (e.g. quinacridone^[15]), no complete quenching of fluorescence takes place for our compounds; instead, the light output reaches a maximum for the films with 40 % **8b**. However, the fluorescence quantum efficiency decreases with increasing concentration (factor of 4 upon going from films with 1 % to 4 % of **8b**).

For the color shift caused by the tempering process we offer the following interpretation: Spin-coating leads to inhomogeneous polymer films with microdomains in which aggregates of various size (stacks) have formed due to the discotic shape of **8b**. These microdomains cause the broad excimer fluorescence at approximately 590 nm (overlap of various transitions!). Assuming a linear relationship between the energy of the fluorescence transition and $1/N$,^[16] N (the number of molecules in an aggregate) can be estimated from the fluorescence spectrum of the films (details are given in the inset of Figure 2b). Accordingly, the untempered films consist mainly of tetramers. Upon tempering of films with low concentrations (1–2 mass %), the material is better homogenized by additional dissolving of the **8b** molecules in the PS matrix; the number of the aggregates decreases in favor of isolated molecules, and their size also decreases (monomers to trimers are present). In contrast, for higher concentrations larger stacks are formed between the discotic molecules, which emit light of longer wavelengths. The overall largest bathochromic shift occurs upon tempering of the pure coronenebis(dicarboximide) layers, as they are capable of forming very long stacks.

Since the photo- and electroluminescence properties of the title compounds match qualitatively—this will be discussed in detail in a separate publication—the emissions of these aggregates could be utilized for a variety of applications: Selective heating allows the emission color to be controlled locally, so that large areas can easily be colored dot by dot. To create multicolored displays, current investigations focus on the long-term stability of aggregate formation as well as how the choice of substituents R^1 and R^2 can possibly lead to large color changes upon aggregate formation, resulting in a drastic increase in the slope of the $E_{\text{max}} - 1/N$ curve.

Experimental Section

7b: In a carefully dried and argon-purged 500-mL Schlenk flask, **6a** (500 mg, 0.7 mmol) was dissolved in a 1:1 mixture (300 mL) of anhydrous THF and anhydrous Et_3N . To this solution was added 4 mol % $[\text{Pd}(\text{PPh}_3)_4]$ (32 mg, 26 μmol) and 5 mol % CuI (6.5 mg, 34 μmol). After two additional cycles of evacuation and purging with argon, 1-dodecyne (466 mg, 2.80 mmol) was added with a syringe through a septum. This mixture was

stirred for 10–14 h at 80 °C. After the starting material had been consumed (TLC), the mixture was added to an ice/HCl mixture (3/1, three times the reaction volume). The mixture was then extracted several times with CH₂Cl₂. The combined CH₂Cl₂ fractions were dried over MgSO₄, and the solvent was removed by distillation. The residue was purified by chromatography on silica gel with CH₂Cl₂ to yield red **7b** (555 mg, 91 %).

8b: Bis(dicarboximide) **7b** (500 mg) was dissolved in 250 mL of toluene. The mixture was heated to 100 °C and 0.5 mL of DBU added with a syringe through a septum. The reaction mixture was stirred for 8–12 h at 100 °C. For the workup, the mixture was added to ice-cooled, dilute HCl and extracted with CHCl₃. The organic layer was dried over MgSO₄, and the product precipitated from CH₃OH to afford orange **8b** in quantitative yield (500 mg).

Spectroscopic investigations: For the film experiments defined amounts of **8b** along with PS (Aldrich, M_w = 280 000, T_g = 100 °C) were dissolved in CHCl₃ and films prepared from these by spin-coating.

For the fluorescence experiments the samples were excited at 413 nm (ca. 10 mW on an irradiation area of 2 mm in diameter) with a krypton-ion laser. The fluorescence spectra were recorded with a computer-integrated spectrometer card (Ocean Optics, model PC1000) under an angle of 30°. A cut-off filter was used to suppress any scattered light of the excitation laser.

Received: October 28, 1997 [Z110921E]

German version: *Angew. Chem.* **1998**, *110*, 1463–1467

Keywords: chromophores • imides • liquid crystals • photoluminescence • polycycles

- [1] a) H. Zollinger, *Color Chemistry*, 2nd ed., VCH, Weinheim, **1991**; b) W. Herbst, K. Hunger, *Industrial Organic Pigments*, VCH, Weinheim, **1993**.
- [2] F. Vögtle, *Reizvolle Moleküle der Organischen Chemie*, Teubner, Stuttgart, **1989**, p. 161.
- [3] For liquid crystalline dyes, see for example C. Göltner, D. Pressner, K. Müllen, H. W. Spiess, *Angew. Chem.* **1993**, *105*, 1722–1724; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1660–1662.
- [4] P. Schlichting, U. Rohr, K. Müllen, *Liebigs Ann.* **1997**, 395–407.
- [5] A. Böhm, H. Arms, G. Henning, P. Blaschka (BASF), patent application DE19547210.
- [6] For analogous reactions of aryethynylarenes, see for example M. B. Goldfinger, K. B. Crawford, T. M. Swager, *J. Am. Chem. Soc.* **1997**, *119*, 4578–4598.
- [7] The direct transformation of **5** with alkynes is also possible; however, the subsequent reaction with DBU does not lead to compounds **9**. This is why the detour via **6** was necessary.
- [8] a) D. Dotcheva, M. Klapper, K. Müllen, *Macromol. Chem. Phys.* **1994**, *195*, 1905–1911; b) G. Karayannidis, D. Stamelos, D. Bikiaris, *Makromol. Chem.* **1993**, *194*, 2789–2796; c) H. Gassemi, A. S. Hay, *Macromolecules* **1994**, *27*, 4410–4412.
- [9] a) W. Neugierar (I. G. Farbe) D.R.P. 486491, **1926** [*Chem. Abstr.* **1930**, *24*, 1870]; b) V. I. Rogovik, *Zh. Org. Khim.* **1974**, *10*, 1072–1075.
- [10] Coronenebis(dicarboximide)s **8** are very photostable. Irradiation of 8×10^{-5} M solutions of **8b** in toluene (quartz cuvettes; UV lamp with $\lambda_{\max}$ = 366 nm), for instance, did not result in a significant decrease in extinction, even after several weeks.
- [11] In the X-ray diffractogram of **8c**, for instance, the alkyl chains cause a reflection at $2\theta = 17.6^\circ$ (halo reflex). The (001) reflex occurs at $2\theta = 25.0^\circ$, and its d value corresponds to the intracolumnar distance (3.6 Å). The very intense (100) reflex at $2\theta = 4.4^\circ$ corresponds to an intercolumnar distance of approximately 20.0 Å ((200) reflex at $2\theta = 8.9^\circ$). The hexagonal superstructure is verified by the weak (110) reflex at $2\theta = 7.7^\circ$. The lattice constant a is given by $a = 1.1547 \times d_{100} = 23.15$ Å.
- [12] a) D. Adam, F. Closs, T. Frey, D. Funhoff, D. Haarer, H. Ringsdorf, P. Schuhmacher, K. Siemensmeyer, *Phys. Rev. Lett.* **1993**, *70*, 457–460; b) D. Adam, P. Schuhmacher, J. Simmerer, L. Häusling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, D. Haarer, *Nature* **1994**, *371*, 141–143.

- [13] a) L. Dähne, *J. Am. Chem. Soc.* **1995**, *117*, 12855–12860; b) L. Dähne, A. Horvath, G. Weiser, G. Reck, *Adv. Mater.* **1996**, *8*, 486–490.
- [14] In contrast, other perylene mesogens show additional bands at higher wavelengths, which suggest the existence of aggregates in solution: a) ref. [3]; b) D. Pressner, C. Göltner, H. W. Spiess, K. Müllen, *Ber. Bunsen-Ges. Phys. Chem.* **1993**, *97*, 1362–1365; c) M. A. Biasutti, S. De Feyter, S. De Backer, G. B. Dutt, F. C. De Schryver, M. Ameloot, P. Schlichting, K. Müllen, *Chem. Phys. Lett.* **1996**, *248*, 13–19.
- [15] U. Keller, K. Müllen, S. De Feyter, F. C. De Schryver, *Adv. Mater.* **1996**, *8*, 490–493.
- [16] The assumption of a linear relationship between the optical transition energy $E_{\max}$ and $1/N$ results from the model of a particle in a box. The relationship also holds true, for example, for π -conjugated oligomers.^[17]
- [17] a) J. Grimme, M. Kreyenschmidt, F. Uckert, K. Müllen, U. Scherf, *Adv. Mater.* **1995**, *7*, 292–295; b) P. Bäuerle, *ibid.* **1992**, *4*, 102.

The Thioesterase of the Erythromycin-Producing Polyketide Synthase: Influence of Acyl Chain Structure on the Mode of Release of Substrate Analogues from the Acyl Enzyme Intermediates**

Kira J. Weissman, Cameron J. Smith, Ulf Hanefeld, Ranjana Aggarwal, Matthew Bycroft, James Staunton,* and Peter F. Leadlay

The polyketide core of the antibiotic erythromycin A is assembled by a polyketide synthase (PKS) from seven C₃ units.^[1] The units are condensed to form a putative enzyme-bound heptaketide product **1**, which is then released through cyclization to the macrolactone, 6-deoxyerythronolide B (**2**) (Scheme 1). The PKS contains a separate catalytic domain for each step in the formation of **2**, housed in three gigantic multifunctional proteins, DEBS 1–3. The ordering of the domains can be analyzed in terms of six chain-extension modules, fronted by a loading domain for the starter acyl group, and terminated by an off-loading thioesterase (TE) responsible for release of the completed product.^[2]

A pivotal step in this biosynthetic scheme is the thioesterase-catalyzed cyclization of the heptaketide **1** to form the macrolide ring **2**. Early in vitro studies with simple substrate

[*] Dr. J. Staunton, K. J. Weissman, C. J. Smith, U. Hanefeld, R. Aggarwal, M. Bycroft
Department of Chemistry, University of Cambridge
Lensfield Road, Cambridge CB2 1EW (UK)
Fax: (+44) 1223-226913
E-mail: js24@cus.cam.ac.uk

Dr. P. F. Leadlay
Department of Biochemistry, University of Cambridge
Tennis Court Road, Cambridge CB2 1QW (UK)
Fax: (+44) 1223-336656
E-mail: pfl10@mole.bio.cam.ac.uk

[**] This work was supported by fellowships to K.J.W. from the Winston Churchill Foundation of the United States and the Howard Hughes Medical Institute, to C.J.S. from the Cambridge Commonwealth Trust, and to U.H., m.B., and R.A. from the Biotechnology and Biological Sciences Research Council (BBSRC) and GlaxoWellcome PLC.