

Novel bisindenocarbazole derivative exhibiting a nematic mesophase

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Abstract—In this letter we describe the synthesis of the first liquid crystalline bisindenocarbazole derivative. The novel bisindenocarbazole exhibits a broad nematic mesophase between 180 and 250 °C, which was characterized by polarizing microscopy and small angle X-ray scattering. The material shows an excellent electrochemical stability and a strong blue fluorescence with a quantum yield of 49% in solution.

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1. Introduction

During the last decade considerable progress has been made in the development of new organic semiconductors. Among these materials, fused aromatics like pentacene and rubrene have received special attention due to their high charge carrier mobilities. In single crystals of pentacene¹ and rubrene² mobilities up to 15 cm²/V s have been demonstrated. In recent years, some fused heterocycles with improved stability towards oxidation have been synthesized.^{3–6} Polycrystalline thin films were obtained by the evaporation of selected indolocarbazole derivatives on heated substrates. Such microcrystalline films exhibit charge carrier mobilities up to 0.1 cm²/V s in organic field-effect transistors.^{5,6} Nevertheless, in polycrystalline films the mobility strongly depends on the morphology, for example, the grain size and packing of the microcrystals and therewith is very sensitive towards the deposition conditions.

An alternative approach to well-ordered thin films are large monodomains formed by liquid crystals (LC). The molecules can be aligned in the LC-phase at elevated temperatures. The orientation is then frozen in either by quenching the LC-phase to room temperature or by photopolymerization of liquid crystalline compounds with photoreactive groups, known as reactive mesogens. High mobilities in discotic liquid-crystal phases from 2,3,6,7,10,11-hexahexylthiotriphenylene were reported by Haarer and co-workers in 1999. Photo-induced charge carrier mobilities up to 0.1 cm²/V s were

obtained in the helical columnar mesophase.⁷ The group of Müllen reported the synthesis of discotic hexabenzocoronene derivatives from which carrier mobilities up to 1 cm²/V s were determined by a pulse-radiolysis time-resolved microwave conductivity technique (PR-TRMC).^{8,9} Besides discotic materials, rod-like calamitic molecules are also able to form highly ordered mesophases. In the smectic G phase of an α,ω -dialkylterthiophene, the carrier mobilities of 2×10^{-2} cm²/V s for both holes and electrons were reported by Funahashi and Hanna in 2000.¹⁰ Furthermore, the orientation of calamitic LC-phases has been adopted to increase charge carrier mobilities in organic field-effect transistors (OFETs). Here liquid crystalline fluorene–bithiophene copolymers like F8T2¹¹ have been used as well as low molar mass oligothiophenes^{12,13} and reactive mesogens.¹⁴ A second field in which ordered LC-phases have already been successfully used, are organic light emitting diodes (OLEDs). Polyfluorenes and fluorene model compounds with nematic mesophases have been used to generate linearly polarized light.^{15–19}

Recently, we have introduced a series of bisindenocarbazoles, which are a new class of fused aromatic heterocycles. By the introduction of different alkyl side chains, the thermal properties of the bisindenocarbazoles can be tailored ranging from crystalline materials to molecular glasses.²⁰ In order to obtain a liquid crystalline bisindenocarbazole derivative, the core molecule has to be extended to increase the length/width ratio. In this letter we present the synthetic access to a novel rod-like bisindenocarbazole derivative, which exhibits a nematic LC-phase together with a saturated blue photoluminescence.

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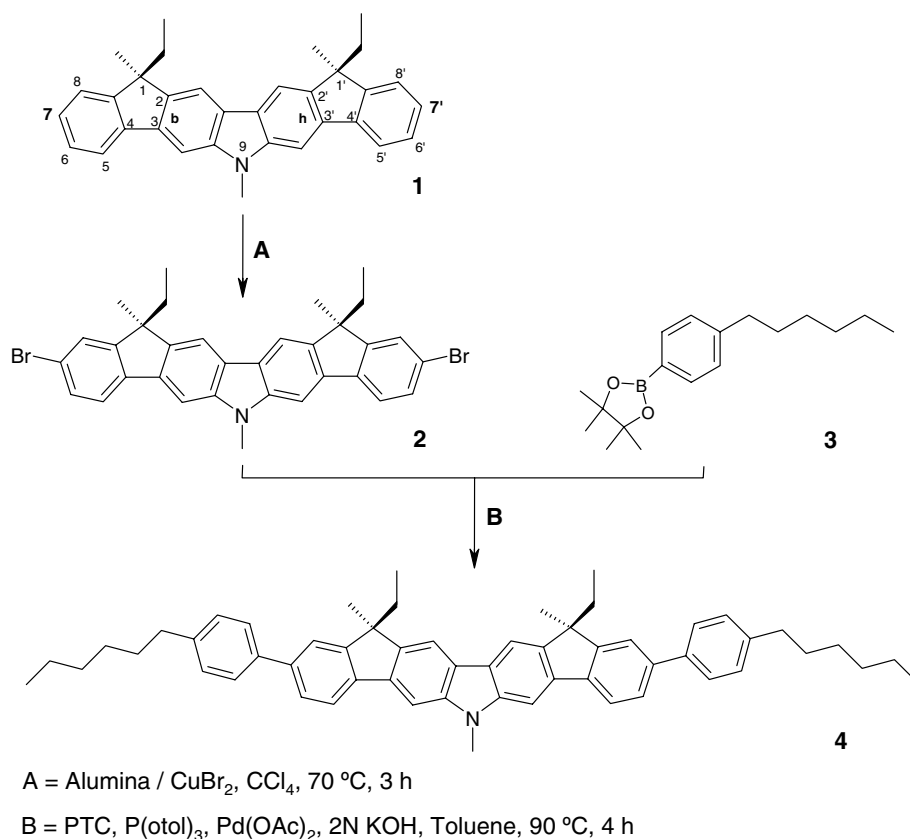
The synthesis of the bisindenocarbazole starting compound **1** is reported elsewhere.²⁰ The new building block **2** was prepared by the reaction of **1** with two equivalents of bromine. For this purpose we used a halogenation reaction with alumina-supported copper(II) bromide in carbon tetrachloride.²¹ The bromination was carried out with the (*R,S*)-bisindenocarbazole isomer shown in Scheme 1. 2D NMR spectroscopy revealed that the bromine was introduced selectively in the 7- and 7'-position of the bisindenocarbazole core. The conversion of 1-bromo-4-hexyl-benzene into the corresponding borolane compound **3** was carried out in with *n*-BuLi and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane in dry THF. Finally the bisindenocarbazole derivative **4** was prepared by a palladium catalyzed Suzuki cross-coupling reaction as depicted in Scheme 1. The product shows an excellent solubility in common organic solvents, which facilitates purification and processing of the material. The target compound **4** was purified by medium pressure liquid chromatography (MPLC) and characterized by IR, ¹H and ¹³C NMR, mass spectrometry and elemental analysis.

Thermogravimetric analysis (TGA) proved the high thermal stability of the novel bisindenocarbazole derivative. In nitrogen atmosphere, decomposition starts at about 310 °C at a heating rate of 10 K/min. Above 180 °C a nematic mesophase is observed by polarizing microscopy (POM) up to a clearing temperature at 251 °C. Upon cooling, the typical Schlieren texture of the nematic mesophase appears at 250 °C and crystal-

lization starts at about 165 °C. Polarizing microscope images are shown in Figure 1. In the DSC measurement, **4** exhibits a melting transition at around 180 °C with an enthalpy of 12.4 kJ/mol and shows recrystallization at 165 °C (8.1 kJ/mol).

Further analysis by small angle X-ray scattering (SAXS) at a temperature of 220 °C confirmed the existence of a nematic LC-phase (Fig. 2). In the small angle region a Bragg peak was observed from which an average end-to-end distance of 34.5 Å at 220 °C can be calculated. This distance is a little bit shorter than the calculated length of the extended molecules (ca. 36 Å), which is consistent with a slightly tilted arrangement of the rigid-rod like bisindenocarbazole molecules in the nematic mesophase. From the broad wide angle Bragg peak a spacing of 5.6 Å is obtained. This peak reflects the average side-to-side distance of the rod-like molecules and is a typical value for a nematic LC-phase.

Absorption and photoluminescence (PL) spectra of **4** were taken from the diluted cyclohexane solutions. The absorption maximum is detected at 395 nm and the maximum of photoluminescence emission at 403 nm (excitation wavelength 390 nm). The optical spectra are shown in Figure 3. The very small Stokes shift of only 8 nm can be explained by the rigid π -electron system of the new material, which allows no major geometrical changes in the transition from the ground to the excited state.^{22,23} For comparison, the bisindenocarbazole core itself has a Stokes shift of 6 nm.²⁰



Scheme 1. Synthesis of the nematic bisindenocarbazole derivative **4**.

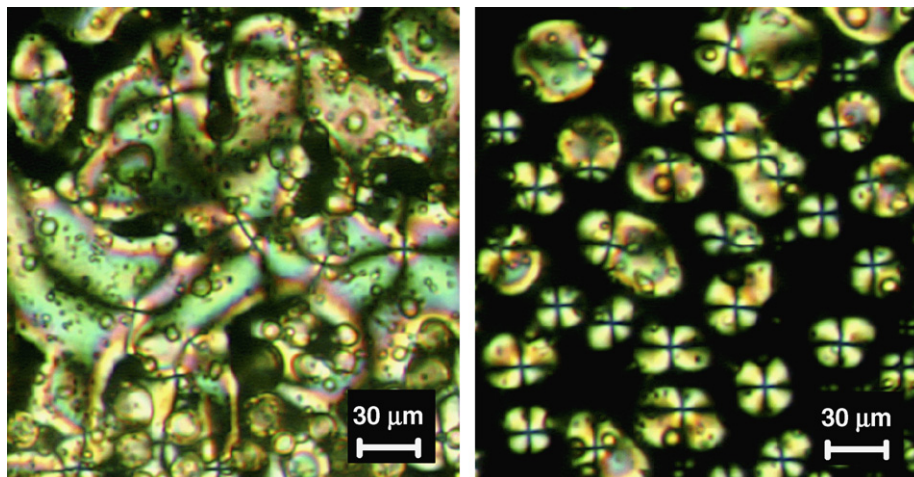


Figure 1. Polarizing microscopy images of **4** upon heating at 220 °C (left) and upon cooling at 248 °C (right) under crossed polarizers.

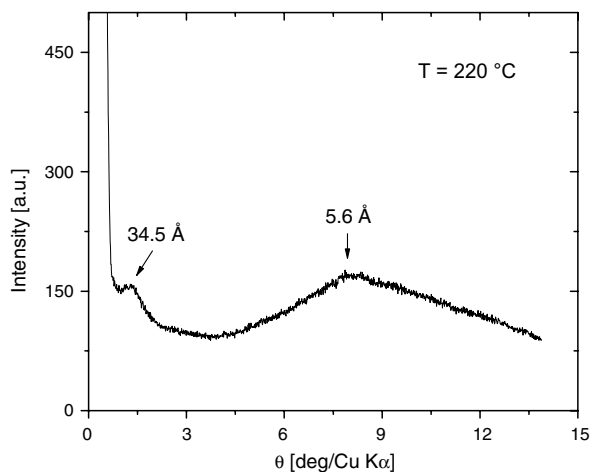


Figure 2. X-ray diffractogram of the bisindenocarbazole derivative **4** at 220 °C.

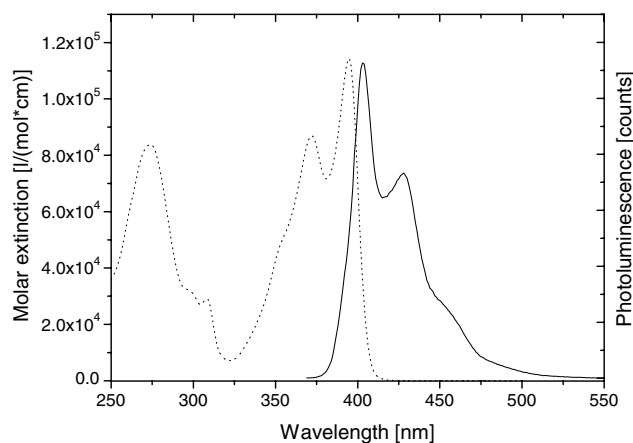


Figure 3. Absorption and fluorescence spectra of the phenylated bisindenocarbazole **4**. The absorption spectrum was taken from 10^{-5} M cyclohexane solution and the fluorescence spectrum was measured from 10^{-6} M cyclohexane solution with an excitation wavelength of 395 nm.

In order to estimate the fluorescence quantum yield (Φ_f) of the bisindenocarbazole derivative **4**, its fluorescence

was compared to the well known laser dye Exalite 428 [7,7''-bis(4-*t*-amylphenyl)-9,9,9',9'',9''-hexapropyl-2,2':7'2''-terfluorene], which has a quantum efficiency of 90% in cyclohexane solution.²⁴ In order to minimize self-absorption it is necessary to measure the fluorescence from highly diluted solutions.²⁵ For the estimation of Φ_f , cyclohexane solutions of Exalite 428 and **4** with an optical density of 0.1 were prepared. From these solutions fluorescence spectra were taken and by integration, a fluorescence quantum yield of 49% was calculated for **4**. The strong blue fluorescence of the liquid crystalline bisindenocarbazole derivative makes it an attractive candidate as blue emitter in polarized organic light emitting devices (OLEDs).

For the investigation of electrochemical properties we have used cyclic voltammetry (CV). The CV curve of **4** measured versus Ag/AgCl shows only one oxidation peak at 443 mV, which is quasireversible (Fig. 4). Repeated oxidation and reduction cycles did not change the CV curve what demonstrates the high electrochemical stability of **4**. Taking -4.8 eV as the

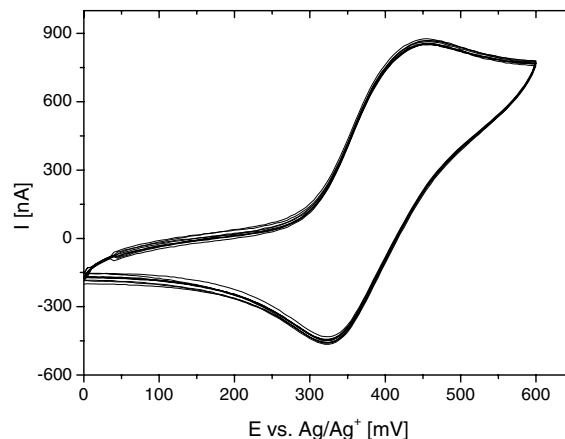


Figure 4. Cyclic voltammetry curves of **4** in $\text{CH}_2\text{Cl}_2/\text{TBAPF}_6$, $\nu = 50$ mV/s. Ten subsequent redox cycles were carried out in order to check the electrochemical stability of the bisindenocarbazole derivative **4**.

HOMO level for the standard ferrocene/ferrocenium redox system²⁶ a HOMO level of -5.4 eV was calculated for **4**. With the optical band gap of 3.0 eV from the absorption spectrum, a LUMO value of -2.4 eV can be estimated.

2. Conclusion

We present a new synthetic route to a novel bisindenocarbazole derivative with a broad nematic mesophase between 180 and 250 °C. Bisindenocarbazoles represent a class of fused aromatics from which no liquid crystalline derivatives have been described before. The material is thermally stable and exhibits excellent electrochemical stability. From the CV measurements a HOMO value of -5.3 eV was calculated. At the moment the synthesis of a number of bisindenocarbazole derivatives is in progress in order to get a better understanding of the structure–property relationship in this new class of materials.

3. Experimental

3.1. General

¹H NMR spectra were recorded with a Bruker AC 250 (250 MHz) apparatus. 2D NMR spectra were recorded with a Bruker AC 300 (300 MHz). All data are given as chemical shifts δ (ppm) downfield from Si(CH₃)₄. The IR spectra were recorded using a Bio-Rad Digilab FTS-40. The UV–vis spectra were recorded with a Hitachi U-3000 spectrophotometer. Emission spectra were obtained from a Shimadzu spectrofluorometer RF-5301PC. Mass spectra (MS) were recorded with a Finnigan MAT 8500 (70 eV) with a MAT 112S Varian. Thermogravimetric analysis (TGA) was performed on a Perkin Elmer TAS-409 at a heating rate of 10 K/min under N₂. For differential scanning calorimetry measurements (DSC), a Perkin Elmer Diamond DSC apparatus was used (heating/cooling rate: 10 K/min). Polarized microscopy was carried out with the Nikon Diaphot 300 equipped with a Linkon hotstage. Cyclic voltammetry measurements (CV) were performed with a glassy carbon working electrode (0.2 mm) in a three-electrode potentiostat configuration from EG&G Princeton Applied Research. All CV experiments were carried out at 25 °C in CH₂Cl₂ solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. Oxidation potentials were measured versus Ag/AgCl as the reference electrode.²⁷ X-ray analysis was carried out with a Huber/Seifert Iso-Debyelex 3003, using a Guinier diffractometer system (Cu K α : 1.5418 Å) with a sealed tube for temperature dependent measurements.

All chemicals and reagents were used as received from Aldrich. Neutral alumina was purchased from ICN Biomedicals (MP Alumina N, Akt. I). Carbon tetrachloride (p.a.) was received from Merck. Tetrahydrofuran (THF) was distilled over potassium before use. The synthesis of (1*R*,1'*S*)-diethyl-(1*S*,1'*R*)-dimethyl-bis-

indeno[3,2-*b*:2'*3'*-*h*]-9-methyl-carbazole (**1**) has been reported elsewhere.²⁰

3.2. Preparation of alumina supported copper(II) bromide²¹

To a solution of copper(II) bromide (10 g) in distilled water (30 ml) neutral alumina (20 g) was added at room temperature. The water was evaporated at 80 °C under reduced pressure with a rotary evaporator. The resulting reagent was dried under high vacuum at 100 °C for 24 h and stored under argon.

3.3. Synthesis of 7,7'-dibromo-(1*R*,1'*S*)-diethyl-(1*S*,1'*R*)-dimethyl-bisindeno[3,2-*b*:2'*3'*-*h*]-9-methyl-carbazole (**2**)

A mixture of the (*R,S*)-bisindenocarbazole isomer **1**²⁰ (0.38 mg, 0.86 mmol), Al₂O₃-CuBr₂ (2.9 g) and carbon tetrachloride (80 ml) was stirred at 70 °C for 3 h. The product mixture was then filtered and the spent reagent was washed with dichloromethane (30 ml) before the solvents from the combined filtrates were evaporated under reduced pressure. Purification by column chromatography on silica gel with hexane/THF ($10:1$) as an eluent yielded 0.4 g (78%) of **2** as pale yellow solid. ¹H NMR (250 MHz, CDCl₃): δ (ppm): 0.38 (t, 6H, $2 \times$ Me, $J = 7.3$ Hz), 1.61 (s, 6H, $2 \times$ Me), 2.15 (q, 4H, $2 \times$ CH₂, $J = 7.3$ Hz), 3.93 (s, 3H, NMe), 7.48 (dd, 2H, $J = 8.0$ Hz and $J = 1.5$ Hz), 7.53 (d, 2H, $J = 1.5$ Hz), 7.64 (s, 2H), 7.68 (d, 2H, $J = 8.0$ Hz), 8.04 (s, 2H); ¹³C NMR (62.5 MHz, CDCl₃): δ (ppm): 8.93 , 27.23 , 29.41 , 34.05 , 50.88 , 99.55 , 113.95 , 120.82 , 120.89 , 123.05 , 126.27 , 130.03 , 137.72 , 139.92 , 141.77 , 142.90 , 154.73 ; IR (KBr): $\tilde{\nu}$ (cm⁻¹): 2957 , 2929 , 2872 , 1584 , 1477 , 1453 , 1260 , 844 ; $m/z = 597/599/601$ (M⁺, $50/100/50\%$), 570 (80), 405 (50), 324 (43), 142 (26), 44 (48). Anal. Calcd for C₃₃H₂₉Br₂N (599.4): C, 66.13 ; H, 4.88 ; N, 2.34 . Found: C, 66.11 ; H, 4.87 ; N, 2.36 .

3.4. Synthesis of 2-(4-hexyl-phenyl)-4,4,5,5-tetramethyl-1,3,2[dioxaborolane (**3**)

1-Bromo-4-hexyl-benzene (1.0 g, 4.1 mmol) was dissolved in absolute THF under argon. The solution was cooled to -78 °C before 3.1 ml (5.0 mmol) *n*-BuLi (1.6 M solution in hexane) were added dropwise. The reaction mixture was stirred for 10 min, before 1.0 ml (5.0 mmol) of 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane was added. The reaction mixture was allowed to warm to room temperature and stirred for another 12 h before it was poured into ice water. The solution was extracted with diethyl ether, the organic phase washed with brine and dried with Na₂SO₄ before the solvent was removed. Purification by column chromatography on silica gel with hexane/THF ($15:1$) as an eluent yielded 1.0 g (85%) of **3** as a colourless oil. ¹H NMR (250 MHz, CDCl₃): δ (ppm): 0.86 (t, 3H, Me, $J = 7.0$ Hz), 1.18 – 1.26 (m, 8H, $4 \times$ CH₂), 1.33 (s, 12H, $4 \times$ Me), 2.62 (t, 2H, CH₂, $J = 7.6$ Hz), 7.20 (d, 2H, $J = 7.6$ Hz), 7.73 (d, 2H, $J = 7.6$ Hz); IR (KBr): $\tilde{\nu}$ (cm⁻¹): 3049 , 2955 , 2925 , 1610 , 1570 , 1460 , 1146 , 1080 ; $m/z = 288$ (M⁺, 100%), 217 (46), 189 (29), 107 (23).

3.5. Synthesis of 7,7'-di-(4-hexyl-phenyl)-(1*R*,1'*S*)-diethyl-(1*S*,1'*R*)-dimethyl-bisindeno[3,2-*b*:2'*3'*-*h*]-9-methyl-carbazole (4)

Dibromo bisindenocarbazole **2** (0.1 g, 0.17 mmol) and 0.1 g (0.35 mmol) of the borolane compound **3** were dissolved in 25 ml toluene. A 2 M K₂CO₃ solution (6 ml) and 0.1 g of trimethylbenzylammonium chloride were added. The reaction mixture was degassed by three freeze/thaw cycles before 1.7 mg (7.3×10^{-6} mol) of palladium(II) acetate and 6.7 mg (2.2×10^{-5} mol) of tri-*o*-tolylphosphine were added under argon. The mixture was stirred for 4 h at 90 °C. The reaction mixture was poured into ice water, extracted with diethyl ether and dried with Na₂SO₄. After evaporation of the solvent, the product was purified by MPLC with hexane/THF (30:1) as an eluent at a pressure of 18 bar. Compound **4** (98 mg, 79%) was obtained as a white solid. ¹H NMR (250 MHz, CDCl₃): δ (ppm): 0.37 (t, 6H, 2 × Me, *J* = 7.3 Hz), 0.83 (t, 6H, 2 × Me, *J* = 6 Hz), 1.18–1.32 (m, 10H, 5 × CH₂), 1.49–1.65 (m, 12H, 2 × Me, 3 × CH₂), 2.09 (q, 4H, 2 × CH₂, *J* = 7.3 Hz), 2.56 (t, 4H, *J* = 7.7 Hz), 3.89 (s, 3H, NMe), 7.18 (d, 4H, *J* = 8.1 Hz), 7.50–7.57 (m, 8H), 7.61 (s, 2H), 7.79 (d, 2H, *J* = 7.6 Hz), 8.00 (s, 2H). ¹³C NMR (62.5 MHz, CDCl₃): δ (ppm): 8.01, 13.10, 21.63, 26.42, 28.04, 28.38, 30.51, 30.75, 33.21, 34.63, 49.62, 98.37, 112.77, 118.73, 120.39, 121.77, 124.90, 125.96, 127.82, 137.40, 138.01, 138.95, 138.99, 140.74, 140.93, 142.53, 152.15; IR (KBr): $\bar{\nu}$ (cm⁻¹): 2959, 2926, 2854, 1559, 1495, 1345, 1260, 841; *m/z* = 761 (M⁺, 100%), 732 (30), 703 (10), 330 (33). Anal. Calcd for C₅₇H₆₃N (762.1): C, 89.83; H, 8.33; N, 1.84. Found: C, 89.40; H, 8.30; N, 2.10.

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