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ARTICLE

Hexaaryl-*carbo*-benzenes revisited: novel synthetic route, crystallographic data, and prospects of electrochemical behavior

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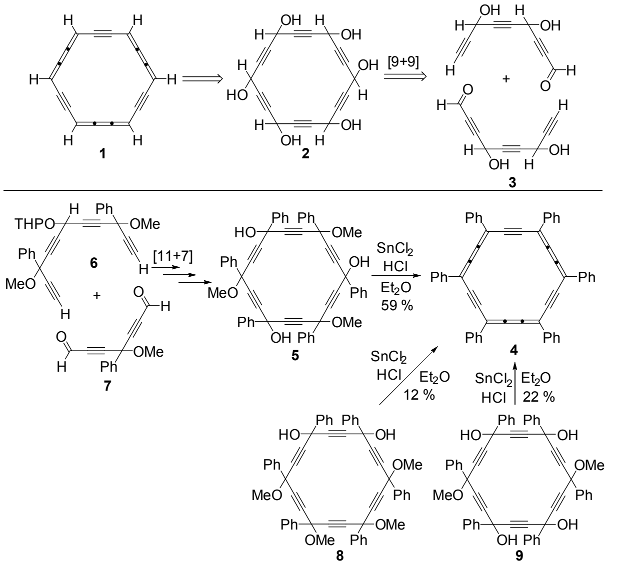
An improved 12-step synthetic route and full characterization of hexaphenyl-*carbo*-benzene (**4**, 8 %) and the *p*-bis-3,5-di-*tert*-butylphenyl homologue (**11**, 4 %), are described. The *carbo*-benzene reference **4** is now accurately described in the crystal state by X-ray diffraction analysis in the chiral space group $P2_12_12_1$, and in comparison to the less symmetric derivative **11** giving a centro-symmetric packing. According to cyclic voltammetry, both hexaaryl-*carbo*-benzenes **4** and **11** can behave as both reversible potent electron acceptors and standard electron donors, with respective potentials of –0.73 ± 1 V and +1.17 ± 2 V/SCE, respectively. Due to an extremely low solubility, solid films of **11** fabricated by the "wet method", with the initial view to studying charge transport properties, were found to display high roughness.

1 Introduction

By January 1995, the title term "*carbo*-benzene" was proposed for **1**, as a putative example of Hückel-aromatic *carbo*-mer,[1] namely a structure devised by D_{6h} symmetry-preserving C_2-expansion of the benzene molecule (Figure 1).[2] In spite of an attempt at synthesis *via* a hexaoxy-[6]pericyclynediol **2** (itself targeted by a [9+9] macro-cyclization route from the triynal **3**),[3] the "bare" *carbo*-benzene **1** could not be obtained and remains hitherto experimentally unknown.[4] Exactly at the same time, Ueda, Kuwatani *et al*. communicated the synthesis of 3,6,9,12,15,18-hexaphenyldodecadehydro[18]annulene **4** and a few congeners,[5] standing as the first examples of *carbo*-benzene derivatives, in tri- or hexa-substituted versions (Scheme 1). The highly chromophoric compound **4** and its [6]pericyclynetriol precursor **5** were described in more details by the same authors in 1998.[6] The employed route was based on a [11+7] macro-cyclization step, where a bis-terminal tetrayne **6** reacts as a dinucleophile with a skipped bis-ynal **7** as a dielectrophile. The original synthetic route thus consisted in 15 steps, with a 1 % overall yield, and a 59 % yield for the **5** → **4** reductive aromatization step.[5,6] In 2007, the same hexaphenyl-*carbo*-benzene **4** was reported to be also accessible by reductive aromatization of a [6]pericyclynediol **8** and a [6]pericyclynetetraol **9**, in 12 and 22 % yield, respectively.[7] The precursors **8** and **9** were themselves obtained through [14+4] macro-cyclization processes, in nine steps with 11 % overall yield, and eight steps with 12 % overall yield, respectively.[8]

A much shorter alternative route would be based on a [8+10] macro-cyclization process and a key [6]pericyclynedione **10**,[9] which more recently proved efficient for the synthesis of centro-symmetric tetraphenyl-*carbo*-benzene targets.[10] Application of this method to the preparation of the *carbo*-benzene paradigm **4** is hereafter described, along with the synthesis of the *a priori* more liphophilic *p*-bis-(di-3,5-*tert*-butylphenyl) derivative **11**.



Scheme 1. Strategies envisaged for the preparation of the unsubstituted *carbo*-benzene **1** (*top*); known syntheses of hexaphenyl-*carbo*-benzene **4** (*bottom*).

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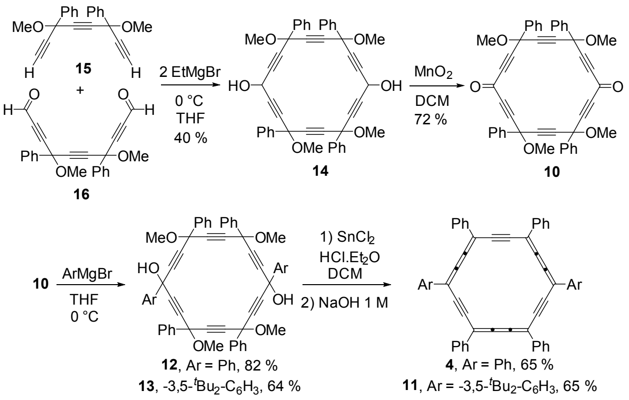
In the 1998 pioneer report,[6] X -ray diffraction (XRD) analysis of a single crystal of **4** allowed confirmation of the quasi-D_{6h} symmetric structure and provided information on bond distances and bond angles. Nevertheless, the quality of the crystallographic structure was likely not sufficient for deposition at the CCDC, where no corresponding cif file is currently available. The challenge of gaining accurate crystallographic data to make a cif file of **4** available at the CCDC is particularly addressed below.

2 Results and discussion

The *carbo*-benzene targets **4** and **11** were thus envisaged by reductive aromatization of the [6]pericyclynediols **12** and **13.** The latter were targeted from the known [6]pericyclynedione **10**, obtainable by oxidation of the corresponding secondary [6]pericyclynediol **14** (Scheme 2).[9] An optimal procedure for the synthesis of **14** is based on a [8+10] macro-cyclization step involving the C_8 triyne **15** and the C_{10} dialdehyde **16**. As compared to the previously used [11+7] and [14+4] strategies (see Introduction), an advantage of the [8+10] strategy is its late divergence character: the sensitive dialdehyde **16** is indeed readily obtained from the triyne **15** just before the macro-cyclization step, which gives the [6]pericyclynediol **14** in *ca* 40 % yield (see SI for a detailed comparison of the original and improved synthesis strategies).[9] The key [6]pericyclynedione **10** is then obtained by oxidation of **14** with MnO_2. From **10**, the targets **4** and **11** were prepared in two steps following a procedure previously experienced for the synthesis of other *carbo*-benzenes.[10] Addition of two equivalents of either PhLi or PhMgBr to the diketone **10** was thus attempted. Treatment of **10** with PhLi was found to induce an opening of the C_{18} ring, allowing access to the diadduct **12** in trace amount only. In contrast, the use of PhMgBr allowed isolation of **12** with a remarkably high 82% yield (Scheme 2). The Grignard reagent was thus also used for anchoring two 3,5-di-*tert*-butylphenyl groups to **10**, providing the [6]pericyclynediol **13** with 64 % yield.

Using a classical procedure,[10] reductive aromatization of **12** and **13** in dichloromethane (DCM) solution with 10 equivalents of $SnCl_2$ and 20 equivalents of $HCl•Et_2O$, followed by neutralization with 1 M aqueous NaOH, gave the targets **4** and **11** with the same 65 % yield. This procedure differs from the original one by the nature of the solvent and the hydrolysis conditions.[6] The results confirm recent observations that the use of DCM as solvent instead of diethyl ether, along with milder hydrolytic conditions (1 M instead of 10 M NaOH), provides higher yields in *carbo*-benzenes, essentially by enhancement of the solubility of both the reagents and products.[10] In comparison with the original method,[5,6] not only the yield in **4** of the last reductive elimination step has been improved from 59 to 65 %, but also the total number of steps has been reduced from 15 to 12, while the global yield has been increased from about 1 % to 8 % (see SI for comparative synthesis schemes).

The hexa-aryl-*carbo*-benzenes **4** and **11** have been isolated as poorly soluble dark red solids. The introduction of two *tert*-butyl groups on two phenyl substituents of **4** thus appears to have a limited effect on the solubility of such rigid carbon-rich compounds. Indeed, the solubility of **11** was determined to be *ca* 0.46 ± 0.03 mg/mL, namely less than twice the solubility of **4** of *ca* 0.29 ± 0.03 mg/mL, in spite of the presence of four *tert*-butyl groups on two of the aromatic substituents of **11**. For comparison, direct anchoring of aliphatic chains at two vertices the C_{18} macrocycle was recently reported to be much more efficient with the view to increasing solubility of *carbo*-benzenes.[13]



Scheme 2. Synthesis of *carbo*-benzene targets through a [8+10] macro-cyclization route.

In spite of this, accurate spectroscopic data were obtained for **4** and **11** (^1H NMR, ^{13}C NMR, UV-vis), thus confirming the data ranges of Ueda, Kuwatani *et al*. for **4**.[5,6] In particular, ^1H NMR spectra of **4** and **11** reveal the characteristic deshielding of the *ortho*-^1H nuclei of the aryl substituents resulting from the magnetic anisotropy induced by the strong diatropic C_{18} ring current (Figure 1).[1,5-7,10]

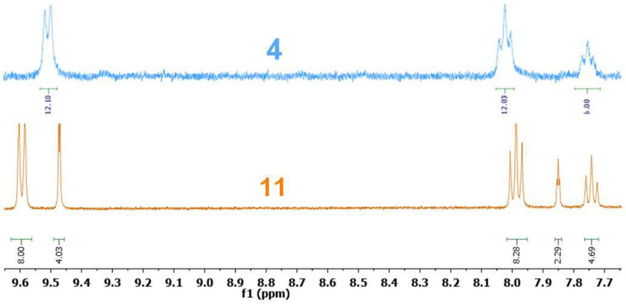


Figure 1. Aromatic region of the ^1H NMR spectra of **4** and **11** in highly diluted $CDCl_3$ solutions (400 MHz, 12 h acquisition time).

The UV-vis absorption spectrum of **4** in chloroform solution confirms the λ_{max} value of 472 nm previously reported (Figure 2).[6] The *carbo*-benzene **11** exhibits an identical spectral profile with the same λ_{max} value. The molar extinction coefficient of **4** was however measured to be lower than the value initially reported (234 000 *vs* 363 000 $L.mol^{-1}.cm^{-1}$).[6] The absorption

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spectra of **4** and **11** are classical for *carbo*-benzenes, and their common maximum absorption wavelength λ_{max} = 472 nm is a median value of all the reported values, varying from 424 nm for the octupolar triphenyl-*carbo*-benzene,[5,6] to 521 nm for the quadrupolar *para-N,N*-dimethylanilinyl-tetraphenyl-*carbo*-benzene.[10b]

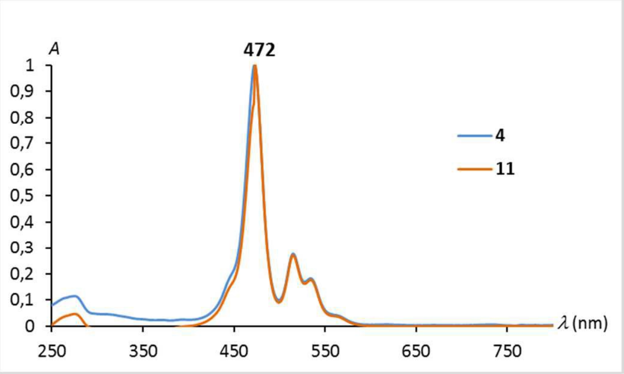
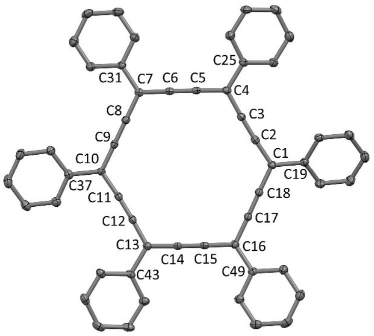


Figure 2. Normalized absorption spectra of **4** and **11** in chloroform solution.

The structures of **4** and **11** were confirmed by XRD analysis of single crystals deposited from chloroform solutions (Figure 3, Table 1).[14] Contrary to the pioneer crystallographic data,[6] the quality of the present crystals of **4** proved sufficient for refined resolution, having allowed deposition at the CCDC.[14] The same allotropic variety, involving one $CHCl_3$ molecule *per* molecule of **4**, was obtained. Noteworthy, the highly planar- and centro-symmetric molecule **4** thus crystallizes in the Sohncke chiral space group $P2_12_12_1$. Crystallization of a highly symmetrical achiral molecule such as **4** in a chiral space group is not common, but examples have been previously reported for other rigid compounds.[15]



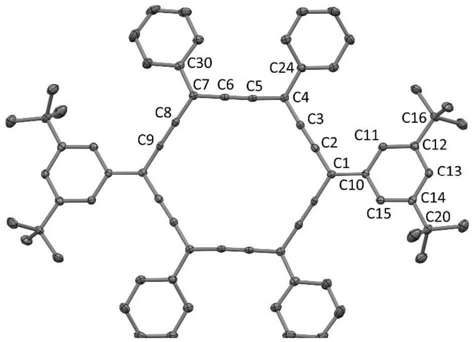


Figure 3. Molecular views of the X-ray crystal structures of the *carbo*-benzenes **4** (*top*) and **11** (*bottom*). Numbering of non-equivalent C atoms are indicative of the crystal symmetry. For clarity, hydrogen atoms and solvent molecules are omitted.

Table 1. Selected crystallographic data for **4** and **11**.[14]

	4	**11**
Empirical formula	$C_{54}H_{30}$,$CHCl_3$	$C_{70}H_{62}$, 2($CHCl_3$)
Formula mass	798.21	1142.02
Crystal system	Orthorhombic	Triclinic
Space group	$P2_12_12_1$	*P* -1
T [K]	100	120
a [Å]	12.4948(5)	10.1720(5)
b [Å]	16.0972(6)	11.8006(8)
c [Å]	20.2765(9)	12.8576(7)
α [°]	90	90.105(5)
β [°]	90	101.559(5)
γ [°]	90	94.484(5)
V [Å^3]	4078.24(18)	1507.20(8)
D_c	1.300	1.258
Z	4	1
μ [mm^{-1}]	0.263	0.327
Refl. measured	97066	23700
Refl. unique/R_{int}	9935/0.048	6699/0.045
Refl. with *I* > 3σ(*I*)	7863	4214
Nb parameters	560	379
R	0.0351	0.045
R_w	0.0369	0.0516
Flack parameter	0.05(5)	/
Nb Friedel-pairs	4448	/
$\Delta\rho_{max}/\Delta\rho_{min}$ [e.Å^{-3}]	0.66/-0.58	0.50/-0.33

Geometrical features of the macrocycle of **4** are typical of generic *carbo*-benzenes, with average sp^2C-*sp*C and *sp*C-*sp*C bond lengths of 1.39 and 1.22 Å respectively. The average angle at the sp^2 vertices of the macrocycle is of 118.9°. The C_{18} ring is slightly distorted: the maximum deviation from planarity mounts to 0.11 Å, while the globally hexagonal shape is not regular, the diameters (between facing sp^2 vertices) varying from 7.79 Å to 8.17 Å. Torsion angles between the phenyl mean planes and the macrocycle mean plane vary from 2.9° to 29.8°. In the crystal of **11**, the molecules pack in a parallel

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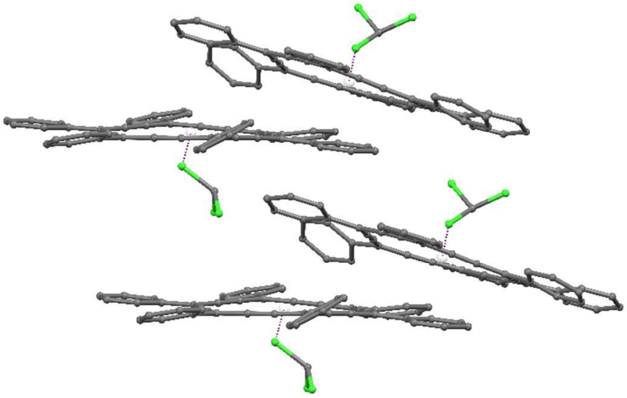
fashion, the distance between the mean planes of two successive *carbo*-benzene macrocycles being of 3.62 Å, i.e. much larger than in the recently reported first examples of π-stacked *carbo*-benzenes.[13a] No π-stacking is indeed here observed between two C18 rings, or between a C18 ring and a C6 ring of the aryl substituents. Instead of a chlorine atom of the chloroform molecule co-crystallized with **4**, (see above), one of the methyl groups of a *tert*-butyl substituent of **11** points towards the center of the C_{18} ring of the nearest molecule: the closest H atom the methyl group reside 1.43 Å away from the centroid and 1.38 Å from the mean plane of the neighboring C_{18} ring (Figure 4).



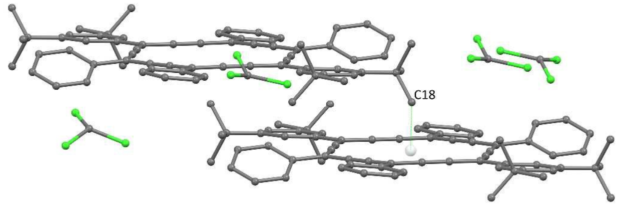


Figure 4. Views of the crystalline molecular packing of **4** (top) and **11** (bottom) evidencing both the absence of π-stacking between the C_{18} rings, and interactions with solvent molecules (for **4**) and between two *carbo*-benzene molecules (for **11**).

The electrochemical behavior of **4** and **11** has also been studied (Table 2). Cyclic (CV) and square-wave (SWV) voltammograms were recorded for **4** and **11** in chloroform solutions (see S.I.). More conventional DCM solutions could indeed not be used because of an extremely low solubility in this solvent. For a reference diethyl-*carbo*-benzene exhibiting sufficient solubility in either solvents, this solvent change was recently shown to make redox processes less reversible, but keep almost unchanged the redox potential values, thus allowing comparison between data obtained from either DCM or chloroform solutions.[13b]

Table 2. CV and SWV data for the *carbo*-benzenes **4** and **11** in chloroform solutions.

Product	Reductions			Oxidations		
	$E_{1/2}$[a] (ΔE_P)[b]	RI_P[c]	E_P[red d]	$E_{1/2}$[a] (ΔE_P)[b]	RI_P[c]	E_P[ox d]
4	- 0.72[e] (0.44)	0.58				1.14[f]
			- 1.15[f]			
11	- 0.74[e] (0.59)	1.01		1.19[e] (0.53)	0.68	
			- 1.30			1.70

[a] Half-wave potential $E_{1/2} = (E_P^{red} + E_P^{ox})/2$, in V/SCE. [b] Separation between the two peak potentials: $\Delta E_P = |E_P^{red} - E_P^{ox}|$, in V. [c] Peak current ratio $RI_P = |I_P^{ox}/I_P^{red}|$. [d] E_P values measured from CV in V/SCE. [e] Reversibility observed at high scan rate only. [f] The compound underwent polymerization and deposited on the electrode.

While the first reduction processes were found to occur reversibly at similar potentials (- 0.72 V for **4**, – 0.74 V for **11**), the second reduction happens to be irreversible for both compounds (Table 2). These values are consistent with previous values reported for other *para*-diaryl-tetraphenyl-*carbo*-benzenes, the first reduction occurring between –0.75 and –0.85 V depending on the nature of the aryl groups.[10a,10b] This process is however made easier upon substitution of the C_{18} ring by acetylenic substituents: the lowest reduction potential (in absolute value) of – 0.60 V observed to date for a *carbo*-benzene was indeed measured for a *para*-bis-fluorenylethynyl-substituted representative.[10f] In oxidation regime, the first potentials of the two *carbo*-benzenes have comparable values (1.14 V for **4** and 1.19 V for **11**), but the process is reversible for **11** only: the oxidation product of **4** indeed undergoes polymerization, leading to a deposit on the electrode. A second non-reversible oxidation process was also observed for **11**. *Carbo*-benzenes generally undergo irreversible oxidation, most of them giving a polymeric film on the electrode after the first oxidation process, the latter occurring at potentials between +0.51 and +0.90 V for donor-substituted hexaaryl-*carbo*-benzenes,[10a,10b] and reaching +1.17 V for a fluorenylethynyl-substituted derivative exhibiting a more extended -conjugation.[10f]

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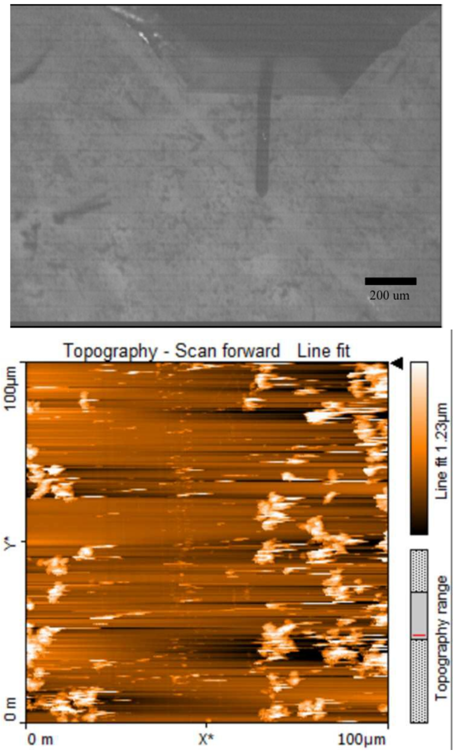

Figure 5. Morphology of spin-casted films of **11** (blended with $PC_{71}BM$: 1:1, w/w ratio) on a glass substrate: microscopic optical image taken by a digital camera installed on the AFM instrument used (*top*), and AFM image showing the film roughness (rms) ~ 355 nm (*bottom*). An additional AFM image is available in the S.I.

The low reduction potential of **4** and **11** (*ca* – 0.73 V) suggests their possible use as electron acceptors, alternatives to C_{60} (and PCBM) for photovoltaics (the first reduction potential of C_{60} is -0.55 V in chloroform).[16] The accessible and possibly reversible character of the first oxidation of **11** (at 1.19 V) might also be compatible with a use as an organic electron donor. However, the very low solubility of these hexa-aryl-*carbo*-benzenes, even that of the slightly more soluble derivative **11**, did not allow preparing highly regular thin solid films by the "wet method", thus preventing measurement of their efficiency for charge transport.[17] Indeed, while microscopic optical images clearly show the non-uniformity of the films, AFM images allowed the measurement of their high roughness, mounting to *ca* 355 nm (Figure 5). This entails a poor optical quality of the films, as evidenced by their UV-vis absorption spectra exhibiting large light scattering competing with absorption (see S.I.).

3 Conclusions

Hexaphenyl-*carbo*-benzene **4** is a fully symmetrical paradigm and model of the *carbo*-benzene family: 20 years after its first description, its synthetic accessibility has been significantly improved through the implementation of a [8+10] macro-cyclization strategy, and its characterization has been completed by accurate crystallographic and electrochemical data. The expected enhancement of solubility upon substitution of **4** by four *tert*-butyl groups was found limited, preventing the use of thin films of **11** for charge transport in organic photovoltaics. Nevertheless, the much higher solubility of recently described *p*-dialkyl-tetraphenyl-*carbo*-benzenes[13] allows consideration of their possible use for such applications. Results of the envisaged studies will be communicated in due course.

4 Experimental

4.1 General remarks

THF, diethyl ether (Et_2O), pentane and dichloromethane (DCM) were dried with a PureSolv-MD-5 Innovative Technology system for the purification of solvents. All other reagents were used as commercially available. In particular, solutions of PhLi were 1.9 M in dibutyl ether, solutions of PhMgBr were 3 M in diethyl ether, solutions of HCl were 2 M in diethyl ether. All reactions were carried out under argon atmosphere using Schlenk and vacuum line techniques. Column chromatography was carried out on silica gel (60 Å, C.C 70-200 µm). Silica gel thin layer chromatography plates (60F254, 0.25 mm) were revealed under UV-light and/or by treatment with an ethanolic solution of phosphomolybdic acid (20%). The following analytical instruments were used, ^1H and ^{13}C NMR: Avance 400 and Avance 400 HD spectrometers; mass spectroscopy: Quadrupolar Nermag R10-10H spectrometer; UV-Visible: Perkin-Elmer UV-Vis Win-Lab Lambda 950; NMR chemical shifts are given in ppm with positive values to high frequency relative to the tetramethylsilane reference. Coupling constants J are in Hertz. UV-Visible extinction molar coefficient ε is in $L\cdot mol^{-1}\cdot cm^{-1}$ and wavelengths λ in nm.

4.2 Experimental procedures and characterization

4.2.1 Hexaphenylcyclooctadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyne (4). A solution of [6]pericyclynediol **12** (77 mg, 0.087 mmol) in DCM (50 mL) was treated with $SnCl_2$ (165 mg, 0.87 mmol) and HCl (0.87 ml, 1.74 mmol, 2 M in Et_2O) at -78 °C. The mixture was stirred at -78 °C for 10 min, then at room temperature for 25 min. After addition of aqueous 1 M NaOH (1.74 mL) and filtration through celite®, the organic layer was washed with brine three times, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by washings with Et_2O (3x5 mL) and pentane (3x5 mL) to give **4** as a dark violet solid with 65% yield (38 mg, 0.057 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.48 (d, J = 7.3 Hz, 12H, *o*-C_6H_5), 8.01 (t, J = 7.7 Hz, 12H, *m*-C_6H_5), 7.74 (t, J = 7.4 Hz, 6H, *p*-C_6H_5). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 140.25 (*i*-C_6H_5), 130.56 (*o*-C_6H_5), 129.92 (*m*-C_6H_5), 129.44 (*p*-C_6H_5), 118.46 (=*C*=*C*=, -*C*≡*C*-), 104.53 (=*C*Ph-). **HRMS** (MALDI-TOF/DCTB): *m/z*: $[M+Na]^+$ calculated for $C_{54}H_{30}Na$: 701.2245, found: 701.2225. **UV-vis** ($CHCl_3$): λ_{max} = 472 nm (ε = 234000 $L\cdot mol^{-1}\cdot cm^{-1}$). **Melting-decomposition temperature**: 221 °C.

4.2.2 1,10-bis(3,5-di-tert-butylphenyl)-4,7,13,16-tetraphenylcyclooctadeca-1,2,3,7,8,9,13,14,15-nonaen-5,11,17-triyne (11). A solution of [6]pericyclynediol **13** (130 mg, 0.123

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mmol) in DCM (100 mL) was treated with $SnCl_2$ (233 mg, 1.23 mmol) and HCl (1.3 mL, 2.453 mmol, 2 M in Et_2O) at -78 °C. The mixture was stirred at -78 °C for 20 min, then at room temperature for 15 min. After addition of 1 M aqueous NaOH (2.6 mL) and filtration through celite®, the organic layer was washed with brine three times, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by washings with Et_2O (3x5 mL) and pentane (3x5 mL) to give **11** as a dark red solid with 65% yield (47 mg, 0.052 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.59 – 9.55 (m, 8H, *o*-C_6H_5), 9.45 (d, *J* = 1.7 Hz, 4H, *o*-C_6H_3), 7.96 (dd, *J* = 8.1, 7.2 Hz, 8H, *m*-C_6H_5), 7.83 (t, *J* = 1.7 Hz, 2H, *p*-C_6H_3), 7.72 (t, *J* = 7.3 Hz, 4H, *p*-C_6H_5), 1.78 (s, 36H, -$C(CH_3)_3$). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 152.55 (*m*-C_6H_3), 140.39 (*i*-C_6H_5), 130.50 (*o*-C_6H_5), 129.85 (*m*-C_6H_5), 129.34 (*p*-C_6H_5), 127.05 (*i*-C_6H_3), 125.02 (*o*-C_6H_3), 124.22 (*p*-C_6H_3), 118.17 (=*C*=*C*=, -*C*≡*C*-), 105.63 (=*C*Ph-), 35.55 (-$C(CH_3)_3$), 31.88 (-$C(CH_3)_3$). **HRMS** (MALDI-TOF/DCTB): *m/z*: $[M]^{+\bullet}$ calculated for $C_{70}H_{62}$ 902.4852, found: 902.4787. **UV-vis** ($CHCl_3$): λ_{max} = 472 nm (ε = 248000 L·mol^{-1}·cm^{-1}). **Melting-decomposition temperature**: 230 °C.

4.2.3 4,7,13,16-tetramethoxy-1,4,7,10,13,16-hexaphenylcyclooctadeca-2,5,8,11,14,17-hexayne-1,10-diol (12). A solution of [6]pericyclynedione **10** (86 mg, 0.126 mmol) in THF (20 mL) was treated with PhMgBr (0.1 mL, 0.291 mmol) at 0 °C. The reaction mixture was stirred for 1 h at this temperature and 0.5 h at room temperature. After addition of a saturated aqueous solution of NH_4Cl, the aqueous layer was separated and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (pentane : ethyl acetate 4 : 1) to give **12** as a yellow oil with 82 % yield (87 mg, 0.104 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 – 7.62 (m, 12H, *o*-C_6H_5), 7.49 – 7.27 (m, 18H, *m*-, *p*-C_6H_5), 3.71 – 3.35 (m, 12H, -OCH_3), 3.35 – 3.05 (m, 2H, -O*H*). **^{13}C{^{1}H} NMR** (101 MHz, $CDCl_3$) δ 140.90 – 140.69 (*i*-C_6H_5-C(OH)<), 139.49 – 139.24 (*i*-C_6H_5-$C(OCH_3)$<), 129.13 – 128.92 (*p*-C_6H_5), 128.73 – 128.49 (*m*-C_6H_5), 126.56 – 126.40 (*o*-C_6H_5-$C(OCH_3)$<), 125.78 – 125.74 (*o*-C_6H_5-C(OH)<), 87.22 – 86.63, 84.65 – 84.37, 82.96 – 82.57 (-*C*≡*C*-), 72.02 – 71.91 (>*C*(OH)Ph), 65.10, 65.07 (>*C*(OCH_3)Ph), 53.48, 53.45 (-O*C*H_3). **HRMS** (MALDI-TOF/DCTB): *m/z*: $[M]^{+\bullet}$ calculated for $C_{58}H_{44}O_6$ 836.3138, found: 836.3015.

4.2.4 1,10-bis(3,5-di-tert-butylphenyl)-4,7,13,16-tetramethoxy-4,7,13,16-tetraphenylcyclooctadeca-2,5,8,11,14,17-hexayne-1,10-diol (13). A solution of [6]pericyclynedione **10** (165 mg, 0.243 mmol) in THF (20 mL) was treated with 3,5-di-tertbutyl-C_6H_3MgBr (0.625 mmol in 1 mL THF) at 0 °C. The reaction mixture was stirred for 1.5 h at this temperature and 0.5 h at room temperature. After addition of a saturated aqueous solution of NH_4Cl, the aqueous layer was separated and extracted with Et_2O. The organic layers were combined, dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by chromatography on silica gel (pentane : ethyl acetate 4 : 1) to give **13** as a yellow oil with 64 % yield (165 mg, 0.156 mmol). **^{1}H NMR** (400 MHz, CD_2Cl_2) δ 7.93 – 7.54 (m, 12H, *o*-C_6H_5), 7.54 – 7.24 (m, 14H, *m*, *p*-C_6H_5, *p*-C_6H_3), 3.70 – 3.40 (m, 12H, -OCH_3), 3.36 – 3.17 (m, 2H, -O*H*), 1.41 – 1.22 (m, 36H, -$C(CH_3)_3$). **^{13}C{^{1}H} NMR** (101 MHz, CD_2Cl_2) δ 151.41 – 151.34 (*m*-C_6H_3), 139.88 – 139.68 (*i*-C_6H_5), 139.62 – 139.52 (*i*-C_6H_3) 129.08 – 128.94 (*p*-C_6H_5), 128.56 – 128.46 (*m*-C_6H_5), 126.45 – 126.26 (*o*-C_6H_5), 123.34, 123.25 (*p*-C_6H_3), 120.24 – 120.10 (*o*-C_6H_3), 87.24 – 86.94, 84.63 – 84.37, 82.65 – 82.54 (-*C*≡*C*-), 72.02 – 71.81 (>*C*(OH)Ph), 65.77 – 65.70 (>*C*(OCH_3)Ph), 53.37 – 53.19 (-O*C*H_3), 34.96, 34.93 (-$C(CH_3)_3$), 31.20 – 31.10 (-$C(CH_3)_3$). **HRMS** (MALDI-TOF/DCTB): *m/z*: $[M+Na]^+$ calculated for $C_{74}H_{76}O_6Na$: 1083.5540, found: 1083.5476.

4.3 Crystal structure determination

Intensity data were collected at low temperature on an Apex2 Bruker diffractometer equipped with a 30W air-cooled microfocus source or on an Oxford-Diffraction Gemini (λ_{Mo} = 0.71073 Å). The structures were solved using SUPERFLIP, and refined by means of least-squares procedures on *F* using the programs of the PC version of CRYSTALS.[11] Atomic scattering factors were taken from the International Tables for X-Ray Crystallography.[12] For **4**, the asymmetric unit consists in a whole *carbo*-benzene molecule. For **11**, it contains half a molecule. Both asymmetric units contain a disordered $CHCl_3$ solvent molecule. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined using a riding model. Absorption corrections were introduced using the program MULTISCAN.

4.4 Voltammetric measurements.

Voltammetric measurements were carried out with a potentiostiat Autolab PGSTAT100 controled by GPES 4.09 software. Experiments were performed at room temperature in a home-made airtight three-electrode cell connected to a vacuum/agon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of *ca* 1 cm^2 apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter). The supporting electrolyte [*n*-Bu_4N][PF_6] was used as received (Fluka, 99 % electrochemical grade) and simply degassed under argon. The chloroform solutions used in the electrochemical study was 10^{-3} M in *carbo*-benzene and 0.1 M in supporting electrolyte. Before each measurement, the solutions are degassed by bubbling argon, and the working electrode was polished with a polishing machine (Presi P230). Typical instrumental parameters for recording square-wave voltammograms were: SW frequency f = 20 Hz, SW amplitude E_{sw} = 20 mV, scan increment *dE* = 5 mV.

4.5 Solid film fabrication and AFM measurements.

Glass substrates were cleaned with ethanol in an ultrasonic bath and were rubbed with alcohol-wetted cotton. Substrates were then dried with clean and dry air and kept at 85 °C over 15 min. Before deposition of the compound layers by spin-cast (blend of 11:PCBM) from a chlorobenzene solution (at 30 mg/mL), substrates were treated with UV oxygen plasma for 5 min. The solution was stirred for 4 h and deposited by spin-coating at 1500 rpm for 30 s in a N_2 glovebox. Morphology, roughness and thickness were analyzed by means of atomic force microscopy (AFM) with a microscope easyscan2 from Nanosurf, with a maximum square scanning area of 110 µm, operating in contact mode under ambient conditions (see S.I.).

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