

Polycyclic Aromatic Hydrocarbons | Hot Paper |

Synthesis and Crystal Structure of Dimorphic Dibenzo[*cde,opq*]rubicene**Joghee R. Suresh,^[a] Glenn Whitener,^[a] Gabriele Theumer,^[a] Dirk J. Bröcher,^[a] Ingmar Bauer,^[a] Werner Massa,^[b] and Hans-Joachim Knölker^{*[a]}

Abstract: Dibenzo[*cde,opq*]rubicene has been synthesized by an eight-step reaction sequence including an iron-mediated [2+2+1] cycloaddition and a flash vacuum pyrolysis as

key steps. Two crystal modifications of the S-shaped, planar polycyclic aromatic hydrocarbon have been obtained and characterized by X-ray diffractometry.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) consisting only of fused aromatic rings without heteroatoms and substituents are an intriguing class of organic compounds with unique properties. They are formed by incomplete combustion of carbon-containing fuels and other carbon-based compounds.^[1] Thus, PAHs represent one of the most abundant and persistent organic pollutants which cause severe health concerns for humans, in particular cancer.^[1] Their interesting electronic and optoelectronic properties have prompted several studies aiming for applications in electronic devices.^[2] Moreover, PAHs are considered to be abundant in interstellar space and components of interstellar dust.^[3] Their contribution to the diffuse interstellar bands (DIBs) has been widely discussed.^[4] Dibenzo[*cde,opq*]rubicene (**1**) (Figure 1) is a prominent representative of uncurved PAHs having an S-shaped structure with C_{2h} symmetry. In spite of the planar structure of molecule **1**, it constitutes in bent form a subunit of the fullerene C_{70} (**2**) but not of C_{60} . Since both, C_{60} and C_{70} fullerenes, have been identified in a planetary nebula,^[5] we assumed that **1** may also be present in interstellar space. Therefore, we performed extensive spec-

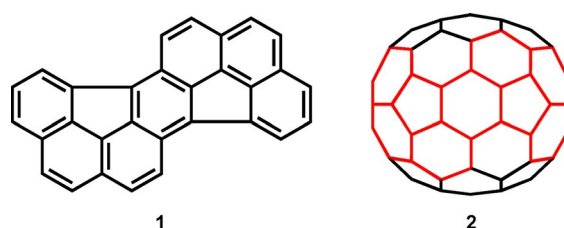


Figure 1. Structures of dibenzo[*cde,opq*]rubicene (**1**) and C_{70} fullerene (**2**).

troscopic studies of **1** and compared the data with those of interstellar spectra.^[4d] Even though we did not find coincidences between the spectral properties of **1** and several interstellar phenomena, the presence in space cannot be completely ruled out. Several bowl-shaped fragments of C_{70} have already become available by targeted organic synthesis.^[6] Yamamoto and co-workers described a previous synthesis of **1** by flash vacuum pyrolysis of 7,14-diethynylacenaphtho[1,2-*k*]fluoranthene or 7,14-bis(1-chlorovinyl)acenaphtho[1,2-*k*]fluoranthene.^[7] They also investigated the redox properties of **1**. However, no spectroscopic details, in particular no ^1H and ^{13}C NMR data, have been provided. To get a reliable access to compound **1** for further analytical investigations, we have devised a new synthetic sequence.

Results and Discussion

The present approach to dibenzo[*cde,opq*]rubicene (**1**) is inspired by our synthesis of corannulene (**3**).^[8] Since corannulene (**3**) was obtained by double cyclization of the bis(ethynyl)fluoranthene **5** under the conditions of flash vacuum pyrolysis, dibenzo[*cde,opq*]rubicene (**1**) should be available from bis(ethynyl)acenaphthofluoranthene **4** (Scheme 1). Both cyclization precursors, **4** and **5**, were obtained from 7,9-bis(trimethylsilyl)-8*H*-cyclopenta[*a*]acenaphthylene-8-one (**6**). Compound **6** as a common intermediate in both syntheses was constructed from bis(ethynyl)naphthalene **7** and carbon monoxide using our iron-mediated [2+2+1] cycloaddition and demetallation protocol.^[9]

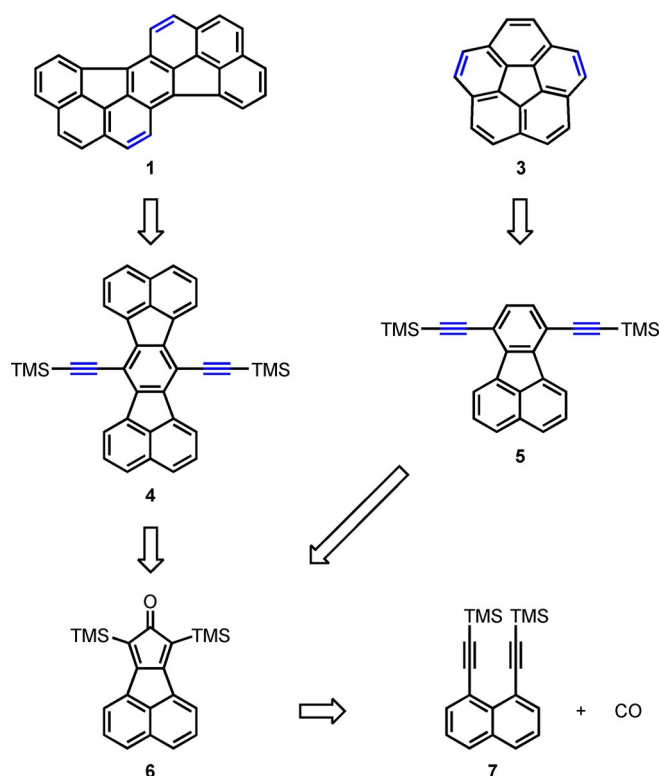
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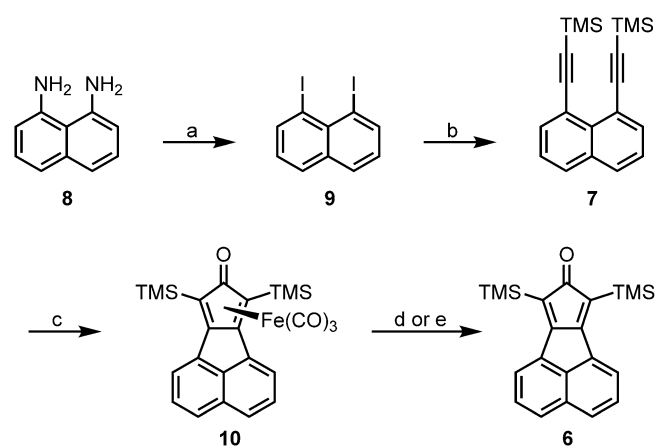
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Scheme 1. Retrosynthetic comparison between the syntheses of corannulene (**3**) and dibenzo[*cde,opq*]rubicene (**1**).

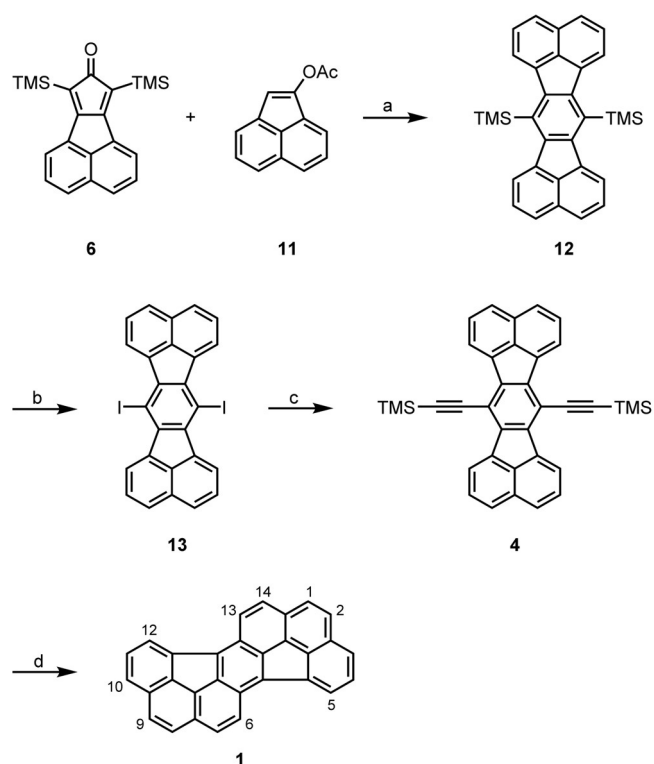
At first, we synthesized intermediate **6** following our sequence reported for the construction of corannulene (**3**).^[8] Thus, 1,8-diaminonaphthalene (**8**) was transformed into 1,8-diiodonaphthalene (**9**) according to a literature protocol (Scheme 2).^[10] 1,8-Bis(trimethylsilylethynyl)naphthalene (**7**) was obtained in excellent yield by a double Sonogashira coupling



Scheme 2. Synthesis of compound **6**. Reagents and conditions: a) NaNO_2 (3.0 equiv), H_2SO_4 , KI (6.1 equiv), H_2O , -20°C to 80°C , 30 min (70%); b) TMSA (3.0 equiv), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (2 mol%), CuI (4 mol%), NEt_3 , RT, 12 h (95%); c) $\text{Fe}(\text{CO})_5$ (2.0 equiv), DME, sealed tube, 140°C , 20 h (89%); d) $(\text{CH}_3)_3\text{NO} \times 2 \text{H}_2\text{O}$ (8.0 equiv), acetone, RT, 2 h (89%); e) 1) 1 M NaOH (8.4 equiv), THF, RT, 2.5 h; 2) $\text{C}_5\text{H}_{11}\text{I}$ (16 equiv), RT, 15 min; 3) H_3PO_4 , RT; 4) air, daylight, $\text{Et}_2\text{O}/\text{THF}$, $\text{Na}_2\text{S}_2\text{O}_8$, Celite, RT, 3 h (91%). DME = 1,2-dimethoxyethane, TMSA = trimethylsilylacetylene.

of **9** with trimethylsilyl acetylene.^[11] The iron-mediated [2+2+1] cycloaddition of **7** with pentacarbonyliron was performed in 1,2-dimethoxyethane in a sealed tube at 140°C and led to the tricarbonyl(η^4 -cyclopentadienone)iron complex **10** in 89% yield. For the demetallation of tricarbonyl(η^4 -cyclopentadienone)iron complexes, we have applied three different methods.^[12,13] Firstly, trimethylamine *N*-oxide was employed for this purpose.^[9a,12] Thus, reaction of the tricarbonyl(η^4 -cyclopentadienone)iron complex **10** with trimethylamine *N*-oxide in acetone at room temperature provided the free cyclopentadienone **6** in 89% yield. Another method proceeds through a photolytically induced threefold ligand-exchange reaction of carbonyl for acetonitrile.^[13a] The resulting (triacetonitrile)iron complexes can be demetallated under very mild conditions at -30°C by injection of air. Finally, the tricarbonyliron fragment can also be removed using our protocol based on a sequence of Hieber base reaction/iodo-hydrido ligand exchange/protonation and finally demetallation of the resulting dicarbonyl(η^5 -hydroxycyclopentadienyl)iodoiron complex by air in the presence of daylight.^[13b] Using this protocol, we were able to obtain the cyclopentadienone **6** in 91% yield.^[8]

Cyclopentadienones have been frequently employed as diene components in Diels–Alder reactions.^[14] They can be smoothly converted to benzene moieties by reaction with alkynes with concomitant loss of carbon monoxide in a cheletropic reaction. This method has been widely used for the construction of larger PAHs.^[15] Following this route, we reported the transformation of 3,4-annulated 2,5-bis(trimethylsilyl)cyclopentadienones into annulated benzene derivatives by reaction with the electron-deficient dimethyl acetylenedicarboxylate (DMDA).^[16] Alternatively, benzene rings can be formed by Diels–Alder reaction of cyclopentadienones with alkenes followed by decarbonylation and aromatization.^[14] The aromatization can be achieved by dehydrogenation at higher temperatures and/or addition of oxidizing agents like 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) or KMnO_4 .^[17] The presence of a leaving group at the dienophile enables an aromatization by an elimination process.^[14] This principle has been exploited for the construction of various 7,14-disubstituted acenaphtho[1,2-*k*]fluoranthenes from 1-haloacenaphthylene and 8*H*-cyclopenta[*a*]acenaphthylen-8-ones.^[18] We used acenaphthylen-1-yl acetate (**11**) (for the synthesis of **11**, see Experimental Section) as dienophile for the Diels–Alder reaction with the cyclopenta[*a*]acenaphthylen-8-one **6** (Scheme 3). The reaction was performed at 200°C under neat conditions resulting in aromatization by in situ cheletropic extrusion of carbon monoxide and elimination of acetic acid to give acenaphtho[1,2-*k*]fluoranthene **12**. The product proved to be labile during column chromatography on silica gel losing the trimethylsilyl groups by protodesilylation. Therefore, compound **12** was not purified and used directly for the subsequent transformation. The *ipso*-substitution of the trimethylsilyl groups using iodine monochloride following a literature procedure^[19] led to the diiodide **13**. Twofold Negishi coupling^[20] of **13** with trimethylsilylethynylzinc chloride afforded 7,14-bis(trimethylsilylethynyl)acenaphtho[1,2-*k*]fluoranthene (**4**). The final twofold cyclization was achieved by flash vacuum pyrolysis (FVP).^[21] This method



Scheme 3. Synthesis of dibenzo[*cde,opq*]rubicene (**1**). Reagents and conditions: a) **11** (1.7 equiv), 200 °C, 45 min; b) ICl (3.0 equiv), CCl₄, 0 °C to RT, 16 h (48%, 2 steps); c) Me₃SiCCZnCl (9.9 equiv), Pd(PPh₃)₄ (10 mol%), THF, reflux, 15 h (94%); d) FVP, 1000 °C, 1–1.2 mbar Ar (10%). FVP = flash vacuum pyrolysis.

has been frequently employed for the construction of geodesic and planar polyarenes.^[21b,d,g]

In agreement with Scott and Zimmermann, we observed that free alkynylarenes and alkynylalkenes are often labile and tend to polymerize under the conditions of FVP.^[22] To circumvent this fact, various types of masked alkynylarenes have been employed such as 2,2-dibromovinylarenes,^[23] 1-chlorovinylarenes,^[7,24] and 1-silyloxyvinylarenes.^[25] Zimmermann and co-workers described the use of trimethylsilyl-protected alkynylalkenes for the synthesis of corannulene (**3**) by FVP.^[22b] We could show for the first time that trimethylsilyl-protected alkynylarenes can be directly introduced to FVP affording corannulene (**3**) in 36% yield.^[8] Thus, in the present synthesis of dibenzo[*cde,opq*]rubicene (**1**) we employed the trimethylsilyl-protected bis(ethynyl)acenaphthofluorene **4** directly for the final cyclization step. The flash vacuum pyrolysis of compound **4** was conducted at 1000 °C in a gentle argon stream at 1 mbar. The carrier gas served to reduce the dwell time of the starting material in the hot pyrolysis zone to reduce decomposition. Dibenzo[*cde,opq*]rubicene (**1**) precipitated in the cold part of the quartz tube and was isolated in 10% yield after column chromatography.

Crystals of two different modifications of **1** (**1a** and **1b**) were both suitable for single-crystal X-ray structure determination. The X-ray analyses revealed only minor variations for the structures **1a** and **1b** with respect to C–C bond lengths and

angles (Figure 2; Tables S1 and S2, Supporting Information). Both molecular structures are nearly perfectly planar with mean deviations from best planes of 0.006(2) (**1a**) and 0.016(2) Å (**1b**). Both modifications show stacking of the mole-

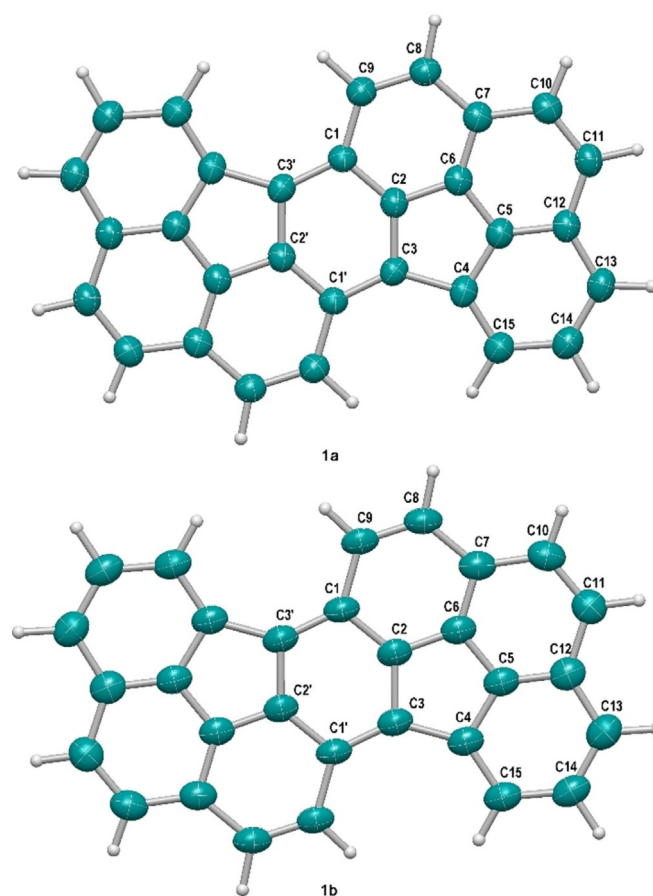


Figure 2. Molecular structure of dibenzo[*cde,opq*]rubicene (**1**) in the structural modifications **1a** and **1b**. Displacement ellipsoids at the 50% probability level.

cules in a parallel offset way, typical for systems with π – π interactions, and a zigzag arrangement of the molecular layers (Figure 3, and Figure S28). The main differences between both forms are the strength of the π – π interactions with distances between the molecular planes of 3.414 (**1a**) and 3.474 Å (**1b**), and the zigzag angles of 88.93(2)° for **1a** and 51.49(3)° for **1b**. The longitudinal axes of the molecules are oriented in the direction of the corrugation in **1a** and orthogonal to it in **1b** (Figure 3, Figure S28). The offset shift of the molecules is in the direction of their longitudinal axis for **1a** and orthogonal to it for **1b** (Figure S29).

Conclusions

We have developed a straightforward eight-step-synthesis of dibenzo[*cde,opq*]rubicene (**1**). Key steps are the iron-mediated [2+2+1] cycloaddition and a flash vacuum pyrolysis. Dibenzo[*cde,opq*]rubicene (**1**) crystallized in two modifications con-

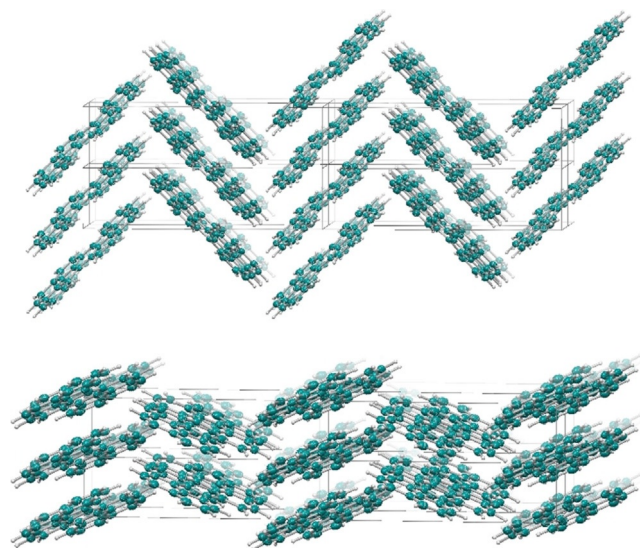


Figure 3. Packing of molecules in **1a** (top) and **1b** (bottom). View approximately along the *a* axes of the unit cells.

taining almost identical molecular structures in different packing modes.

Experimental Section

General: All reactions were carried out in oven-dried glassware using anhydrous solvents under an argon atmosphere, unless stated otherwise. Dichloromethane and tetrahydrofuran were dried using a solvent purification system (MBraun-SPS). TLC was performed with TLC plates from Merck (60 F254) using UV light for visualization. Melting points were measured on the melting point apparatuses Büchi Type 535 or Gallenkamp MPD 350, respectively. Ultraviolet spectra were recorded on a PerkinElmer 25 UV/Vis spectrometer. IR spectra were recorded on Bruker IFS 88 FT-IR or Thermo Nicolet Avatar 360 FT-IR spectrometers using the DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) or ATR (Attenuated Total Reflectance) method, respectively. NMR spectra were recorded on Bruker AM 400, DRX 500, and Avance III 600 spectrometers. Chemical shifts δ are reported in parts per million (ppm) with the solvent signal as internal standard. Standard abbreviations were used to denote the multiplicities of the signals. Mass spectra (nominal masses) and high-resolution mass spectra were recorded on Finnigan MAT-90 and MAT-95 spectrometers (electron impact, 70 eV). Mass spectra with nominal masses were also obtained by GC-MS coupling using an Agilent Technologies 6890 N GC System equipped with a 5973 Mass Selective Detector (electron impact, 70 eV). Elemental analyses were measured on Heraeus CHN-Rapid or EuroVector EuroEA3000 elemental analyzers. X-ray analysis: Data collection on area detector system IPDS-II (Stoe). Structures solved with direct methods (*SIR2002*)^[26] and refined with *SHELXL2018/3*.^[27]

1,8-Diiodonaphthalene (9): 1,8-Diaminonaphthalene (**8**) (1.00 g, 6.32 mmol) was suspended in 6.9 M sulfuric acid (12 mL) and cooled to -20°C . A solution of sodium nitrite (1.29 g, 18.7 mmol) in water (5 mL) was added dropwise. During this process, the temperature was kept below -15°C . Subsequently, a solution of potassium iodide (6.42 g, 38.7 mmol) in water (6 mL) was added at the same temperature. If required, small amounts of sulfuric acid were added to avoid freezing of the solution. The mixture was heated to

80°C and stirred for 30 min. Then, the solution was cooled to 0°C and adjusted to pH 10 by addition of a concentrated sodium hydroxide solution. The black precipitate was filtered off, ground, and extracted five times with 10 mL of diethyl ether. The combined organic layers were washed with 10% hydrochloric acid, a saturated aqueous solution of sodium thiosulfate, and dilute aqueous sodium hydroxide, dried over magnesium sulfate and concentrated in vacuum. The resulting brown residue was recrystallized from hexane to afford compound **9** (1.68 g, 4.42 mmol, 70%) as red-brown crystals. M.p. $109\text{--}110^{\circ}\text{C}$; UV (CHCl_3): $\lambda = 221, 240, 311\text{ nm}$; IR (DRIFTS): $\tilde{\nu} = 3827, 3436, 3052, 2360, 2112, 1930, 1871, 1800, 1700, 1595, 1555, 1534, 1489, 1432, 1418, 1363, 1348, 1318, 1249, 1215, 1180, 1132, 1091, 1050, 970, 936, 907, 827, 810, 803, 768, 746, 670, 642, 607\text{ cm}^{-1}$; $^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 7.07$ (br t, $J = 7.7\text{ Hz}$, 2H), 7.83 (dd, $J = 8.1, 1.1\text{ Hz}$, 2H), 8.42 ppm (dd, $J = 7.3, 1.1\text{ Hz}$, 2H); $^{13}\text{C NMR}$ and DEPT (125 MHz, CDCl_3): $\delta = 96.00$ (2C), 126.95 (2CH), 131.03 (2CH), 132.12 (C), 135.80 (C), 144.04 ppm (2CH); MS (EI): m/z (rel. int. %) = 380 (78, $[\text{M}]^+$), 253 (34), 127 (13), 126 (100), 74 (10); HRMS (EI): m/z calcd for $\text{C}_{10}\text{H}_6\text{I}_2$: 379.8559; found: 379.8564; elemental analysis calcd (%) for $\text{C}_{10}\text{H}_6\text{I}_2$: C 31.61, H 1.59; found: C 32.09, H 1.79.

1,8-Bis(2-trimethylsilylethynyl)naphthalene (7): 1,8-Diiodonaphthalene (**9**) (1.00 g, 2.63 mmol) was dissolved in triethylamine (10 mL) followed by the addition of trimethylsilylacetylene (1.09 mL, 775 mg, 7.89 mmol). The mixture was stirred for 10 min at RT and then bis(triphenylphosphane)palladium dichloride (37.0 mg, 0.053 mmol) and copper(I) iodide (20.0 mg, 0.105 mmol) were added. After 12 h of stirring at RT, diethyl ether (20 mL) was added. The organic solution was washed successively with saturated aqueous solutions of NH_4Cl , NaHCO_3 , and NaCl (20 mL each). The combined aqueous layers were extracted with diethyl ether (20 mL). The combined organic layers were dried (MgSO_4) and the solvent was evaporated. Purification of the residue by column chromatography (silica gel, pentane) afforded compound **7** (800 mg, 2.50 mmol, 95%) as red-black oil. UV (CHCl_3): $\lambda = 221, 240, 271, 330, 345\text{ nm}$; IR (DRIFTS): $\tilde{\nu} = 3314, 3058, 2959, 2899, 2143, 1939, 1565, 1502, 1426, 1407, 1370, 1351, 1262, 1249, 1162, 1121, 1030, 1009, 856, 827, 765, 709, 651, 627, 614\text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 0.33$ (s, 18H), 7.39 (dd, $J = 8.0, 7.3\text{ Hz}$, 2H), 7.77 (dd, $J = 8.3, 1.1\text{ Hz}$, 2H), 7.81 ppm (dd, $J = 7.2, 1.1\text{ Hz}$, 2H); $^{13}\text{C NMR}$ and DEPT (100 MHz, CDCl_3): $\delta = 0.16$ (6 CH_3), 103.00 (2C), 105.38 (2C), 120.64 (2C), 125.36 (2CH), 129.76 (2CH), 130.34 (C), 133.79 (C), 136.90 ppm (2CH); MS (EI): m/z (rel. int. %) = 320 (100, $[\text{M}]^+$), 305 (29), 288 (12), 286 (25), 284 (12), 248 (44), 234 (18), 233 (90), 217 (37), 205 (13), 189 (15), 126 (17), 73 (75); HRMS (EI): m/z calcd for $\text{C}_{20}\text{H}_{24}\text{Si}_2$: 320.1417; found: 320.1427.

Tricarbonyl[η^4 -7,9-bis(trimethylsilyl)-8H-cyclopenta[*a*]acenaphthylen-8-one]iron (10): 1,8-Bis(2-trimethylsilylethynyl)naphthalene (**7**) (1.72 g, 5.37 mmol), pentacarbonyliron (1.42 mL, 2.06 g, 10.5 mmol) and 1,2-dimethoxyethane (25 mL) were heated in a sealed tube (borosilicate glass Schott Duran 50, $15 \times 2.4\text{ cm}$, wall thickness 1.8 mm) at 140°C for 20 h. After evaporation of the solvent, the crude product was purified by column chromatography (silica gel, hexane/ethyl acetate, 10:1). The iron complex **10** (2.34 g, 4.79 mmol, 89%) was obtained as yellow crystals. M.p. $188\text{--}189^{\circ}\text{C}$ (dec.); UV (CHCl_3): $\lambda = 231, 314\text{ nm}$; IR (DRIFTS): $\tilde{\nu} = 3421, 3060, 2957, 2901, 2058, 2009, 1995, 1987, 1966, 1955, 1819, 1744, 1632, 1599, 1487, 1432, 1371, 1348, 1293, 1248, 1212, 1199, 1187, 1155, 1060, 1045, 964, 911, 846, 828, 778, 765, 744, 722, 703, 637, 608\text{ cm}^{-1}$; $^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 0.52$ (s, 18H), 7.64 (br t, $J = 7.6\text{ Hz}$, 2H), 7.93 (d, $J = 8.3\text{ Hz}$, 2H), 7.96 ppm (d, $J = 7.1\text{ Hz}$, 2H); $^{13}\text{C NMR}$ and DEPT (100 MHz, CDCl_3): $\delta = 0.09$ (6 CH_3), 69.53 (2C), 110.34 (C), 123.91 (2CH), 128.14 (2CH), 128.45 (2CH), 130.58 (2C),

132.50 (2C), 136.01 (C), 183.00 (C), 208.43 ppm (3C); MS (EI): m/z (rel. int. %) = 488 (11, $[M]^+$), 460 (15), 433 (23), 432 (69), 405 (34), 404 (100), 376 (14), 333 (15), 317 (15), 73 (15); HRMS (EI): m/z calcd for $C_{24}H_{24}FeO_4Si_2$: 488.0563; found: 488.0541; elemental analysis calcd (%) for $C_{24}H_{24}FeO_4Si_2$: C 59.01, H 4.95; found: C 59.06, H 5.00.

7,9-Bis(trimethylsilyl)-8H-cyclopenta[*a*]acenaphthylen-8-one (6): By demetallation with trimethylamine *N*-oxide (Scheme 2, step d): Tricarbonyl[η^4 -7,9-bis(trimethylsilyl)-8H-cyclopenta[*a*]acenaphthylen-8-one]iron (**10**) (359 mg, 0.735 mmol) and trimethylamine *N*-oxide dihydrate (653 mg, 5.88 mmol) were dissolved in acetone and stirred at room temperature for 2 h. After filtration through a short pad of silica gel and removal of the solvent, the crude product was purified by column chromatography (silica gel, *n*-hexane). Compound **6** (229 mg, 0.657 mmol, 89%) was obtained as dark red crystals.

Demetallation through Hieber base reaction (Scheme 2, step e): Tricarbonyl[η^4 -7,9-bis(trimethylsilyl)-8H-cyclopenta[*a*]acenaphthylen-8-one]iron (**10**) (200 mg, 0.409 mmol) was dissolved in tetrahydrofuran (10 mL) and a 1 M aqueous solution of sodium hydroxide (3.44 mL, 3.44 mmol) was added. The mixture was vigorously stirred for 2.5 h at room temperature and then 1-iodopentane (0.85 mL, 1.29 g, 6.52 mmol) was added causing a rapid color change to brown. After 15 min the mixture was acidified with concentrated phosphoric acid (0.85 mL, 16.2 mmol), extracted with diethyl ether, dried (Na_2SO_4), and filtered through a short pad of silica gel. The resulting solution was diluted with diethyl ether to give a total volume of 250 mL. Sodium thiosulfate pentahydrate (175 mg, 0.705 mmol) and Celite (175 mg) were added and the mixture gently stirred for 3 h at room temperature in the presence of daylight and air. After filtration through a short pad of silica gel and removal of the solvent, the crude product was purified by column chromatography (silica gel, *n*-hexane). Compound **6** (130 mg, 0.373 mmol, 91%) was obtained as dark red crystals.

M.p. 182–183 °C (dec.); UV ($CHCl_3$): $\lambda = 224, 250, 285, 344, 353, 363, 383, 486$ nm; IR (DRIFTS): $\tilde{\nu} = 3346, 3058, 2958, 2898, 2493, 1928, 1872, 1792, 1682, 1618, 1604, 1560, 1486, 1411, 1353, 1245, 1211, 1180, 1141, 1098, 1067, 1045, 1000, 968, 847, 771, 731, 698, 635$ cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$): $\delta = 0.41$ (s, 18H), 7.63 (br t, $J = 7.7$ Hz, 2H), 7.84 (d, $J = 7.1$ Hz, 2H), 7.85 ppm (d, $J = 8.2$ Hz, 2H); ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): $\delta = -0.42$ (6 CH_3), 122.32 (2CH), 125.27 (2C), 127.33 (2CH), 128.39 (2CH), 131.99 (C), 132.02 (2C), 144.35 (C), 169.15 (2C), 212.74 ppm (C); MS (EI): m/z (rel. int. %) = 348 (100, $[M]^+$), 334 (19), 333 (66), 332 (15), 331 (42), 317 (18), 275 (10), 217 (14), 216 (14), 215 (11), 159 (10), 133 (37), 117 (19), 73 (48); HRMS (EI): m/z calcd for $C_{21}H_{24}OSi_2$: 348.1366; found: 348.1379; elemental analysis calcd (%) for $C_{21}H_{24}OSi_2$: C 72.36, H 6.94; found: C 72.34, H 7.11.

Acenaphthylen-1-yl acetate (11): Butyllithium (5.10 mL, 1.58 M in hexane, 8.06 mmol) was slowly added to a solution of diisopropylamine (1.30 mL, 936 mg, 9.25 mmol) in tetrahydrofuran (10 mL) at $-78^\circ C$. The mixture was stirred for 15 min at this temperature. A solution of commercially available acenaphthylen-1-one (1.00 g, 5.95 mmol) in tetrahydrofuran (20 mL) was slowly added and stirring was continued at $-78^\circ C$ for 2 h. After warming to $0^\circ C$, acetic anhydride (0.800 mL, 864 mg, 8.46 mmol) was added. The mixture was allowed to warm to room temperature and stirred for 14 h. After addition of water and dichloromethane, the layers were separated and the aqueous layer was extracted three times with dichloromethane. The combined organic layers were dried ($MgSO_4$) and the solvent was evaporated. Purification by column chromatography (silica gel, petroleum ether/diethyl ether, 20:1), provided compound **11** (800 mg, 3.81 mmol, 64%) as a yellow solid. M.p. $46^\circ C$; IR (ATR): $\tilde{\nu} = 3043, 1760, 1744, 1521, 1479, 1464, 1429, 1371,$

$1304, 1190, 1129, 1072, 1012, 876, 829, 758, 707, 663, 588$ cm^{-1} ; 1H NMR ($CDCl_3$, 500 MHz): $\delta = 2.39$ (s, 3H), 6.93 (s, 1H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.58 (d, $J = 6.8$ Hz, 1H), 7.67 (d, $J = 6.9$ Hz, 1H), 7.74 (d, $J = 8.3$ Hz, 1H), 7.83 ppm (d, $J = 8.1$ Hz, 1H); ^{13}C NMR and DEPT ($CDCl_3$, 125 MHz): $\delta = 21.27$ (CH_3), 112.96 (CH), 121.80 (CH), 124.16 (CH), 124.87 (C), 126.64 (CH), 127.23 (CH), 127.71 (C), 127.97 (CH), 128.26 (CH), 133.54 (C), 136.54 (C), 150.96 (C), 168.16 ppm (C); MS (EI): m/z (rel. int. %) = 210 (6, $[M]^+$), 168 (100), 139 (49), 113 (5).

7,14-Diiodoacenaphtho[1,2-*k*]fluoranthene (13): Cyclopenta[*a*]acenaphthylen-8-one **6** (800 mg, 2.29 mmol) and acenaphthylene **11** (800 mg, 3.81 mmol) were stirred at $200^\circ C$ for 45 min. After cooling to RT, the mixture was treated with diethyl ether (100 mL). The solid was filtered off and washed with diethyl ether to give 520 mg (1.10 mmol) of 7,14-bis(trimethylsilyl)acenaphtho[1,2-*k*]fluoranthene (**12**) as a dark brown solid of which a sample of 470 mg was used for the next transformation without further purification. A solution of iodine monochloride (490 mg, 3.02 mmol) in carbon tetrachloride (50 mL) was added to a solution of 7,14-bis(trimethylsilyl)acenaphtho[1,2-*k*]fluoranthene (**12**) (470 mg, 0.998 mmol) in carbon tetrachloride (100 mL) at $0^\circ C$ within 5 min. The mixture was stirred at room temperature for 16 h and then washed successively with saturated aqueous solutions of $Na_2S_2O_3$, $NaHCO_3$, and NaCl. The aqueous layers were extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$. Evaporation of the solvent afforded compound **13** (580 mg, 1.00 mmol, 48%, two steps) as a brown solid. M.p. $355\text{--}360^\circ C$ (dec.); IR (ATR): $\tilde{\nu} = 3049, 2920, 2844, 1457, 1425, 1345, 1229, 1179, 1107, 1047, 954, 905, 818, 761, 687, 629, 577, 537$ cm^{-1} ; 1H NMR (500 MHz, 1,1,2,2- $[D_2]$ tetrachloroethane, $80^\circ C$): $\delta = 7.84$ (t, $J = 7.7$ Hz, 4H), 8.03 (d, $J = 8.2$ Hz, 4H), 9.39 ppm (d, $J = 7.3$ Hz, 4H); ^{13}C NMR and DEPT (125 MHz, 1,1,2,2- $[D_2]$ tetrachloroethane, $80^\circ C$): $\delta = 87.30$ (2C), 124.88 (4CH), 127.14 (4CH), 128.39 (4CH), 129.79 (2C), 133.46 (2C), 136.65 (4C), 142.14 ppm (4C); MS (EI): m/z (rel. int. %) = 578 (100, $[M]^+$), 452 (11), 324 (68), 322 (13), 289 (10), 162 (27), 161 (14); elemental analysis calcd (%) for $C_{26}H_{12}I_2$: C 54.01, H 2.09; found: C 53.68, H 2.22.

7,14-Bis(trimethylsilyl)ethynyl)acenaphtho[1,2-*k*]fluoranthene (4): Butyllithium (3.60 mL, 1.6 M in hexane, 5.76 mmol) was slowly added to a solution of trimethylsilylacetylene (540 mg, 5.50 mmol) in dry tetrahydrofuran (13 mL) at $-78^\circ C$. The mixture was stirred at $-78^\circ C$ for 40 min and then warmed to $0^\circ C$. A solution of zinc chloride (7.86 mL, 0.7 M in THF, 5.50 mmol) was added and the mixture was stirred for 3 h at $0^\circ C$. The resulting solution of trimethylsilyl ethynylzinc chloride was slowly added to a solution of diiodide **13** (320 mg, 0.553 mmol) and tetrakis(triphenylphosphine)palladium (66.0 mg, 0.057 mmol) in dry tetrahydrofuran (13 mL) at $0^\circ C$. The mixture was heated at reflux for 15 h. After cooling to room temperature, the mixture was filtered through a short pad of Celite. The crude product obtained after removal of the solvent was purified by column chromatography (basic alumina, activity grade 4, petroleum ether/dichloromethane, 20:1) to provide compound **4** (270 mg, 0.520 mmol, 94%) as a yellow solid. M.p. $351\text{--}352^\circ C$; IR (ATR): $\tilde{\nu} = 3049, 2956, 2148, 1435, 1427, 1246, 1191, 1139, 1036, 983, 877, 837, 821, 768, 755, 704, 635$ cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$): $\delta = 0.52$ (s, 18H), 7.71 (dd, $J = 7.3, 7.9$ Hz, 4H), 7.92 (d, $J = 8.1$ Hz, 4H), 8.73 ppm (d, $J = 7.0$ Hz, 4H); ^{13}C NMR and DEPT (125 MHz, $CDCl_3$): $\delta = 0.03$ (6 CH_3), 102.55 (2C), 105.39 (2C), 112.98 (2C), 123.65 (4CH), 127.40 (4CH), 127.89 (4CH), 129.47 (2C), 132.96 (2C), 135.48 (4C), 139.10 ppm (4C); MS (EI): m/z (rel. int. %) = 518 (100, $[M]^+$), 487 (6), 429 (5), 422 (6), 416 (7), 415 (11), 413 (6), 73 (12); elemental analysis calcd (%) for $C_{36}H_{30}Si_2$: C 83.34, H 5.83; found: C 83.38, H 5.73.

Dibenzo[cde,opq]rubicene (1): The apparatus for flash vacuum pyrolysis (FVP)^[21] consisted of a quartz tube (100×4 cm o.d.) connected to a cooling trap (liquid nitrogen) and a vacuum pump on the one end and an argon supply on the other. The quartz tube was inserted into two quartz tube furnaces, a sublimation oven (30×5 cm i.d.) on the side of the argon supply and a pyrolysis oven (40×7 cm i.d.) on the side of the cooling trap. 7,14-Bis(trimethylsilylethynyl)acenaphtho[1,2-k]fluoranthene (**4**) (270 mg, 0.520 mmol) was given into a porcelain boat which was placed in a quartz tube in the center of the sublimation oven. At the start of the pyrolysis experiment, the system was evacuated to 5×10^{-3} mbar. Then, the argon supply was opened to adjust a gentle flow of argon up to a final pressure of 1–1.2 mbar. The pyrolysis oven was turned on and equilibrated at 1000 °C. Then the sublimation oven was heated to 380 °C. The sample was kept at this temperature for 4 h and then at 420 °C for another 2 h. The product precipitated at the cold part of the quartz tube. Subsequently, the tube was cooled to room temperature, vented, opened, and the product was dissolved in dichloromethane. Evaporation of the solvent provided 100 mg of crude product. Column chromatography (silica gel, pentane/dichloromethane, 15:1) afforded dibenzo[cde,opq]rubicene (**1**) (20.0 mg, 0.053 mmol, 10%) as a dark red solid. M.p. > 370 °C; UV (CHCl₃): $\lambda = 283, 316, 342, 425, 449$ nm; IR (ATR): $\tilde{\nu} = 3031, 1633, 1552, 1456, 1419, 1324, 1256, 1215, 1188, 1163, 1135, 1016, 957, 933, 903, 859, 821, 766, 731, 625, 590, 556$ cm⁻¹; ¹H NMR (600 MHz, CDCl₃): $\delta = 7.77$ (t, $J = 7.4$ Hz, 2H, H-4), 7.97 (d, $J = 8.0$ Hz, 2H, H-5), 7.97 (d, $J = 8.6$ Hz, 2H, H-14), 8.01 (d, $J = 8.5$ Hz, 2H, H-13), 8.09 (d, $J = 8.7$ Hz, 2H, H-1), 8.46 (d, $J = 6.8$ Hz, 2H, H-3), 8.56 ppm (d, $J = 8.8$ Hz, 2H, H-2); ¹³C NMR and DEPT (150 MHz, CDCl₃): $\delta = 125.13$ (C-2), 125.52 (C-14), 125.61 (C-3), 127.02 (C-5), 127.11 (C-13), 127.29 (C-1), 128.87 ppm (C-4) (chemical shifts derived from the HSQC spectrum, assignment achieved by COSY, NOESY, HSQC, and HMBC measurements); MS (EI): m/z (rel. int. %) = 347 (100, [M]⁺), 372 (39), 370 (18), 368 (6), 221 (8), 204 (17), 186 (32), 59 (10); HRMS (EI): m/z calcd for C₃₀H₁₄: 374.1096; found: 374.1084. Detailed IR and UV/Vis spectroscopic studies of **1** have been published by us previously.^[4d] Crystallization afforded two different modifications of **1** which were analyzed by X-ray diffractometry.

Crystallographic data for **1a**: CCDC: 1917204,^[29] C₃₀H₁₄, $M = 374.41$ g mol⁻¹, crystal size: 0.50×0.07×0.03 mm³, monoclinic, space group $P2_1/n$, $a = 9.1654$ (18) Å, $b = 4.8663$ (6) Å, $c = 19.186$ (4) Å, $\beta = 93.268$ (16)°, $V = 854.3$ (3) Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.455$ g cm⁻³, $\mu = 0.08$ mm⁻¹, $\lambda = 0.71073$ Å, $T = 100$ K, θ range: 2.1–25.0°, reflections collected: 6309, independent: 1508 ($R_{\text{int}} = 0.091$), 158 parameters. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 ; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.048$, $wR_2 = 0.111$; maximal residual electron density: 0.20 e Å⁻³.

Crystallographic data for **1b**: CCDC: 1917209,^[29] C₃₀H₁₄, $M = 374.41$ g mol⁻¹, crystal size: 0.50×0.15×0.02 mm³, monoclinic, space group $P2_1/c$, $a = 14.198$ (3) Å, $b = 3.8562$ (5) Å, $c = 16.196$ (4) Å, $\beta = 106.75$ (2)°, $V = 849.1$ (3) Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.464$ g cm⁻³, $\mu = 0.08$ mm⁻¹, $\lambda = 0.71073$ Å, $T = 100$ K, θ range: 1.5–25.0°, reflections collected: 3572, independent: 1491 ($R_{\text{int}} = 0.072$), 157 parameters. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 ; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.049$, $wR_2 = 0.124$; maximal residual electron density: 0.15 e Å⁻³.

Conflict of interest

The authors declare no conflict of interest.

Keywords: cycloadditions · flash vacuum pyrolysis · polycyclic aromatic hydrocarbons · polymorphism · X-ray diffraction

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