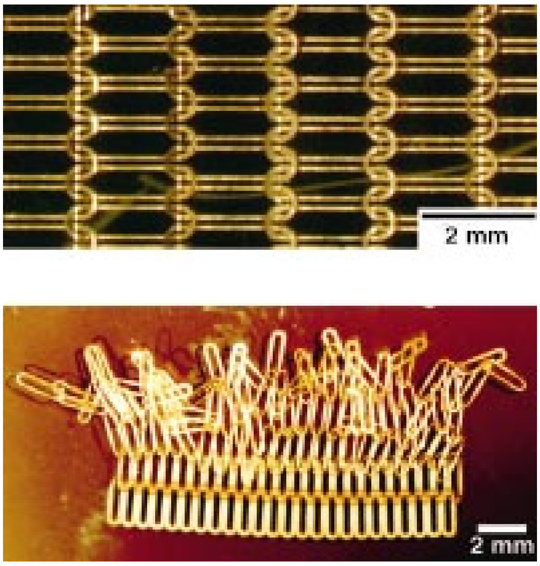

Figure 2. Top: A freely interlocked chain mail (5 × 24 ovals) fabricated by using one glass slide and five cylinders; bottom: a blow-up image of the chain mail.

Experimental Section

The masks for photolithography were produced with a rapid prototyping technique: we designed the patterns with a CAD program; the files containing these designs were sent to a commercial high-resolution printer (5010 dpi) and printed onto transparencies.[3, 6] By UV photolithography, we transferred patterns into negative photoresist (NANO XP SU-8, MicroChem Corp., Newton, MA) on silicon wafers for microcontact printing, and patterns into positive photoresist (Shipley 1813, Microlithography Chemical Corporation, Newton, MA) on a glass slide coated with a thin layer of gold by ebeam evaporation. The surface of these patterned silicon wafers was made more hydrophobic by exposing them to a vapor of perfluoro-1,1,2,2-tetrahydrooctyltrichlorosilane (United Chemical Technologies, Inc., Bristol, PA) in a vacuum desiccator; poly(dimethylsiloxane) (PDMS) prepolymer (Sylgard 184, Dow Corning, Midland, MI) was cast against the silanized silicon wafers and cured at 60 °C for about 3 h, and the elastomeric PDMS replica were peeled from the silicon wafers to be used as stamps for microcontact printing.[3] We coated the glass slide with about 1.5 nm of titanium and about 15 nm of gold by ebeam evaporation; the capillaries were mounted on a stage that rotated about two orthogonal axes during the evaporation, and coated with about 50 nm of titanium and about 70 nm of silver.[7] We used a laser-aligned arrangement of precision translation and rotation stages and hexadecanethiol (hexadecyl mercaptan, technical grade, 92 %, Aldrich) as an "ink" for microcontact printing patterns onto the capillaries.[8] Subsequent wet-chemical etching was accomplished by immersing the printed substrates in an aqueous ferri-/ferrocyanide bath (0.001 M $K_4[Fe(CN)_6]$, 0.01 M $K_3[Fe(CN)_6]$, 0.1 M $Na_2S_2O_3$) for about 30 s to remove the underivatized silver. We aligned the patterns on the substrates manually under a stereoscope and immobilized them by applying 5-min epoxy at the ends of the capillaries and the glass slide. After making electrical connections to the metal with silver epoxy (SPI Supplies, West Chester, PA), we electroplated nickel onto the areas defined by the photoresist on the slide and the silver patterns on the cylinders from a nickel sulfamate-based plating bath (Techni-Nickel "S", Technic Inc., Providence, RI) at 45 °C for about 4 h at a current density of about 20 mA cm^{-2} until the matched ends on different substrates were welded. We released the fully formed chain mail from the substrates by dissolving the photoresist in acetone and dissolving the titanium and glass in concentrated HF solution. **Caution**: concentrated HF is highly corrosive to skin, tissues and bones; avoid exposure. The thin layer of gold was removed by sonication for about 1 min.

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Color-Tuned Electroluminescence from Columnar Liquid Crystalline Alkyl Arenecarboxylates[**]

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Columnar liquid crystals consisting of a polycyclic aromatic core surrounded by flexible side chains combine the good charge-transport properties of aromatic single crystals with the good film-forming properties of viscous liquids.[1] Thus, thin films made of large well-aligned monocrystalline domains can be obtained at room temperature after annealing the material in the liquid crystalline state at elevated temperature. The columns generally align perpendicular to the surface. Thus, the direction of maximum charge mobility, which is along the column axis due to the proximity of the aromatic cores of neighboring molecules, is normal to the plane of the film.

Such semiconducting materials may be used in light-emitting diodes,[2] where an organic film or a stack of organic layers is confined between an anode with high work function (usually formed from transparent indium–tin oxide) and a cathode with low work function (for example, Al or Mg).[3] In devices containing only a single organic layer, the fluorescent organic material needs to exhibit both sufficient hole and electron affinity to allow injection of charges of both signs into the organic layer. It is useful to prepare multilayer devices[4] in order to efficiently confine the recombination of charges in

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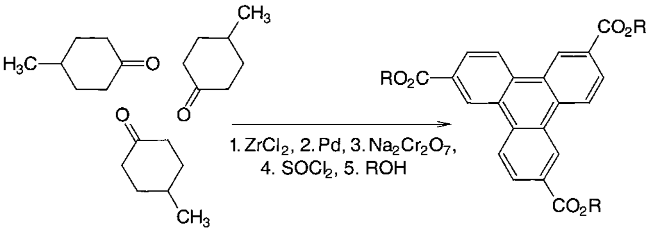
the interior of the device, near the interface of a hole-transporting layer (HTL) with an electron-transporting layer (ETL). Appropriate stacks of several emitting layers may be used to achieve white electroluminescence through additive color mixing.[5]

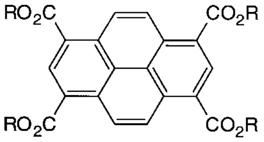
We have developed liquid crystalline aromatic esters which show luminescence in different wavelength ranges between the violet and the red end of the visible spectrum, to combine the excellent charge-transport and film-forming properties of columnar liquid crystals with the ability to emit light.

We prepared alkyl esters of triphenylene 2,6,10-tricarboxylic acid **1a–h** (Scheme 1) to obtain luminescence in the violet–blue range. In contrast to well-known electron-rich (hole-transporting) hexaethers and hexathioethers of triphenylene,[2] these compounds contain weakly electron-withdrawing alkoxycarbonyl groups that diminish the electron density of the aromatic system and, thus, enable electron transport. For emission at longer wavelengths, we made the liquid crystalline (LC) and nonmesomorphic alkyl esters of pyrene 1,3,6,8-tetracarboxylic acid **2a–h** and perylene 3,4,9,10-tetracarboxylic acid **3a–h** ($R = C_nH_{2n+1}$). Dilute solutions of the pyrene derivatives emit in the blue region, while the pure compounds show a green to yellow emission due to the formation of oligomolecular aggregates. The emission colors of the perylene derivatives are green for solutions and orange to red for the pure compounds, respectively. Appropriate mixtures between the derivatives of triphenylene and pyrene or triphenylene and perylene show fluorescence in a broad spectral range.

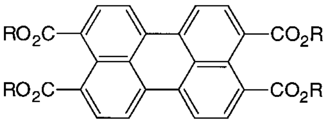


1a – h

Scheme 1. Synthesis of the triphenylene derivatives **1a–h** ($R = C_nH_{2n+1}$).



2a – h



3a – h

Triphenylene 2,6,10-tricarboxylic acid and its trialkyl esters **1a–h** (Scheme 1) were synthesized by a) dehydrating cyclotrimerization of 4-methylcyclohexanone with $ZrCl_2$ (12 h reflux, 50% yield; a simplification of the procedure of Shirai et al.[6]); b) dehydrogenation with Pd/C; c) oxidation in aqueous $Na_2Cr_2O_7$ under pressure;[7] and d) treatment with thionyl chloride followed by treatment with the appropriate alcohol. The ethyl derivative **1b** (NMR data are shown in Table 2) shows a monotropic columnar LC phase, the *n*-propyl and *n*-butyl esters **1c** and **1d** are monotropic nematic, the *rac*-2-ethylhexyl derivative **1h** exhibits an enantiotropic columnar LC phase, and the other derivatives (methyl, *n*-pentyl, *n*-hexyl, *n*-octyl) are not mesomorphic (Table 1). The monotropic mesophases of **1b** and **1c** are metastable against crystallization (glassy) at room temperature. Crystallization sets in upon heating to about 60 °C. The nematic phase of **1d** gives way to crystals upon standing at ambient temperature. Most interestingly, the crystalline phase of **1h**, which forms when cooling an aligned sample below the liquid crystal–crystal transition temperature, is sufficiently similar in its lattice parameters to the mesophase to make the transition nearly undetectable in the polarizing microscope. This made us expect that the columnar structure of the liquid crystal is unusually well maintained in the crystal, and no significant reorientation or formation of grain boundaries (which both would impair the charge-transport properties of the film) takes place in thin films. This assumption of an isomorphic columnar crystalline structure is confirmed by powder X-ray diffraction measurements; these show that the main reflection in the LC phase, which corresponds to the spacing of a hexagonal columnar lattice, is maintained nearly unchanged in the crystalline state (Figure 1). This new family of triphenylene esters offers, in the ethyl and *rac*-2-ethylhexyl homologues **1b** and **1h**, two compounds that are well suited for use in semiconducting thin films because they form solid phases (glassy and crystalline, respectively) at room temperature that maintain the uniform alignment obtained when cooling through the phase transition.

Table 1. Phase-transition temperatures [°C] of the three series of compounds (on heating).[a]

R	**1a–h**	**2a–h**	**3a–h**
methyl (**a**)	cr-258-i	cr-266-[col-262-]i	cr-322-i
ethyl (**b**)	cr-161-[col-135-]i	cr-190-col-204-i	cr-244-col-313-i
n-propyl (**c**)	cr-137-(n-82-)i	cr-181-i	cr-193-col-287-i
n-butyl (**d**)	cr-86-[n-59-]i	cr-101-i	cr-161-col-242-i
n-pentyl (**e**)	cr-111-i	cr-101-i	cr-114-col-203-i
n-hexyl (**f**)	cr-101-i	cr-104-i	cr-72-col-177-i
n-octyl (**g**)	cr-77-i	cr-88-i	cr-62-col-132-i
rac-2-ethylhexyl (**h**)	cr-111-col-124-i	col-94-i	col-240-i

[a] cr = crystalline, col = columnar liquid crystalline, n = nematic liquid crystalline, i = isotropic liquid.

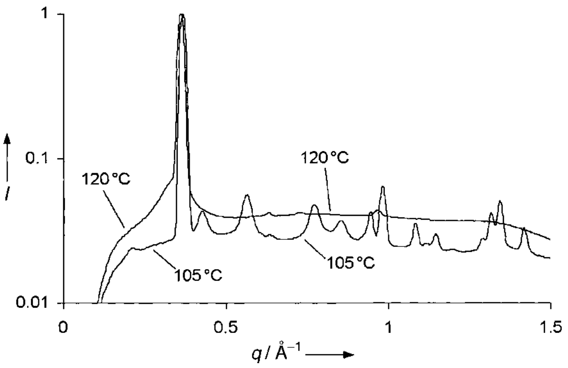


Figure 1. Powder X-ray diffraction study of compound **1h** at 120 °C and at 105 °C. *q* = wave vector, *I* = intensity.

Pyrene 1,3,6,8-tetracarboxylic acid was synthesized following the procedure of Vollmann et al.[8] and esterified with $SOCl_2$/ROH. We again made the methyl, ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *n*-octyl, and *rac*-2-ethylhexyl esters, **2a**–**h** (NMR data of **2b** are shown in Table 2). The methyl, ethyl, and *rac*-2-ethylhexyl homologues **2a**, **2b**, and **2h** are columnar liquid crystalline, while the other compounds are not mesogenic. Compound **2a** is monotropic, and **2b** and **2h** are enantiotropic. Both **2a** and **2b** crystallize with loss of the homeotropic alignment, whilst **2h** does not crystallize and is a mesomorphic fluid at room temperature.

Table 2. ^{1}H NMR data for ethyl esters **1b**, **2b**, and **3b** (300 MHz, Me_4Si, $CDCl_3$).

	$\delta(CH_3)$	$\delta(CH_2)$	δ(ArH)
1b	1.52 (t, $J = 7$ Hz, 9H)	4.52 (q, $J = 7$ Hz, 6H)	8.33 (dd, $J = 9$, 1.5 Hz,3H), 8.75 (d, $J = 9$ Hz, 3H), 9.32 (d, $J = 1.5$ Hz, 3H)
2b	1.56 (t, $J = 7$ Hz, 12H)	4.62 (q, $J = 7$ Hz, 8H)	9.20 (s, 2H), 9.37 (s, 4H)
3b	1.46 (t, $J = 7$ Hz, 12H)	4.41 (q, $J = 7$ Hz, 8H)	7.82 (d, $J = 8$ Hz, 4H), 7.85 (d, $J = 8$ Hz, 4H)

Perylene 3,4,9,10-tetracarboxylic esters **3a**–**h** were obtained from the dianhydride by treatment with K_2CO_3 in a 1:1 mixture of RI and ROH (3 days at approximately 80 °C; NMR data for **3b** are given in Table 2). The mesomorphic behavior of the *n*-alkyl series has been published previously.[9] In addition, we made the *rac*-2-ethylhexyl homologue **3 h**, which does not crystallize and is a columnar liquid crystalline fluid over a very large temperature range (from room temperature to the liquid transition at 240 °C). Columnar LC room temperature glasses can be obtained by mixing different short-chain *n*-alkyl homologues (for example, **3b**/**3e** in a 1:1 ratio).

The photoluminescence wavelengths of the compounds presented here are distributed over the entire visible spectrum, and the respective chromaticity coordinates make a nearly uninterrupted arc of points through the chromaticity diagram from blue to red (Figure 2). This allowed us to prepare electroluminescent samples with a wide range of colors.

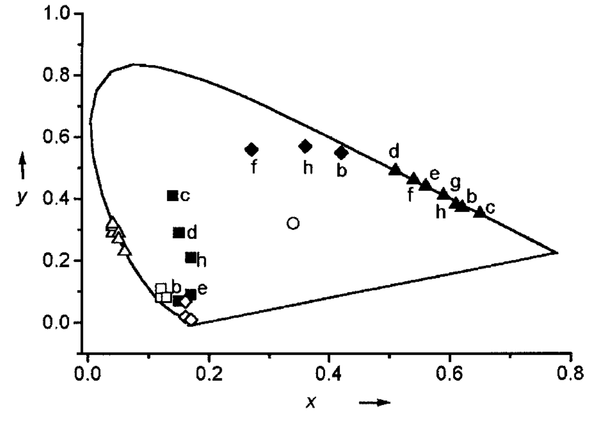


Figure 2. Chromaticity coordinates (x = red, y = green) for the photoluminescence of solutions (open symbols) and thin films (closed symbols) of the triphenylene (squares), pyrene (diamonds), and perylene (triangles) derivatives. The open circle in the center represents the panchromatic point (white).

We prepared light-emitting diodes consisting of a glass substrate coated with an indium–tin oxide (ITO) electrode layer, one to three organic layers, and an aluminum layer serving as the negative electrode. The perylene derivatives **3a**–**h** show a strong electroluminescence even in single-layer samples (Figure 3). They were made by deposition of a layer (about 50 nm thick) on top of the ITO substrate by thermal evaporation under high vacuum, followed by evaporation of a thin (approximately 100 nm) Al electrode on top of the organic layer. Compounds **1a**–**h** and **2a**–**h** were used in two-layer samples containing an HTL (approximately 50 nm; produced by spin coating) such as poly-3,4-ethylene dioxythiophene (Baytron P, Bayer AG) or *N*,*N*′-diphenyl-*N*,*N*′-bis(3-methylphenyl)-1,1′-biphenyl-4,4′-diamine (TPD, SynTec) between the ITO and the emitting layer. The HTl serves to improve the charge-carrier injection at the ITO anode. Subsequently, the emitting layer (20–50 nm) consisting of the aromatic ester and then the Al top electrode (100 nm) were evaporated onto the HTL. In addition, we prepared and tested three-layer devices that contained an HTL and two emitting layers, in order to combine the emission of different compounds and, thereby, broaden the emission spectra towards a nearly white appearance.

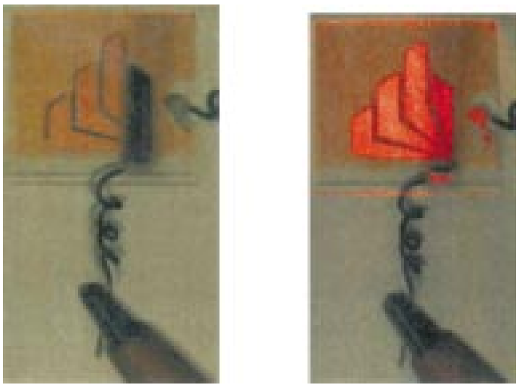


Figure 3. Photograph of a light-emitting diode that contains compound **3b**, without (left) and with (right) applied voltage.

Measurements of the current and the emission intensity versus voltage show typical diode characteristics for the prepared devices, with a threshold voltage where the current starts rising abruptly and where electroluminescence sets in. For example, bilayers with **2b** and **2f** as the emitting ETL show electroluminescence if the voltage exceeds a threshold value of about 5–6 V. For a single-layer light-emitting diode of **3b** with a film thickness of about 50 nm, we observed emission above a threshold of 7–8 V, and the maximum luminance was 100 cd cm^{-2} at a voltage of 20 V. By subsequent evaporation of **3b** on top of a bilayer of HTL and **1b**, light emission in a wide spectral range could be obtained. The corresponding three-layer diode appears nearly panchromatic (Figure 4). Most of the samples can be operated in air under laboratory conditions for several hours at about 10 V.

In conclusion, the compounds presented here prove to be very useful for preparing organic light-emitting devices of different colors, including red, green, blue, and almost white. The color-tuning towards white emission, the color stability,

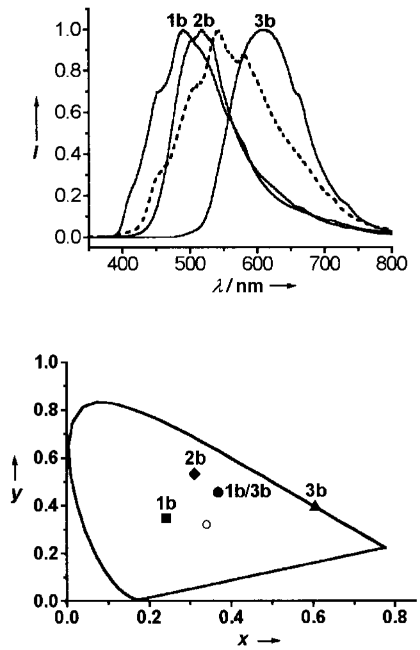


Figure 4. Top: Electroluminescence spectra of diodes (solid lines) that contain an emitting layer of the compounds **1b**, **2b**, and **3b**, and a light-emitting diode that contains two emitting layers made of compound **1b** and compound **3b** (dashed line). Bottom: Chromaticity coordinates of the electroluminescence for **1b**, **2b**, **3b**, and a sample with two emitting layers made of **1b** and **3b**. The open circle in the center represents the panchromatic point (white).

and the lifetime of the device may be improved by simultaneous codeposition of several of these compounds of presumably very similar electro- and photochemical stability. The extent to which the self-organization of the liquid crystalline mesophase can be used, through annealing or similar procedures, to further improve the uniformity of the films and thus the efficiency of these materials, is the subject of forthcoming investigations.

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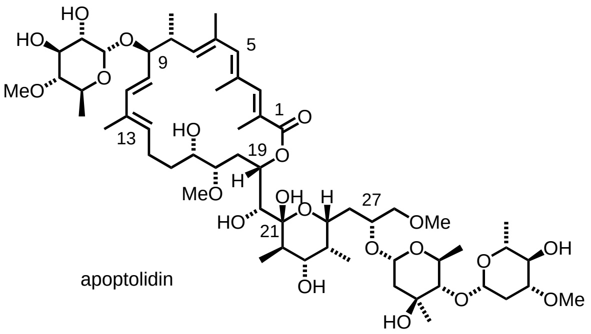
Synthesis of Apoptolidinone[**]

Julia Schuppan, Hermut Wehlan, Sonja Keiper, and Ulrich Koert*

Programmed cell death or apoptosis is a basic biological process that regulates, for example, the homeostasis and morphogenesis of organisms.[1] One very promising application of apoptosis control is in tumor therapy.[2] Apoptolidin, a natural product isolated from *Nocardiopsis sp.*, induces apoptosis in rat glia cells transformed with the E1A oncogene ($IC_{50} = 11\,ng\,mL^{-1}$), but not in untransformed cell lines.[3] Khosla and co-workers identified the mitochondrial F_1F_0 ATPase as one possible target to explain the biological action.[4] Apoptolidin is a 20-membered macrolide with a side chain at C19 containing a 6-membered cyclic hemiketal. A disaccharide from D-oleandrose and L-olivomycose is located at C27, while 6-deoxy-4-*O*-methyl-L-glucose is attached at C9. Here we report on the synthesis of apoptolidinone, the aglycon of apoptolidin.[5]



apoptolidin

Our retrosynthetic analysis of apoptolidinone is based on a macrolactonization and a disconnection between C11 and C12

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