

Supramolecular Chemistry

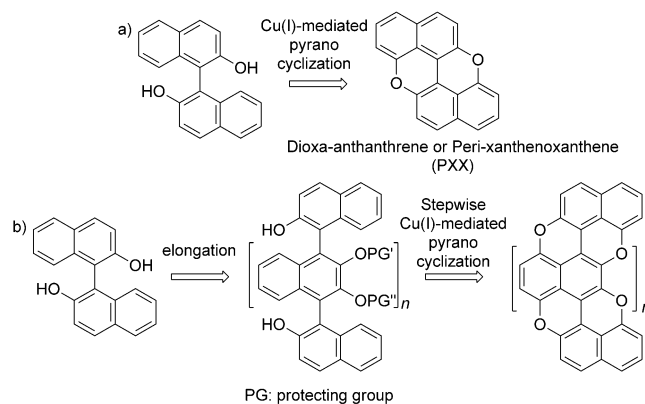
International Edition: DOI: 10.1002/anie.201509517
German Edition: DOI: 10.1002/ange.201509517

Extended O-Doped Polycyclic Aromatic Hydrocarbons

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Abstract: The synthesis of O-doped benzorylenees, in which peripheral carbon atoms have been replaced by oxygen atoms, has been achieved for the first time. This includes key high-yielding ring-closure steps which, through intramolecular C–O bond formation, allow stepwise planarization of oligonaphthalenes. Single-crystal X-ray diffraction showed that the tetraoxa derivative forms remarkable face-to-face π – π stacks in the solid state, a favorable solid-state arrangement for organic electronics.

Discrete and extended polycyclic all-carbon aromatic hydrocarbons (PAHs)^[1,2] have polarized great interest^[3–7] as ultralight materials for engineering flexible optoelectronic devices. Replacing the carbon atoms with other isostructural atoms at given positions^[8,9] is now developing as a versatile functionalization strategy to control the chemical, charge-carrier, and self-assembly behaviors of PAHs.^[10] Specifically, in the last years, we took note of the renaissance of O-doped aromatics such as peri-xanthenoxanthene (PXX; Scheme 1). These molecules are in fact characterized by excellent carrier-transport and injection properties, as well as easy processability, chemical inertness, and high-thermal stability.^[11] Because of these properties, PXX has proven exceptional performance when used as an active organic semiconductor (OSC) in transistors for rollable OLEDs.^[12–14] However, the expansion of PXX into larger O-doped frameworks has so far remained unexplored (Figure 1), although understanding and controlling the O-doping ratio could provide the conceptual basis to engineer a new family of OSCs with tunable optoelectronic properties.



Scheme 1. a) Pyranopyran-fusing approach for preparing a PXX core. b) Synthetic strategy toward the O-doped benzorylenees.

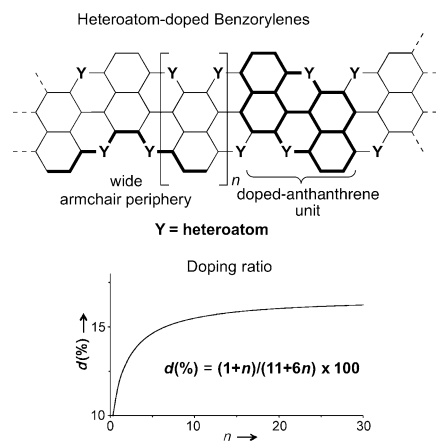


Figure 1. Heteroatom-doped benzorylenees and its distinctive doping ratio (d) as function of the number (n) of dihydroxynaphthalenyl units.

Herein we describe the synthesis of unprecedented O-doped benzorylenees (Scheme 1), like pentaphenopentaphene and naphotetraphenopyranthrene ($n = 1$ and 2 , respectively), featuring a tailored topological periphery and doping ratio, d , with the latter being controlled by the number of the monomeric units. Generally, controlled doping patterns in discrete graphene substructures are obtained through bottom-up synthesis involving monomeric aromatic heterocycles which are preorganized in a covalent scaffold and successively planarized through oxidative C–C bond formation.^[10,15–17] In our approach, we instead considered the O-doped benzorylenees derived from oligonaphthalenes with 2,3-dihydroxynaphthalene and 2-hydroxynaphthalene moieties as the key monomeric and capping units, respectively (Scheme 1b). At the synthetic planning level, this consideration guided us to contemplate the oxidative metal-mediated formation of C–O bonds in a pyranopyran motif (Scheme 1a)

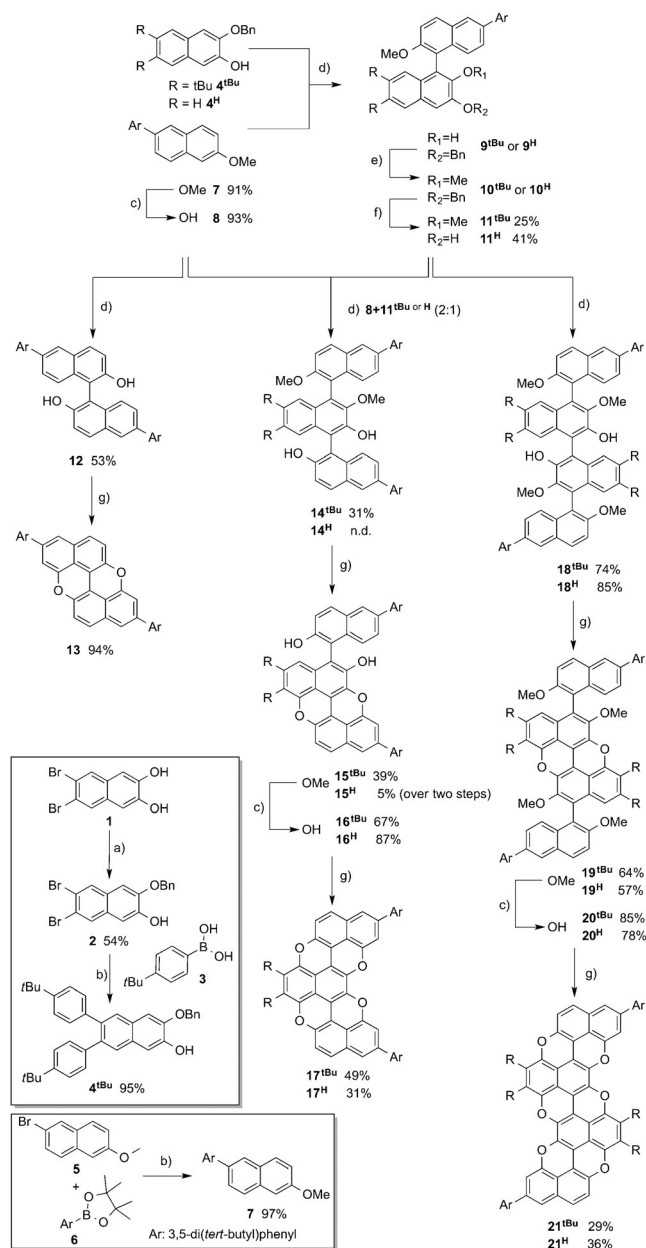
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Supporting information for this article can be found under:
<http://dx.doi.org/10.1002/anie.201509517>.

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as the planarization reaction. As we anticipated potential susceptibility of the 2,3-dihydroxynaphthalenyl moieties under oxidative conditions, a decision was made to protect the hydroxy groups and to follow a two-step planarization protocol (Scheme 1b).

Specifically, two classes of molecules were prepared (Scheme 2): one bearing only 3,5-di(*tert*-butyl)phenyl substituents (**13**, **17^H**, and **21^H**) and another with extra 4-*tert*-butylphenyl side groups (**17^{tBuPh}** and **21^{tBuPh}**) to favor solubility. The key 1,4-linked oligonaphthalene skeletons (**12**, **14**, and **18**) were synthesized by sequential oxidative coupling



Scheme 2. Synthetic path for **13**, **17^X**, and **21^X** ($X = \text{H}$ or $t\text{BuPh}$). In the frames: synthesis of the naphthol building blocks. a) NaHCO_3 , BnBr , DMF , 100°C ; b) Cs_2CO_3 , $[\text{Pd}(\text{PPh}_3)_4]$, $\text{toluene}/\text{DMF}/\text{EtOH}$, microwave, 100°C ; c) BBr_3 , CH_2Cl_2 , 0°C ; d) CuCl_2 , (\pm)-1-phenylethylamine, MeOH , CH_2Cl_2 , 0°C ; e) K_2CO_3 , MeI , acetone, reflux; f) H_2 , Pd/C , CHCl_3 , AcOH ; g) CuI , PivOH , DMSO , $130\text{--}145^\circ\text{C}$.

reactions in the presence of racemic phenylethylamine and CuCl_2 .^[18] It should be noted that the intermediates **9–12** were prepared and used as racemates. The same applies for the molecules **14–16** and **18–20**.

To commence, the naphthol **8** (prepared starting from 6-bromo methoxynaphthalene **5** by a Suzuki cross-coupling reaction followed by cleavage of the methoxy group with BBr_3) was dimerized by copper(II)-mediated oxidative coupling into binaphthyl **12**, which was used as model substrate. Despite numerous works describing the preparation of dibenzofurans,^[19] only a few synthetic strategies have been developed to date for the formation of benzopyranes.^[20] Amongst those, the modified protocol described by Pummerer and co-workers^[21] with CuO allowed the transformation of **12** into the PXX derivative **13** in 42% yield. However, when CuI was used in the presence of O_2 and PivOH in DMSO at 140°C ,^[22] we exceptionally improved the yield to 94%. In any circumstances, CuOAc gave inferior yields while other transition metals gave either low yields or no conversion.

For preparing the quaternaphthalene derivatives, **8** was cross-coupled with either the monobenzyl dihydroxynaphthalene **4^H** or **4^{tBuPh}** (the latter prepared from the 6,7-dibromo precursor, **1**,^[23] through double Suzuki cross-coupling and monobenylation reactions) by copper(II)-promoted cross-coupling to yield the monohydroxy binaphthalenes **11^H** and **11^{tBuPh}**, respectively, after methylation and cleavage of the benzyl ether. Subsequent oxidative dimerization of **11^H** and **11^{tBuPh}** gave the quaternaphthalenes **18^H** (85%) and **18^{tBuPh}** (74%), respectively, as isomeric mixtures. Intramolecular etherification of **18^H** and **18^{tBuPh}** afforded the intermediates **19^H** and **19^{tBuPh}**, respectively, as diastereoisomeric mixtures where the *cis*-(*cis*-**19^H** and *cis*-**19^{tBuPh}**) and *trans*-(*trans*-**19^H** and *trans*-**19^{tBuPh}**) isomers could be easily separated. Small transparent crystals of both isomers of **19^{tBuPh}** were obtained by vapor diffusion. X-ray analysis confirmed the presence of the central pyranopyran cycle with two naphthalenyl substituents in the *cis* and *trans* configurations (Figure 2). Removal of the

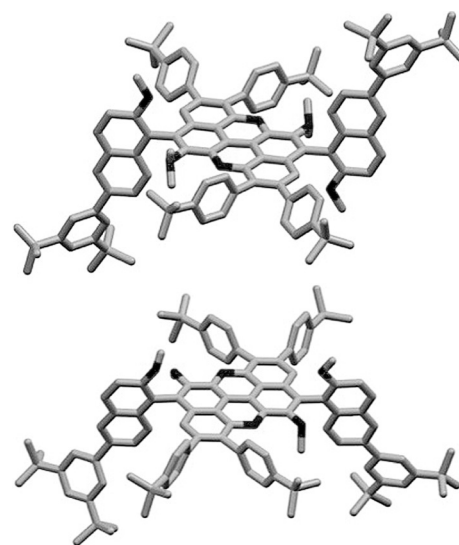


Figure 2. Crystal structures of *trans*-**19^{tBuPh}** (above) and *cis*-**19^{tBuPh}** (below).^[25] Space groups $P21/c$ and $P\bar{1}$, respectively. C gray, O black.

methyl protecting groups by BBr_3 and subsequent the CuI-mediated ring-closure reaction led to the formation of the tripyranopyran derivatives $\mathbf{21}^{\text{H}}$ and $\mathbf{21}^{\text{tBuPh}}$ in 36% and 29% yield, respectively. The fully conjugated tetramers $\mathbf{21}^{\text{H}}$ and $\mathbf{21}^{\text{tBuPh}}$ were unambiguously identified by HR-MALDI through the detection of the peaks corresponding to the molecular ions (M^+) at m/z 966.3935 ($\text{C}_{68}\text{H}_{54}\text{O}_6^+$, calc.: 966.3920) and 1494.7526 ($\text{C}_{108}\text{H}_{102}\text{O}_6^+$, calc.: 1494.7556), respectively.

In parallel, the fused bispyranopyran $\mathbf{17}^{\text{H}}$ and $\mathbf{17}^{\text{tBuPh}}$ were also prepared. The naphthol **8** was cross-coupled with $\mathbf{11}^{\text{H}}$ and $\mathbf{11}^{\text{tBuPh}}$ to afford the dihydroxyternaphthalenes $\mathbf{14}^{\text{H}}$ and $\mathbf{14}^{\text{tBuPh}}$, respectively, as isomeric mixtures (dimer **12** and tetramers $\mathbf{18}^{\text{H}}$ and $\mathbf{18}^{\text{tBuPh}}$ were also obtained as side-products). Successive pyranopyran fusion led to the corresponding intermediates $\mathbf{15}^{\text{H}}$ and $\mathbf{15}^{\text{tBuPh}}$. BBr_3 -promoted cleavage of the methyl groups followed by the oxidative cyclization yielded $\mathbf{17}^{\text{H}}$ and $\mathbf{17}^{\text{tBuPh}}$ in 31% and 49% yield, respectively. Again, $\mathbf{17}^{\text{H}}$ and $\mathbf{17}^{\text{tBuPh}}$ were clearly identified by HR-MALDI through detection of the peaks related to the molecular ions (M^+) at m/z 812.3848 ($\text{C}_{58}\text{H}_{52}\text{O}_4^+$, calc.: 812.3866) and 1076.5760 ($\text{C}_{78}\text{H}_{76}\text{O}_4^+$, calc.: 1076.5744), respectively. Surprisingly, ^1H NMR investigations of the final molecules were inconclusive as only broad peaks were observed after planarization.

However, upon addition of a few drops of NH_2NH_2 to a $[\text{D}_8]$ THF solution of some samples of $\mathbf{17}^{\text{tBuPh}}$, a sharpening of the proton resonances was observed. As shown in Figure 3, the ^1H NMR spectrum of the sample containing NH_2NH_2 features well-resolved peaks, thus perfectly integrating the 22 aromatic proton resonances expected for $\mathbf{17}^{\text{tBuPh}}$. This spectrum could suggest that a fraction of the compound is present as a radical cation. Notably, for $\mathbf{17}^{\text{H}}$, $\mathbf{21}^{\text{H}}$ and $\mathbf{21}^{\text{tBuPh}}$ the addition of NH_2NH_2 was fruitless, and only broad resonances in the ^1H NMR spectra were observed. To further corroborate

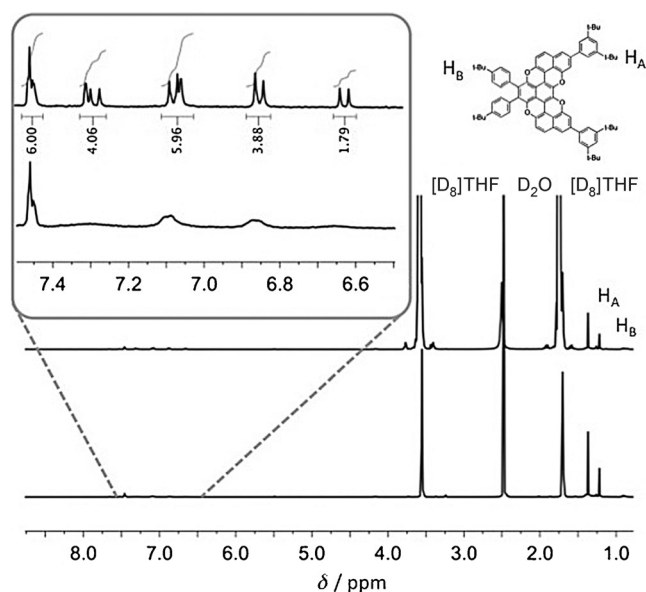


Figure 3. ^1H -NMR spectra (400 MHz, $[\text{D}_8]$ THF) of $\mathbf{17}^{\text{tBuPh}}$ before (below) and after addition of NH_2NH_2 (above).

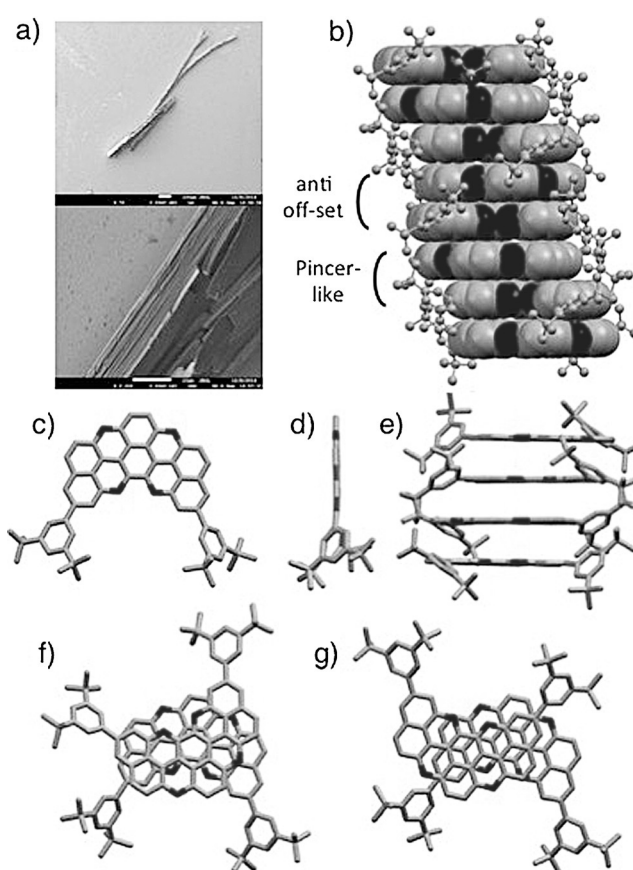


Figure 4. a) SEM images of the crystals of $\mathbf{17}^{\text{H}}$ displaying a lamellar-like texture. b–e) Solid-state columnar π - π stacks with an interplanar distance of 3.3 Å. c, d) Top- and side-view of the crystal structure. f) Pincerlike and g) *anti* off-set π - π stacking arrangements. Space group: $P\bar{1}$. C gray, O black.

the chemical structure of the bis(pyranopyran) derivative, crystals suitable for X-ray diffraction analysis were obtained by vapor diffusion of *i*PrOH into a CH_2Br_2 solution of $\mathbf{17}^{\text{H}}$ (Figure 4). The X-ray structure confirms the nearly flat boomerang-like shape of the pentaphenopentaphene framework, in which four oxygen atoms have replaced four carbon atoms at the peripheries.

Looking at its organization at the solid state (Figures 4b and e), one can clearly evidence the presence of a columnar arrangement in which the molecules are organized in π - π stacks, with an average interplanar spacing of 3.3 Å. Two face-to-face stacking modes are apparent: a pincerlike stack (Figure 4f), in which two crystallographically independent molecules are facing each other in an antiparallel fashion with a relative angle of about 36°, and an *anti* offset shift (Figure 4g), where two molecules stack in an antiparallel arrangement with a lateral offset of about 3.4 Å and 0.8 Å for the other crystallographically independent molecule.

UV-vis steady-state absorption spectra of $\mathbf{13}$, $\mathbf{17}^{\text{X}}$, $\mathbf{21}^{\text{X}}$ are shown in Figure 5. While the spectrum of the PXX derivative features the typical electronic transitions at $\lambda = 392$, 421 and 449 nm, the spectra for conjugates $\mathbf{17}^{\text{X}}$ and $\mathbf{21}^{\text{X}}$ appear much broader. In particular, the absorption spectra of $\mathbf{17}^{\text{H}}$ and $\mathbf{17}^{\text{tBuPh}}$ display unstructured low-intensity red-shifted bands at

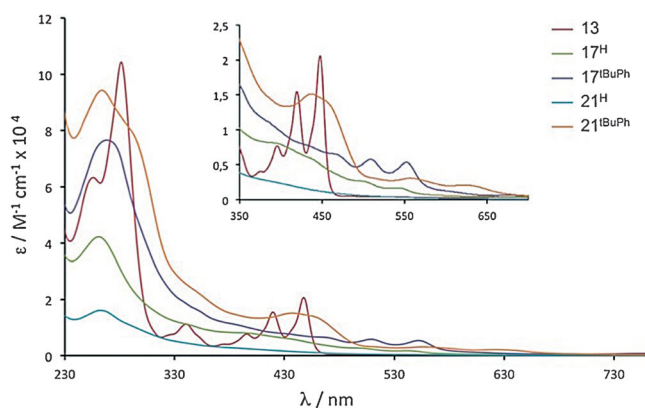


Figure 5. Steady-state UV-vis absorption spectra of **13**, **17^H**, and **21^H** in CH_2Cl_2 .

$\lambda = 412$, 509 and 552 nm, whereas only a long absorption tail reaching $\lambda = 650$ nm is observed for both **21^H** and **21^{tBuPh}**. Variable-temperature measurements did not display any significant sharpening of the electronic transitions even at elevated temperatures (80 °C; see Figure S15 in the Supporting Information). Together with the ^1H NMR results, the intense broadening of the electronic transitions suggests that these O-doped molecules most likely undergo strong aggregation. This aggregation can possibly occur either by simple π -stacking interactions between neutral molecules or between a radical-cation with its neutral counterparts in mixed-valence complexes,^[24] or through the formation of covalent oligomers possibly deriving from a radical recombination followed by proton elimination.

While the formation of mixed-valence species can be realistically excluded because of the absence of electronic transitions fingerprinting a charge transfer in the NIR spectral region (see Figure S12),^[24] HRMS-MALDI and tandem mass (MSMS) measurements unambiguously displayed the presence of oligomeric species, and are supportive of the presence of aggregates even in the gas phase. In particular, peaks at m/z 1624 and 3247 could be discerned, thus suggesting the presence of dimeric and tetrameric species for **17^H** (Figure S18a). MSMS analysis at m/z 3247 and 1624 suggest that the dimers are formed by a combination of covalent [**17^H**]₂-2H and noncovalent [**17^H**]₂ complexes (Figure S18c,d,e,f,h). In contrast, the tetrameric species (Figure S18b,g,h) are constituted by noncovalent complexes of covalent dimers, [(**17^H**)₂-2H]₂.

In conclusion, we have described the first methodology to prepare unprecedented O-doped benzorlylenes by using a stepwise planarization strategy. This approach involves the simultaneous formation of C–O bonds through an intramolecular copper(I)-mediated oxidative reaction originating pyranopyran rings. First X-ray diffraction showed that the tetraoxa derivative undergoes strong π -stacking in the solid state to form lamellar-like microstructures. The remarkable propensity of this class of molecules to undergo self-aggregation is intriguing in view of the design of organic materials to be used in optoelectronic devices. Detailed electron paramagnetic resonance, electrochemical, and conductivity studies are under investigation to fully understand the

chemical behavior of this class of O-doped π -conjugated framework, as well as their potential for engineering transistors.

Acknowledgments

D.B. gratefully acknowledges the EU through the ERC Starting Grant “COLORLANDS” project, the FRS-FNRS (FRFC contract n° 2.4.550.09), the Science Policy Office of the Belgian Federal Government (BELSPO-IAP 7/05 project), and the “TINTIN” ARC project (09/14-023). D.S. thanks the FNRS for her doctoral fellowship. We thank B. Norberg and Prof. J. Wouters (UNamur) for the crystal structure n° 1415364.

Keywords: copper · cyclization · macromolecules · nanostructures · supramolecular chemistry

How to cite: *Angew. Chem. Int. Ed.* **2016**, *55*, 5947–5951
Angew. Chem. **2016**, *128*, 6051–6055

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- [25] CCDC 1415364 (*trans*-**19**^{BuPh}), 1416668 (*cis*-**19**^{BuPh}), 1416669 (**17**^H) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Received: October 11, 2015

Revised: December 29, 2015

Published online: April 8, 2016