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A C_{78} Fullerene Precursor: Toward the Direct Synthesis of Higher Fullerenes

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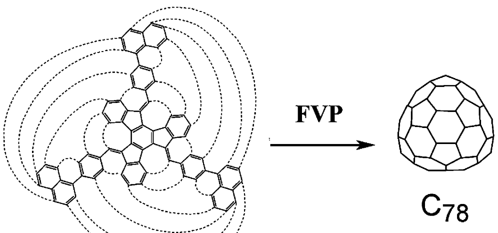
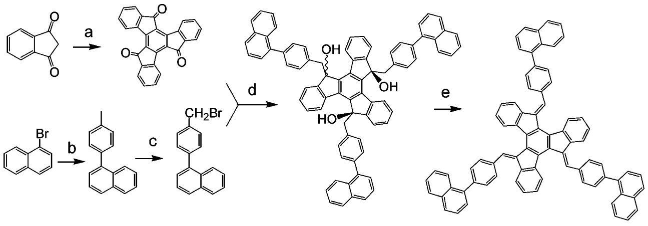


A C_{78} fullerene related structure (of C_{78}:1 and C_{78}:4, the last undiscovered C_{78} IPR isomer) has been synthesized and investigated as a pyrolytic precursor. The pyrolysis of precursor containing all 78 carbon atoms in the required positions and 93 of the 117 C−C bonds, needed for fullerene formation, showed selectivity for C_{78} fullerene formation. In independent experiments it has been shown that the flash pyrolysis of C_{78} fullerene is not affected by Stone−Wales rearrangement and loss of C_2 fragments and, thus, is very promising for the synthesis of individual isomers of higher fullerenes.

Direct synthesis of fullerenes is of practical interest as a prospective method to access new fullerenes which cannot be obtained in the uncontrolled process of graphite evaporation, as well as to higher fullerenes which are formed in low yields as hard-to-isolate mixture. As it was shown previously, many geodesic polyarenes can be obtained by intramolecular C_{aryl}−C_{aryl} condensation of suitable polynuclear aromatic hydrocarbons (PAH) under flash vacuum pyrolysis (FVP) conditions.[1−4] This methodology was successfully employed by Scott et al. for the first rational C_{60}-fullerene synthesis.[5] The pyrolytic precursor containing all 60 carbon atoms at the desired positions, was obtained through an 11-step synthesis. After the FVP of this precursor, C_{60} with 0.1−1% yield was obtained. Despite the relatively low yields, the high selectivity (formation of other fullerenes was not noticeable), makes this approach appear rather promising. Although the successful synthesis of C_{60} was presented more than 5 years ago, until now no attempts were made to synthesize higher fullerenes by using the FVP technique. Recently, we have shown that truxenone can be used as a prospective starting unit for the synthesis of C_{60}-fullerene pyrolytic precursors.[6] Herein we report the synthesis of the C_{78}-fullerene precursor on the base of truxenone and its 20-fold tandem cyclization to C_{78}-fullerene by FVP. The potentiality of using the FVP technique for the direct synthesis of higher fullerenes is discussed.



1 **2** **3** **4**

FIGURE 1. Synthetic route to the C_{78} precursor **4**: (a) H_2SO_4, 80 °C, 80%; (b) $CH_3C_6H_4MgBr/Et_2O$, Ni(acac)$_2$, 78%; (c) NBS, 78%; (d) Mg/Et_2O, 30%; (e) H^+/AcOH, 86%.

The synthetic route of a C_{78} precursor (compound **4**) is presented on Figure 1. Compound **1** can be obtained by Kumada coupling of tolylmagnesium bromide and 1-bromonaphthalene in the presence of a Ni catalyst as well as by Suzuki coupling of naphthylboronic acid and 4-bromotoluene. In the case of Kumada coupling, the resulting product contains about 10% 4,4′-dimethylbiphenyl (dimerization of the Grignard reagent), which can be removed chromatographically at the next step after bromination with NBS. Subsequent transformation of compound **2** into a Grignard reagent and addition to truxenone yields triol **3** as a mixture of syn and anti isomers and noticeable amount of bis(naphthylphenyl)ethane (**5**) as a byproduct. Both of the isomers of compound **3** were isolated in pure form by flash chromatography. The structure of syn isomer was confirmed by single-crystal X-ray structure analysis (CCDC-661369). As a final step the dehydration of triol **3** in glacial acetic acid gives compound **4** as a mixture of cis/trans isomers (for details see the Supporting Information).

The structure of compound **4** is structurally related to C_{78}-fullerene. It contains all 78 carbon atoms in the required positions and 93 out of 117 C−C bonds, which corresponds to 80% of all bonds in the C_{78}-fullerene molecule. Formally, the intramolecular cyclodehydrogenation of the precursor leads to the C_{78}-fullerene cage. The presence of cis/trans isomers did not affect the results of the pyrolysis experiment, because at high temperatures the isomers equilibrate rapidly. Rotation around the single bond between naphthyl and phenyl units and around the single bond between phenyl and truxene moieties results in four possible conformers, two of which can give close carbon structures during intramolecular condensation. Depending on the orientation of units before cyclization either the C_{78}:1 (D_3) or the C_{78}:4 (D_{3h}) fullerene can be obtained, as represented on Figure 2. Statistically, the formation of these two isomers, out of a possible five,[7] occurs with equal probability. The first

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[1] Scott, L. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 4994.
[2] Mehta, G.; Rao, S. R. *Tetrahedron* **1998**, *54*, 13325.
[3] Scott, L. T. *Pure Appl. Chem.* **1996**, *68*, 291.
[4] Tsefrikas, V. M.; Scott, L. T. *Chem. Rev.* **2006**, *106*, 4868.
[5] Scott, L. T.; Boorum, M. M.; McMahon, B. J.; Hagen, S.; Mack, J.; Blank, J.; Wegner, H.; de Meijere, A. *Science* **2002**, *295*, 1500.
[6] Amsharov, K. Yu.; Jansen, M. *Z. Naturforsch.* **2007**, *62b*, 1497.
[7] Fowler, P. W.; Manolopoulous, D. E. *An Atlas of Fullerenes*; Clarendon: Oxford 1995.

10.1021/jo7027008 CCC: $40.75

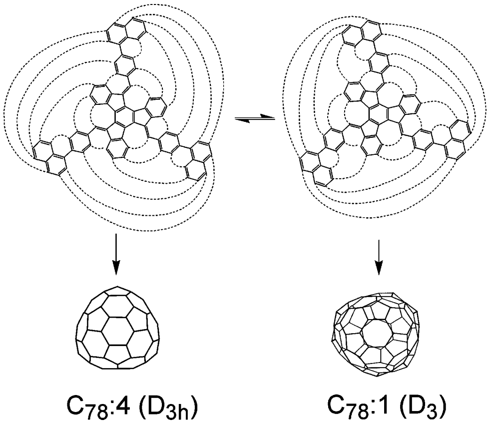

FIGURE 2. Two different conformations of **4** which can give fullerene structures via intramolecular cyclization.

one, C_{78}:1 (D_3), represents the chiral fullerene cage which is known to be stable and soluble. This isomer can be extracted from fullerene soot and separated from the other two soluble C_{78} fullerenes: C_{78}:2 (C_{2v}) and C_{78}:3 (C_{2v}).[8,9] The next known stable but nonsoluble isomer is C_{78}:5 (D_{3h}) which was recently separated and characterized in the form of $C_{78}(CF_3)_{12}$ derivative.[10,11] Thus, only the C_{78}:4 (D_{3h}) isomer remains unexplored in the family of IPR (isolated pentagon rule) C_{78} fullerenes. According to a DFT calculation the HOMO−LUMO gap of this isomer is large (2.47 eV) and close to the HOMO−LUMO gap of C_{70} and C_{60}, 2.69 and 2.76 eV, respectively.[12] Taking into account that the insolubility of fullerenes has been attributed to polymerization due to small (or zero) HOMO−LUMO gap,[13,14] C_{78}:4 (D_{3h}) is presumably soluble. The absence of this isomer in fullerene extracts of raw soot indicates that this fullerene does not form during conventional fullerene synthesis. Although C_{78}:4 (D_{3h}) is predicted to be the least stable among all C_{78} IPR isomers for a wide temperature interval,[15] its energy per carbon atom is comparable to C_{70}-fullerene. Conceivably, the reason why this isomer has not been observed yet lies in kinetic factors.[12] Thus, it is very probable that this isomer does not form under graphite vaporization, but can be achieved by direct synthesis.

LDI (laser desorption ionization) analysis of the products obtained after FVP of precursor **4** at 800 °C shows nine main groups of signals in the mass spectrum (Figure 3). The first group corresponds to the initial precursor **4** and the products of its intramolecular condensation accompanied by loss of hydrogen. The lowest mass detected in this group is 974.3 Da and corresponds to $C_{78}H_{38}$, which is a result of eliminating ten hydrogen atoms and generating five new C−C bonds in the initial precursor. The other eight groups of signals correspond to the products of partial fragmentation of the precursor and products of their subsequent condensation. As it can be concluded from LDI spectra analysis, the main decomposition process is the cleavage of a single bond between phenylnaphthyl radical and truxenene moiety as well as the cleavage of a single bond between naphthalene and phenyl fragments. Thus, the loss of a naphthalene fragment leads to $C_{68}H_{42}$ ($m/z = 858.3$) which subsequently gives $C_{68}H_{42-2n}$ by intramolecular cyclization. The lowest mass in this group corresponds to $C_{68}H_{32}$ ($m/z = 848.3$) which is a result of five new C−C bonds forming. The loss of phenylnaphthalene or methylphenylnaphthalene fragments with subsequent condensation leads to $C_{62}H_{38}$−$C_{62}H_{30}$ and $C_{61}H_{38}$−$C_{61}H_{30}$ species, correspondingly. Combination of such fragmentations gives five further groups of signals: $C_{52}H_{32}$−$C_{52}H_{24}$, $C_{51}H_{32}$−$C_{51}H_{22}$, $C_{46}H_{28}$−$C_{46}H_{20}$, $C_{45}H_{28}$−$C_{45}H_{18}$ and $C_{44}H_{28}$−$C_{44}H_{20}$ (for details see the Supporting Information).

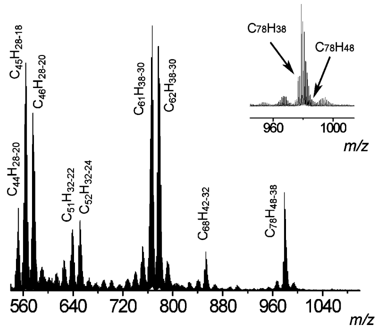

FIGURE 3. LDI mass spectrum of pyrolysis products of **4** at 800 °C (negative mode).

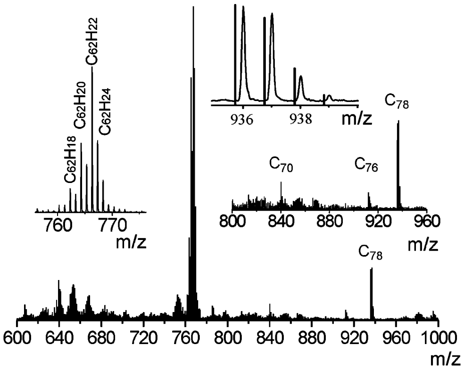

FIGURE 4. LDI mass spectrum of pyrolysis products of **4** at 1000 °C (negative mode). The theoretical isotopic distribution pattern of C_{78} is shifted for clarity (right top).

Increasing the pyrolysis temperature to 1000 °C results in fullerene formation according to LDI data. As can be seen from Figure 4, the signals of C_{78} dominate among the other fullerene signals. The weak signals of C_{70} and C_{76} and absence of C_{60}-fullerene signal confirm the direct formation of the C_{78} cage from compound **4**. The more intense signals in the mass spectra correspond to loss of one phenylnaphthalene fragment and products of subsequent intramolecular condensation. The lowest mass detected in this group is 762.1 Da which corresponds to a loss of 20 hydrogen atoms and formation of ten new bonds. This fact clearly points out that a high degree of condensation takes place at the given conditions and the formation of C_{78} is a result of intramolecular condensation of precursor **4**. Despite the relatively intense signals corresponding to C_{78} in the mass

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(8) Kikuchi, K.; Nakahara, N.; Wakabayashi, N.; Suzuki, N.; Shiromaru, H.; Miyake, Y.; Saito, K.; Ikemoto, I.; Kainosho, M.; Achiba, Y. *Nature* **1992**, *357*, 142.

(9) Diederich, F.; Whetten, R. L.; Thilgen, C.; Ettl, C.; Chao, I.; Alvarez, M. M. *Science* **1991**, *254*, 1768.

(10) Shustova, N. B.; Kuvychko, I. V.; Bolskar, R. D.; Seppelt, K.; Strauss, S. H.; Popov, A. A.; Boltalina, O. V. *J. Am. Chem. Soc.* **2006**, *128*, 15793.

(11) Shustova, N. B.; Newell, B. S.; Miller, S. M.; Anderson, O. P.; Bolskar, R. D.; Seppelt, K.; Popov, A. A.; Boltalina, O. V.; Strauss, S. H. *Angew. Chem.* **2007**, *119*, 4189; *Angew. Chem., Int. Ed.* **2007**, *46*, 4111.

(12) Sun, G.; Kertesz, M. *J. Phys. Chem. A* **2000**, *104*, 7398.

(13) Saito, S.; Okada, S.; Sawada, S.-I.; Hamada, N. *Phys. Rev. Lett.* **1995**, *75*, 685.

(14) Diener, M. D.; Alford, J. M. *Nature* **1998**, *393*, 668.

(15) Uhlik, F.; Slanina, Z.; Osawa E. *Eur. Phys. J. D* **2001**, *16, 349.*

spectra the attempts to isolate one by HPLC were unsuccessful. We regard the low fullerene yield to be probably connected to the presence of weak bonds in the initial precursor, which are not stable enough under FVP conditions, and/or the existence of the fullerene in form of derivatives.[16]

Although the MS data clearly show the selective condensation of compound **4** to C_{78}-fullerene, the yield was not sufficient for determination of the isomer composition. Taking into account that the separation of individual higher-fullerene isomers represents an almost unfeasible task, the isomerization of the fullerene cage during synthesis can completely nullify the effort of direct synthesis. One of the plausible processes for isomerization of fullerenes under FVP conditions is the so-called Stone-Wales (SW) or "pyracylene" rearrangement, which is a 90° rotation of C_2 unit.[17] The SW rearrangement proceeds via an antiaromatic 4-electron-4-center transition state and thus is thermally forbidden under the Woodward−Hoffmann rules for concerted reactions.[18] However, according to quantum mechanical calculations such kind of rearrangement can be realized through a route different from the one originally suggested. The multistep SW rearrangement can be characterized by relatively low activation energy,[19] especially in the presence of radicals.[20,21] The C_{78} cage represents the smallest fullerene in which SW rearrangement can give stable IPR isomers: C_{78}:5 (D_{3h}) $\leftrightarrow$ C_{78}:3 (C_{2v}) $\leftrightarrow$ C_{78}:2 (C_{2v}) $\leftrightarrow$ C_{78}:4 (D_{3h}).[22] For other higher fullerenes the number of IPR isomers which can be transformed one into another by SW rearrangement grows drastically. Thus, SW isomerization gives nine stable isomers in the case of C_{82}, 21 isomers in the case of C_{84}, etc.[7] Although it was shown that no SW transformation takes place in C_{84} (D_2) at 700 °C,[23] there are no data about the stability of higher fullerenes at higher temperatures. For verification of the possibility of SW rearrangement to take place under pyrolysis conditions, the C_{78}:2(C_{2v}) and C_{78}:3(C_{2v}) were isolated and subjected to pyrolysis. According to HPLC data of the pyrolysis products, both of the fullerenes proved to be stable under FVP conditions at 1100 °C. No transformation of one isomer into another was observed. Obviously, SW rearrangement does not take place in fullerene molecules under FVP condition, at least at a temperature lower than 1100 °C. Moreover, no decomposition processes with loss of C_2 clusters and formation of lower fulerenes (C_{60} and C_{70}) were detected during FVP. Thus, FVP technique is very promising for the synthesis of individual isomers of higher fullerenes.

Summing up, the C_{78}-fullerene related structure was obtained through a 5-step synthesis and investigated as a pyrolytical precursor. Taking into account that C_{78} fullerene is not being formed by random assembling during pyrolysis of different aromatic compounds unlike C_{60} fullerene,[24] the results obtained are evidence of the direct fullerene formation by FVP.

We are optimistic that optimization of the precursors structure by removing less stable single bonds and introducing radical promoters will allow the pyrolysis temperature to be reduced and increase the selectivity of fullerene formation.

Experimental Section

The MALDI-TOF MS spectra were obtained by using DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile) or mixture of DCTB with silver triflate as the matrix. The fullerene-containing samples were analyzed in the LDI mode. Chromatographic purifications were carried out with flash grade silica gel Kieselgel 60 (0.06−0.2 mm), Roth. The multistep separation with recycling system (Buckyprep, toluene) was used for isolation of C_{78}:3 and mixture of C_{78}:1 and C_{78}:2. The separation of C_{78}:2 from the mixture and further HPLC analysis were carried out on reverse phase column - Supelcosil LC-18-DB, size 4.6 × 250 mm, mobile phase of toluene/methanol (1:1), UV-detection. Truxenone (Diindeno[1,2-a;1′,2′-c]fluorene-5,10,15-trione) was prepared according to the described procedure.[25] Details of the pyrolysis apparatus are reported elsewhere.[16] In a typical experiment 10−20 mg of compound **4** were pyrolyzed. The resulting products were extracted with toluene, filtered through microfilters (0.2 μm) and analyzed by LDI-TOF MS and HPLC. In the case of fullerene pyrolysis samples of 1 mg were used.

4-(1-Naphthyl)toluene (1). Method A.1-Bromonaphthalene (8.3 g, 40 mmol) was added to freshly prepared 4-methylphenylmagnesium bromide (40 mmol) in 30 mL of Et_2O. After addition of 10 mg of $Ni(acac)_2$, the mixture was stirred for 2 h at room temperature and then heated under reflux for 1 h. The solution was cooled, diluted with 0.05 M HCl, and extracted with ether. The extract was dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography using 20:1 mixture of hexane/DCM. Resulting product containing about 10% of 4,4′-dimethylbiphenyl was used in the next step without further purification (colorless oil, 6.8 g, 78%). **Method B.** 4-Bromotoluene (1.7 g, 10 mmol) and 1-naphthaleneboronic acid (2.1 g, 15 mmol) were dissolved in a mixture of 40 mL of acetone and 40 mL of water. $Pd(OAc)_2$ (10 mg, 0.045 mmol) and Na_2CO_3 (2.1 g, 20 mmol) were added, and the resulting mixture was stirred at room temperature for 18 h. The separation of the product was the same as in method A: colorless oil (1.8 g, 84%) was obtained which slowly solidified; white solid; $R_f = 0.53$ (hexane/DCM 20:1); ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 2.44$ (s, 3H), 7.27−7.29 (m, 2H), 7.37−7.52 (m, 6H), 7.81−7.93 (m, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) $\delta = 21.21$, 125.37, 125.68, 125.89, 126.09, 126.86, 127.42, 128.23, 128.95, 129.94, 131.64, 133.82, 136.88, 137.78, 140.21.

4-(1-Naphthyl)benzyl Bromide (2). Compound **1** 6.5 g (30 mmol) was dissolved in 30 mL of CCl_4. NBS (13.0 g) and catalytic quantities of benzoyl peroxide were added. The resulting mixture was refluxed for 2−3 h, cooled, filtered, and washed with water. The solution was dried over Na_2SO_4 and evaporated. The crude product was purified by silica gel chromatography using 10:1 mixture of hexane/DCM: yellowish oil (6.9 g, 78%); $R_f = 0.34$ (hexane/DCM, 20:1); ^{1}H NMR ($CDCl_3$, 300 MHz) $\delta = 4.54$ (s, 2H), 7.36−7.49 (m, 8H), 7.83−7.87 (m, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) $\delta = 33.37$, 125.33, 125.81, 125.82, 126.12, 126.91, 127.86, 128.30, 128.95, 130.46, 131.41, 133.78, 136.71, 138.82, 140.96; MALDI-TOF MS (DCTB/Ag-triflate) $m/z = 402.87$ [M + Ag]$^+$.

5,10,15-Triol-5,10,15-tris(4-(1-naphthyl)benzyl)-10,15-dehydro-5*H*-diindeno[1,2-*a*; 1′,2′-*c*]fluorene (3). Magnesium (0.36 g, 15 mmol) was activated by catalytic quantities of I_2 in 10 mL of dry diethyl ether. Compound **2** (3.0 g, 10 mmol) as a solution in 10 mL of Et_2O was added slowly under intensive stirring. After being refluxed for 1 h, the mixture was cooled and filtrated.

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[16] Amsharov, K. Yu.; Simeonov, K.; Jansen, M. *Carbon* **2007**, *45*, 337.

[17] Stone, A. J.; Wales, D. J. *Chem. Phys. Lett.* **1986**, *128*, 501.

[18] Woodward, R. B.; Hoffmann, R. *The conservation of orbital symmetry*; Verlag Chemie: Weinheim, 1970.

[19] Murry, R. L.; Strout, D. L.; Odom, G. K.; Scuseria, G. E. *Nature* **1993**, *366*, 665.

[20] Adler, R. W.; Harvey, J. N. *J. Am. Chem. Soc.* **2004**, *126*, 2490.

[21] Nimlos, M. R. *J. Phys. Chem. A* **2005**, *109*, 9896.

[22] Fowler, P. W.; Manolopoulos, D. E.; Ryan, R. P. *Carbon* **1992**, *30*, 1235.

[23] Hawkins, J. M.; Nambu, M.; Meyer, A. *J. Am. Chem. Soc.* **1994**, *116*, 7642.

[24] Osterodt, J.; Zett, A.; Vögtle, F. *Tetrahedron* **1996**, *52*, 4949.

[25] Dehmlow, E. V.; Kelle, T. *Synth. Commun.* **1997**, *27*, 2021.

Truxenone (0.40 g, 1 mmol) was suspended in 6 mL of absolute diethyl ether in an ultrasonic bath and added to Grignard reagent in one step. The resulting mixture was refluxed for 4 h, cooled, and hydrolyzed by addition of NH_4Cl solution. The products were extracted with ether and dried over Na_2SO_4. The solvent was removed, and the residue was purified by silica gel chromatography using mixture of hexane/DCM/acetone 6:4:1. Compound **3** was obtained with summary yield of 30% (syn isomer **3a**, 12%, anti isomer **3b**, 18%).

***syn*-5,10,15-Triol-5,10,15-tris(4-(1-naphthyl)benzyl)-10,15-dehydro-*5H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3a):** yellowish solid (120 mg, 12%); $R_f = 0.23$ (hexane/Et_2O, 1:1); ^1H NMR ($CDCl_3$, 300 MHz) $\delta = 2.43$ (s, 3H), 3.02 (d, $J = 13.2$, 3H), 3.56 (d, $J = 13.2$, 3H), 6.68 (d, $J = 7.9$, 6H), 7.02−7.36 (m, 27H), 7.56 (d, $J = 8.2$, 3H), 7.69 (d, $J = 8.2$, 3H), 7.77 (d, $J = 8.2$, 3H), 8.59 (d, $J = 8.0$, 3H); ^{13}C NMR ($CDCl_3$, 300 MHz) $\delta = 43.02$, 83.19, 124.07, 125.15, 125.52, 125.77, 125.82, 126.20, 126.78, 127.29, 127.53, 128.07, 129.01, 129.09, 130.41, 131.39, 133.64, 134.96, 137.04, 137.25, 138.66, 139.82, 143.31, 148.50; MALDI-TOF MS (DCTB/Ag-triflate) $m/z = 1144.91$ $[M + Ag]^+$. Anal. Calcd for $C_{78}H_{54}O_3$: C, 90.14; H, 5.24. Found: C, 90.06; H, 5.30. Crystal data: monoclinic; space group $C2/c$; $a = 21.5273(15)$ Å, $b = 19.4257(13)$ Å, $c = 27.1517(19)$ Å; $\beta = 98.0570(10)°$, $V = 11242.3(13)$ Å,^{3} $Z = 8$; $2\theta_{max} = 41.15°$; $-20 < h < 20$, $-18 < k < 18$, $-26 < l < 26$; $\lambda = 0.71073$ Å; $T = 100(2)$ K; final R value 0.0988 ($R_w = 0.1221$). CCDC-661369. The crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

***anti*-5,10,15-Triol-5,10,15-tris(4-(1-naphthyl)benzyl)-10,15-dehydro-*5H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (3b):** yellowish solid (185 mg, 18%); $R_f = 0.42$ (hexane/Et_2O, 1:1); ^1H NMR ($CDCl_3$, 300 MHz) $\delta = 2.16$ (s, 1H), 2.35 (s, 1H), 2.47 (s, 1H), 2.95 (d, $J = 13.2$), 3.54−3.85 (m, 5H), 6.72−7.03 (m, 6H), 7.0−7.5 (m, 36H), 8.82 (d, $J = 7.9$, 1H), 8.89 (d, $J = 7.9$, 1H), 8.92 (d, $J = 7.9$, 1H); ^{13}C NMR ($CDCl_3$, 300 MHz) $\delta = 42.85$, 43.29, 43.36, 83.20, 84.04, 84.20, 124.04, 124.46, 125.14, 125.27, 125.30, 125.53, 125.59, 125.64, 125.68, 125.75, 125.83, 125.88, 125.90, 126.53, 126.56, 126.63, 126.79, 126.88, 127.32, 127.40,127.43, 127.50, 127.65, 127.74, 128.22, 128.75, 128.94, 128.95, 129.03, 130.15, 130.23, 130.64, 131.34, 131.61, 131.65, 133.65, 133.71, 133.74, 134.86, 134.94, 135.05, 137.46, 137.58, 137.69, 137.81, 138.07, 138.48, 138.67, 138.71, 139.72, 139.94, 140.06, 142.10, 142.71, 143.13, 148.72, 148.99, 149.04 (14 signals were not observed due to overlapping); MALDI-TOF MS (DCTB/Ag-triflate) $m/z = 1144.83$ $[M + Ag]^+$. Anal. Calcd for $C_{78}H_{54}O_3$: C, 90.14; H, 5.24. Found: C, 89.87; H, 5.35.

5,10,15-Tris(4-(1-naphthyl)benzylidene)-10,15-dihydro-5*H*-diindeno[1,2-*a*;1′,2′-*c*]fluorene (4). Compound **3** (as a mixture of syn/anti isomers) (250 mg) was dissolved in small amount of acetic acid. After addition of a catalytic amount of H_2SO_4, the mixture was reflux at 110 °C under stirring. After 3 h, the resulting mixture was diluted with water, filtrated, washed with water, and dried. The crude product was purified by silica gel chromatography using mixture of hexane/benzene 1:1: orange solid (204 mg, 86%); $R_f = 0.68$ (hexane/Et_2O 1:1); ^1H NMR ($CDCl_3$, 300 MHz) $\delta = 6.96-7.19$ (m, 3H), 7.24−8.03 (m, 42H), 8.59−8.66 (m, 3H); MALDI-TOF MS (DCTB/Ag-triflate) $m/z = 984.48$ $[M + H]^+$, 1091.30 $[M + Ag]^+$. Anal. Calcd for $C_{78}H_{48}$: C, 95.09; H, 4.91. Found: C, 94.22; H, 4.65.

4,4′-Di(1-naphthyl)-1,2-diphenylethane (5): white crystals; $R_f = 0.26$ (hexane); ^1H NMR ($CDCl_3$, 300 MHz) $\delta = 3.13$ (s, 4H), 7.37−7.53 (m, 16H), 7.85−7.95 (m, 6H); ^{13}C NMR ($CDCl_3$, 300 MHz) $\delta = 37.71$, 125.39, 125.71, 125.95, 126.08, 126.90, 127.50, 128.26, 128.36, 130.09, 131.73, 133.85, 138.47, 140.19, 140.81.

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Supporting Information Available: Presumable mechanism of precursor decomposition during the FVP process, HPLC data, ^1H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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