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Benzocyclobutenoacenaphthylene Stilbenes. 1. Synthesis and Thermal Properties

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In this paper the synthesis and characterization of a new class of molecules based on 6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (DBCA) with potentially interesting optical and electronic properties are described. The mentioned compounds contain one or two DBCA units linked via a double bond to an aromatic system. The synthesis of these compounds is mainly carried out by Heck and/or Wittig reactions. The introduction of DBCA units in molecules is interesting in two respects: (1) It will influence the electronic and optical properties of the compounds, and (2) it will induce dimerization (polymerization) because DBCA can, upon thermolysis or photolysis, be converted into a biradicaloid species ("pleiadene") which dimerizes. Thus suitable compounds could be used as monomers for photochemically or thermally induced polymerization.

Introduction

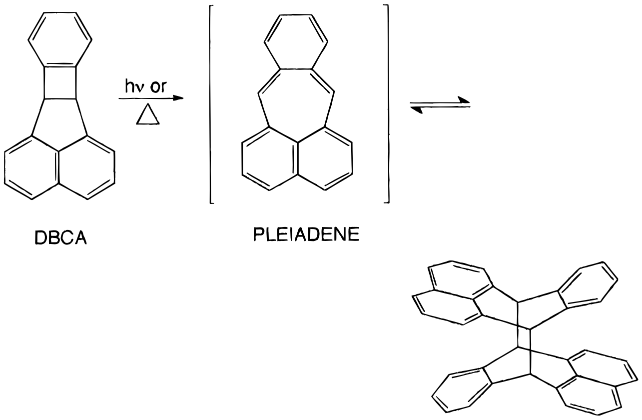
The molecule 6b,10b-Dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (DBCA)[1,2] is one of the precursors for the generation of pleiadene, a π,π-biradicaloid hydrocarbon that was studied theoretically and experimentally during the seventies.[3−5] Since it is a highly reactive molecule, it immediately dimerizes upon formation[6] (Scheme 1).

So far there are very few examples of the synthetic use of the pleiadene unit generated from the DBCA ring system. The pleiadene dimerization has been applied by Stille's group for a chain extension reaction in polymer synthesis,[7] and the reaction of pleiadene with fullerene C_{60} was reported by Müllen's group.[8]

The driving force to synthesize the compounds incorporating one or two DBCA units—shown in Scheme 2—was to study their influence on electronic and optical properties compared to analogues with benzene rings. In this respect the preparation of 8-styryl-DBCA (**1**) gave us the opportunity to compare its properties with *trans*-stilbene. The analogues with another DBCA unit (**2**) and with one anthracene system (**3**) instead of a benzene ring served for comparative studies as well. In addition, we prepared monomers **5** and **6** containing two DBCA units that could serve as polymer building blocks under pleiadene dimerization conditions. Especially for electronic applications a "clean" thermally or photochemically induced polymerization step is of great advantage in the preparation of high-strength materials.

The detailed investigation of electronic and/or optical properties of the DBCA-based molecules described below, as well as the properties of derived polymers, are to be discussed elsewhere. In this paper we concentrate on their preparation and characterization.

Scheme 1



Results and Discussion

The starting materials, 8-halo-6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (8-X-DBCA, X = Br, I), employed in the synthesis of the DBCA-based derivatives were prepared according to the procedure of Upshaw and Stille.[7] The preparation of the compounds with one or two DBCA units linked via double bonds to an aromatic system was carried out by Heck and/or Wittig reactions.

In the case of compound **1** the Pd-catalyzed coupling reaction of 8-I-DBCA and styrene by a Heck coupling[9] gave the target molecule in 75% yield (Scheme 3). We could increase the original yield by using DMF instead of acetonitrile[9] since it is a better solvent for the iodo derivative and a better stabilizer for the palladium complex intermediate.

The characterization data for **1** are given in the Experimental Section. Differential scanning calorimetry

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(1) Kolc, J.; Michl, J. *J. Am. Chem. Soc.* **1970**, *92*, 4147−4148.

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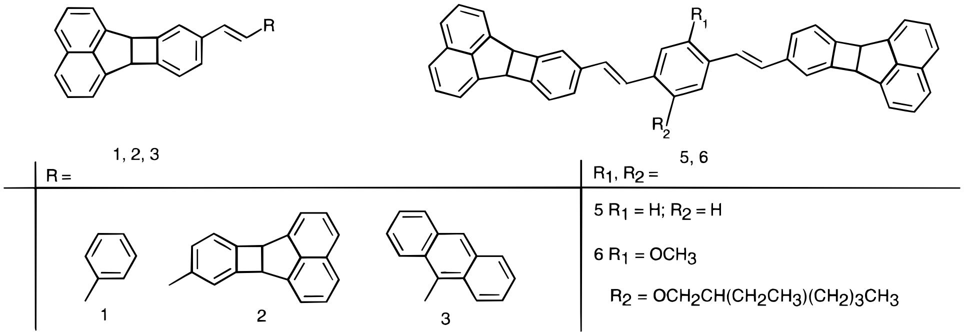
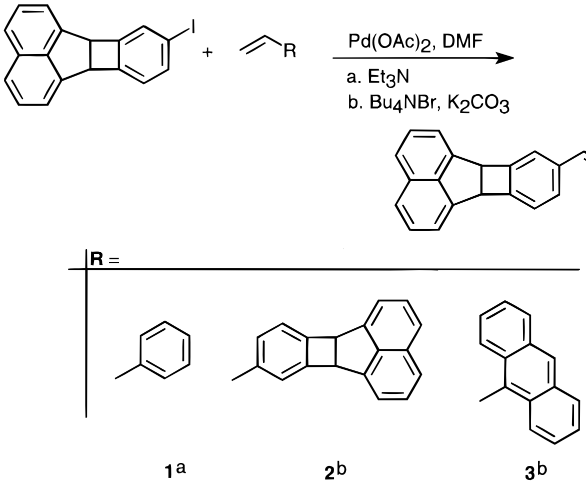
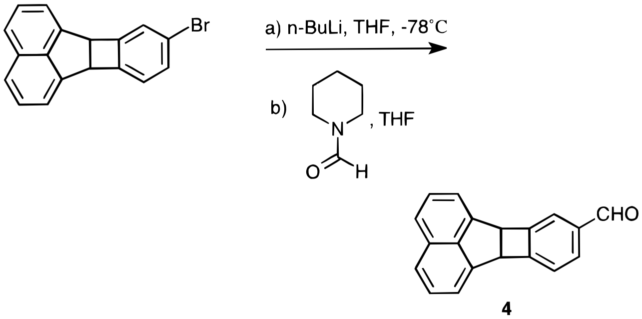
Scheme 2



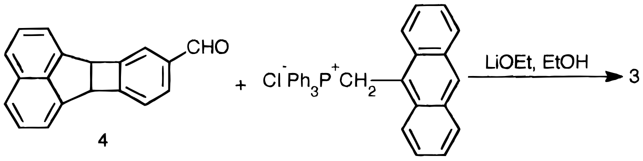
Scheme 3



Scheme 4



Scheme 5



(DSC) was carried out on a sample from 40 to 300 °C under nitrogen, at a heating rate of 5 °C/min. The melting endotherm appeared at 155 °C, and the maximum of the ring-opening or dimerization exotherm occurred at 214 °C. In the case of **2**, the homogeneously catalyzed Heck reaction employed for compound **1** did not proceed as well as before, so we used an alternative phase-transfer catalytic system[10] (Scheme 3). This approach provided compound **2** with a satisfactory yield and complete characterization.

In the course of our research we were also interested in compound **3**, 8-(2′-(9″-anthryl)ethenyl)-DBCA. As in the prior case, the yield of the coupling reaction of 8-I-DBCA and 9-vinylanthracene was improved by a change from the homogeneous palladium(II) acetate/triethylamine catalyst to the phase transfer catalytic system palladium(II) acetate/tetrabutylammonium bromide/potassium carbonate.[11] A Wittig reaction was an even better approach to synthesize the DBCA derivative **3**. For this route the originally obtained 8-halo derivative was converted into the aldehyde **4** in 85−90% yield by a straightforward reaction with *n*-butyllithium and *N*-formylpiperidine. For the Wittig reagent, (9-chloromethyl)anthracene was converted to the triphenylphosphonium chloride and allowed to react with 8-DBCA-carboxaldehyde to give the fluorescent compound **3** in 73% yield (Scheme 5).

Differential scanning calorimetry was carried out from 40 to 400 °C under nitrogen at a heating rate of 10 °C/min. The ring-opening exotherm of the four-membered ring was observed at 223 °C, followed by a continuous increase in the heat flow. Another exothermic peak was observed at 374 °C which could be due to a reaction of the anthracene with a pleiadene resulting from reversal of a dimer.

According to the synthesis of compound **1** the preparation of the corresponding derivative containing two DBCA units (**5**) could be carried out by a Heck reaction of 2 equiv of 8-I-DBCA with *p*-divinylbenzene. Since the commercially available *p*-divinylbenzene is only 80% pure, it was prepared in-house. The olefin was used immediately after the preparation, but under the common Heck reaction conditions (palladium catalyst, about 100 °C) the *p*-divinylbenzene is not stable and leads to a complex mixture of products. Alternatively, the reaction could be carried out by coupling 8-vinyl-DBCA with 1,4-diiodobenzene. The 8-vinyl derivative was prepared according to the procedure described in the literature[11] and allowed to react with 1,4-diiodobenzene to give the product (**5**) in 25% yield (Scheme 6).

A Wittig reaction of 8-DBCA carboxaldehyde (**4**) with the corresponding commercially available *p*-xylenebis(triphenylphosphonium bromide) according to the procedure for *p*-distyrylbenzene[12] (Scheme 7) afforded **5** in 78% yield and consisted of three isomers that differed in the configuration of the double bonds. In contrast to the Heck reaction, which leads only to the *trans*/*trans*-isomer, we could separate the *cis*/*cis*-, *cis*/*trans*-, and *trans*/*trans*-isomers by HPLC (Cosmosil column; solvent 10/90 toluene/

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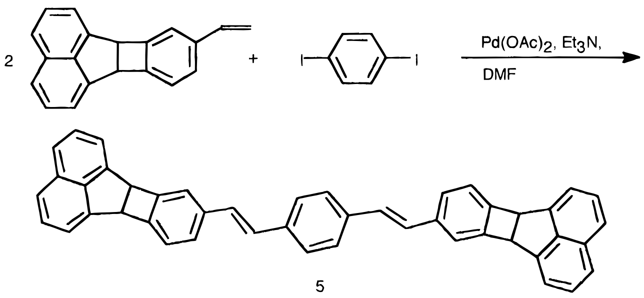
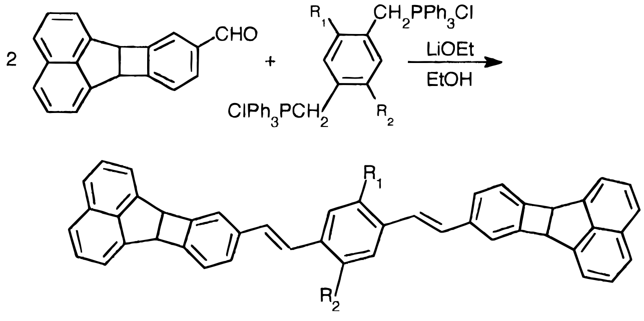
Scheme 6



Scheme 7



R_1, R_2 =

5 R_1 = H; R_2 = H

6 R_1 = OCH_3
R_2 = $OCH_2CH(CH_2CH_3)(CH_2)_3CH_3$

hexane). Refluxing the isomer mixture for several hours in toluene in the presence of a trace of iodine afforded pure, fluorescent *trans-trans-β,β′*-bis-8,8′-DBCA-1,4-divinylbenzene (**5**).

The expected exothermic peak at 240 °C, corresponding to the ring-opening of the DBCA unit, was observed by DSC. A total weight loss of about 4% until 500 °C (TGA) indicated a high thermal stability of the polymer that is formed by the dimerization of the generated pleiadene units on both monomer termini.

Since **5** is not very soluble, we expect that polymers derived from it will be even less soluble. For a possible application in electronics a polymer with a low solubility and the corresponding monomer that tends to crystallize might be a disadvantage. For this reason we introduced substituents in the monomer in order to increase the solubility and the film-forming properties. Hence, α,α′-dichloro-*p*-[5-((2′-ethylhexyl)oxy)-2-methoxy]xylene, which was also used for the preparation of MEH−PPV,[13] was synthesized.[14] This educt was converted to the corresponding bis(triphenylphosphonium chloride) and allowed to react with 8-DBCA-carboxaldehyde (**4**), following the procedure used for the unsubstituted analogue (Scheme 7) to produce **6** in 70% yield. The four isomers, a *cis*/*cis*-, two *cis*/*trans*- (depending on the location of the cis double bond relative to the substituents), and one *trans*/*trans*-isomer, could be separated and analyzed by HPLC (Cosmosil column; 10/90 toluene/hexane). The isomerization to the pure fluorescent *trans-trans-β,β′*-(bis-8,8′-DBCA-MEH DVB), **6**, was carried out as for **5**, above. The resulting product (**6**) was fully characterized, and the DSC evaluation (40−400 °C, 10 °C/min) showed an exothermic transition corresponding to the ring-opening of the pleiadene unit, at 226 °C. As expected, the presence of substituents in **6** increased the solubility and improved the film-forming properties compared to **5**. The 2,5-substitution with alkoxy groups in **6** led to a shift of the peak maximum in the UV/vis spectrum of about 30 nm compared to **5** and enhanced the fluorescence dramatically. Further studies and applications of this highly luminescent material will be published in due course.

In conclusion, the preparation and characterization of a new class of compounds based on DBCA are described. The synthesis of these molecules containing one or two DBCA units linked via a double bond to an aromatic system was carried out by Heck and/or Wittig reactions. The introduction of a DBCA unit in a molecule is interesting in two respects: (1) The cyclobutane ring of the DBCA can be thermally or photochemically opened to give a biradicaloid species ("pleiadene") that dimerizes (or polymerizes), and (2) the influence of a DBCA unit on the electronic and optical properties of the resulting stilbenes, compared to analogues with benzene rings, revealed an enhanced photoluminescence.

Experimental Section

All catalysts were obtained from Strem Chemicals, Alfa A*ESAR*, or Aldrich. Solvents and reagents were from commercial sources and were used as obtained, unless purified as mentioned for a particular preparation.

8-Styryl-6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (1). A solution of 15 mg (0.067 mmol) of palladium(II) acetate in 2 mL of dry dimethylformamide (DMF) was added to a mixture of 1 g (2.8 mmol) of 8-iodo-DBCA, 0.6 mL (4.3 mmol) of dry triethylamine, and 0.4 mL (3.5 mmol) of freshly distilled styrene in 5 mL of dry DMF. The mixture turned orange and became homogeneous at 30 °C and was heated to reflux. The reaction mixture was refluxed for 17 h.

After cooling of the mixture to room temperature, 50 mL of water and 50 mL of diethyl ether were added and the aqueous layer was extracted with ether. The organics were combined and dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by flash column chromatography (SiO_2, 20:1 petroleum ether/CH_2Cl_2): yield 75%; white solid; mp 148−150 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 5.32 (s, 2H), 7.17 (d, J = 7.6 Hz, 1H), 7.26−7.18 (m, 3H), 7.32 (t, 1H), 7.38 (s, 1H), 7.4−7.53 (m, 8H), 7.61 (d, J = 7.6 Hz, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.8, 54.0, 119.9, 122.8, 123.91, 123.95, 126.6, 127.1, 127.6, 128.0, 128.1, 128.2, 128.8, 129.5, 132.7, 137.3, 137.6, 139.2, 143.0, 146.9, 147.7 ppm; FAB-MS (3-NOBA) m/z 330 [M$^+$, 100]; UV/vis (n-hexane) λ 228 (max), 310 nm; IR (KBr) ν 3041, 2942, 1603, 1493, 960, 785, 773, 690 cm^{-1}; DSC (40−300 °C, 5 °C/min) 155 °C (endotherm), 214 °C (exotherm). HRMS: calcd, 330.141; found, 330.140.

8-(2′-(8-(6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthyl)ethenyl)-6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (2). To a mixture of 372 mg (1.05 mmol) of 8-iodo-DBCA, 5 mg (0.02 mmol) of palladium(II) acetate, 284 mg (0.88 mmol) of tetrabutylammonium bromide, and 290 mg (2.1 mmol) of dry potassium carbonate in 10 mL of dry DMF was added 380 mg (1.5 mmol) of 8-vinyl-DBCA.[11] The mixture turned orange-brown and was heated to 100 °C for 63 h. After cooling of the mixture to room temperature, 100 mL of dichloromethane and 100 mL of water were added. The organics were washed with water and dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by flash column chromatography (SiO_2, 3:1 petroleum ether/CH_2Cl_2): yield 47%; light yellow solid; ^1H NMR (400 MHz,

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$CDCl_3$) δ 5.3 (s, 4H), 6.84 (s, 2H), 7.05−7.15 (m, 6H), 7.35−7.5 (m, 8H), 7.55 (d, $J = 8.0$ Hz, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.9, 54.0, 119.8, 119.9, 122.8, 123.91, 123.95, 127.0, 128.0, 128.9, 132.7, 137.4, 139.2, 143.0, 146.7, 147.7 ppm; FAB-MS (3-NOBA) *m/z* 480 [M$^+$, 100]; UV/vis (*n*-hexane) λ 226 (max), 294, 306 (sh) nm.

Preparation of 8-(2′-(9′′-Anthryl)ethenyl)-6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (3). By Heck Reaction. To a mixture of 0.5 g (1.4 mmol) of 8-iodo-DBCA, 6 mg (0.03 mmol) of palladium(II) acetate, 0.38 g (1.2 mmol) of tetrabutylammonium bromide, and 0.39 g (2.8 mmol) of dry potassium carbonate in 20 mL of dry DMF was added 0.41 g (2.0 mmol) of 9-vinylanthracene. The mixture turned brown at once and was heated to 100 °C for 63 h. After cooling of the mixture to room temperature, 150 mL dichloromethane was added and the solids were filtered off. The organics were washed with water and dried over Na_2SO_4, and the solvent was removed in vacuo. The residue was purified by flash column chromatography (SiO_2, 10:1 petroleum ether/CH_2Cl_2): yield 56%; yellow, fluorescent ($\lambda = 366$ nm) solid; for characterization, see below.

By Wittig Reaction. A solution of 9-(chloromethyl)anthracene (1 g, 4.4 mmol) and 1.27 g (4.8 mmol) of triphenylphosphine in 8 mL of dry DMF was heated for 4 h at reflux and cooled. The product was precipitated in diethyl ether and centrifuged: yield 90%; yellow solid.

To a suspension of 0.46 g (1.8 mmol) of carboxaldehyde **4** and 0.8 g (1.6 mmol) of (9′-anthrylmethyl)triphenylphosphonium chloride in 30 mL of dry ethanol was added 3.3 mL (3.3 mmol) of lithium ethoxide (1 M in ethanol). The reaction solution was heated for 20 h at reflux. After cooling of the solution to 25 °C, half of the ethanol was removed in vacuo and 50 mL of water was added. The aqueous solution was extracted with dichloromethane and the organics were dried over Na_2SO_4. The product was purified by flash column chromatography (SiO_2, 5:1 petroleum ether/CH_2Cl_2). Investigation by HPLC (UV detection) showed that the product was a mixture of the *cis*- and *trans*-isomers. Even though the isomers were separable by HPLC on a Cosmocil Buckyprep column (4:1 hexane/toluene), refluxing the mixture in toluene for several hours in the presence of a trace of iodine gave the pure *trans*-isomer: yield 73%; yellow, fluorescent ($\lambda = 366$ nm) solid; mp 220 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.46 (s, 2H), 6.86 (d, $J = 16.2$ Hz, 1H), 7.38−7.7 (m, 13H), 7.80 (d, $J = 17.3$ Hz, 1H), 7.99 (d, $J = 8.1$ Hz, 2H), 8.28 (d, $J = 8.6$ Hz, 2H), 8.38 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 54.0, 54.2, 120.0, 120.1, 123.0, 124.0, 124.1, 124.3, 125.4, 125.6, 126.2, 126.6, 127.2, 128.09, 128.13, 128.8, 129.9, 131.7, 132.8, 133.1, 137.3, 138.2, 139.2, 142.9, 147.3, 148.0 ppm; FAB-MS (3-NOBA) *m/z* 430 [M$^+$, 100]; UV/vis (*n*-hexane) *trans*-isomer $\lambda = 294$ (max), 385 nm, *cis*-isomer (HPLC, Cosmocil Buckyprep column, 4:1 hexane/toluene) $\lambda = 294$ (max), 387 nm; IR (KBr) ν 3044, 2929, 1620, 1602, 1468, 1441, 1367, 969, 883, 843, 783, 772 cm^{-1}; DSC (40−400 °C, 10 °C/min) 223 °C (exotherm), continuous endothermic heat flow, 374 °C (exotherm). HRMS: calcd, 430.1722; found, 430.1721.

8-(6b,10b-Dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene)-carbaldehyde (4). In a three-neck flask, 1.04 g (3.4 mmol) of 8-bromo-DBCA was dissolved in 10 mL of dry THF and cooled to −78 °C. Then 2.2 mL of *n*-butyllithium (1.7 M in pentane; 3.7 mmol) was added slowly and the solution stirred for 1 h at −78 °C. Following this, a solution of 0.8 mL (7.2 mmol) of *N*-formylpiperidine in 5 mL of dry THF was added via syringe. The color changed from brownish to pale-yellow, and the solution was stirred for 10 min at −78 °C, another 2 h at 0 °C, and at room temperature overnight.

The reaction mixture was quenched with 3 N HCl (pH = 2−3) and extracted with diethyl ether. The organics were washed with saturated aqueous $NaHCO_3$ solution, water, and saturated aqueous NaCl solution and were dried over Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by flash column chromatography (SiO_2, 2:1 hexane/Et_2O): yield 88%; white solid; mp 144−146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (s, 2H), 7.35 (d, $J = 7.57$ Hz, 1H), 7.44−7.59 (m, 4H), 7.60−7.66 (m, 4H), 9.86 (s, 1H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.8, 54.5, 120.23, 120.25, 123.07, 123.12, 124.26, 124.34, 128.16, 128.23, 131.5, 132.6, 136.5, 139.0, 141.6, 142.0, 148.2, 154.6, 192.3 ppm; FAB-MS (3-NOBA) *m/z* 256 [M$^+$, 100], 226 [M + H$^+$ − CHO, 16]; IR (KBr) ν 3051, 2949, 2845, 1694, 1492, 1425, 1214, 1192, 828, 785, 771 cm^{-1}; DSC (40−400 °C, 10 °C/min) 145 °C (endotherm), 218 °C (exotherm), 374 °C (exotherm). HRMS: calcd, 256.0888; found, 256.0887.

***β,β′*-Bis[8,8′-(6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene)]-1,4-divinylbenzene (5). By Heck Reaction.** To a solution of 135 mg (0.41 mmol) of 1,4-diiodobenzene, 5 mg (0.022 mmol) of palladium(II) acetate, and 0.17 mL (1.2 mmol) of dry triethylamine in 7 mL of dry DMF was added 250 mg (0.98 mmol) of 8-vinyl-6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthylene (prepared according to ref 11. The mixture was heated to 110 °C and kept stirring at this temperature for 17 h. After cooling of the mixture to room temperature, 100 mL of water and 100 mL of diethyl ether were added and the aqueous layer was extracted with ether. The organic extracts were washed with 2 N aqueous HCl, water, and aqueous saturated NaCl solution, followed by drying over Na_2SO_4 and solvent removal in vacuo. The product (*trans*/*trans*-isomer) was isolated by flash column chromatography (SiO_2, 5:1 petroleum ether/CH_2Cl_2): yield 25%; yellow, fluorescent ($\lambda = 366$ nm) solid; for characterization, see below.

By Wittig Reaction. To a suspension of 0.5 g (1.95 mmol) of the carboxaldehyde **4** and of 0.7 g (0.9 mmol) of *p*-xylenebis(triphenylphosphonium bromide) in 30 mL of USP ethanol was added 3.5 mL (1 M in EtOH, 3.5 mmol) of lithium ethoxide. The reaction mixture was heated for 17 h at reflux. After cooling of the reaction to 25 °C, half of the ethanol was removed in vacuo and 50 mL of water was added. The aqueous solution was extracted with diethyl ether, and the organics were dried over Na_2SO_4. The product (a mixture of the *cis*/*cis*-, the *cis*/trans-, and the *trans*/*trans*-isomers) was purified by flash column chromatography (SiO_2, 10:1 petroleum ether/CH_2Cl_2). The mixture of isomers was dissolved in toluene and refluxed for several hours in the presence of a trace of iodine to give the pure *trans-trans* isomer: yield 78%; yellow solid; mp 225 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (s, 4H), 6.99 (dd, 4H), 7.17 (d, $J = 7.82$ Hz, 2H), 7.21−7.28 (m, 2H), 7.41 (d, $J = 4.07$ Hz, 6H), 7.43−7.55 (m, 8H), 7.63 (d, $J = 7.84$ Hz, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.9, 54.1, 119.9, 120.0, 122.8, 123.9, 124.0, 126.9, 127.1, 127.8, 128.1, 129.4, 132.7, 136.8, 137.3, 139.2, 143.0, 146.9, 147.8 ppm; FAB-MS (3-NOBA) *m/z* 582 [M$^+$, 100]; UV/vis (*n*-hexane) *trans*/*trans*-isomer $\lambda = 320$ (sh), 360 (max), *cis*/*trans*-isomer $\lambda = 293$, 341 (max), *cis*/*cis*-isomer $\lambda = 293$ (max), 330 (sh); IR (KBr) ν 3026, 2929, 1603, 1467, 1260, 957, 820, 739 cm^{-1}; DSC (40−400 °C, 10 °C/min) 240 °C (exotherm), starting from 260 °C (continuous endotherm); TGA (35−500 °C, 20 °C/min) weight loss of 2.18% until 250 °C, plateau until 333 °C, weight loss of another 1.5% until 500 °C. HRMS: calcd, 582.2347; found, 582.2345.

Preparation of *β,β′*-[Bis(8′′,8′′′-(6b,10b-dihydrobenzo[*j*]cyclobut[*a*]acenaphthyl)]-5-((2′-ethylhexyl)oxy)-2-methoxy-1,4-divinylbenzene (6). A solution of 5 mL of 0.5 g (1.5 mmol) of α,α′-dichloro-*p*-[5-((2′-ethylhexyl)oxy)-2-methoxy]xylene and 0.86 g (3.3 mmol) of triphenylphosphine in dry DMF was heated for 4 h at reflux and cooled to 25 °C. The product was precipitated in diethyl ether, centrifuged, and dried in vacuo: yield 97%; light yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.6−1.3 (m, 15H), 2.89 (s+d, 5H), 5.40 (s, 4H), 6.69 (s, 1H), 6.84 (s, 1H), 7.7 (m, 30H) ppm; FAB-MS (3-NOBA) *m/z* 523 [M − 2Cl − PPh_3, 100], 785 [M − 2Cl, 30].

To a suspension of 0.46 g (1.8 mmol) of carbaldehyde **4** and 0.7 g (0.82 mmol) of *p*-[5-((2′-ethylhexyl)oxy)-2-methoxyxylene]-bis(triphenylphosphonium chloride) in 35 mL of dry ethanol was added 3.3 mL (1 M in EtOH; 3.3 mmol) lithium ethoxide. The reaction was heated for 4 h at reflux. After cooling of the sample to 25 °C, half of the ethanol was removed in vacuo and 50 mL of water was added. The aqueous solution was extracted with dichloromethane, and the organics were dried over Na_2SO_4. The product was purified by flash column chromatography (SiO_2, 5:1−3:1 petroleum ether/CH_2Cl_2) and consisted of a mixture of four isomers (*cis*/*cis*-, two *cis*/*trans*-, *trans*/*trans*-

isomers; determined by HPLC). The isomers were dissolved in toluene and refluxed for several hours in the presence of a trace of iodine to give the pure *trans-trans*-isomer: yield 70%; yellow solid; mp 215 °C, ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.8−1.0 (m, 6H), 1.2−1.6 (m, 8H), 1.77 (m, 1H), 3.86 (s, 3H), 3.89 (d, $J = 5.57$ Hz, 2H), 5.38 (s, 4H), 7.03 (dd, 4H), 7.16 (m, 2H), 7.21−7.4 (m, 6H), 7.41−7.55 (m, 8H), 7.63 (d, $J = 7.82$ Hz, 4H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.6, 14.4, 23.3, 29.5, 31.1, 40.0, 53.9, 54.1, 56.6, 72.1, 119.9, 122.76, 122.8, 123.0, 123.9, 126.7, 127.0, 127.2, 128.0, 129.65, 129.67, 132.7, 137.86, 137.88, 139.2, 143.0, 146.6, 147.7, 151.4, 151.5 ppm; FAB-MS (3-NOBA) m/z 740 [M^+, 100]; UV/vis (*n*-hexane) *trans-trans*-isomer $\lambda = 323$, 392 (max), *cis-trans*-isomers $\lambda = 294$, 377 (same intensity); *cis-cis*-isomer $\lambda = 292$ (max), 361 nm; IR (KBr) 3042, 2953, 2869, 2859, 1602, 1495, 1464, 1414, 1365, 1237, 1204, 1037, 964, 784, 775 cm^{-1}; DSC (40−400 °C, 10 °C/min) 226 °C (exotherm), starting from 250 °C (continuous endotherm); TGA (35−500 °C, 20 °C/min) weight loss of 2.38% until 400 °C, weight loss of another 41.42% until 600 °C. HRMS: calcd, 740.3654; found, 740.3654.

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