Abstract: Herein we report a versatile concept for the synthesis of fourfold functionalized, soluble pyrenes, peropyrenes, terropyrenes, and quarterropyrenes. They were obtained by a modular stepwise approach towards the rylene scaffold via Suzuki–Miyaura cross–coupling, oxidative cyclodehydrogenation in the presence of caesium hydroxide under air, and finally zinc-mediated reductive silylation. The silylated reaction products were characterized by X-ray crystallography. The first example of a synthesized and crystallized quarterropyrene is presented and its oxidation reaction investigated. The functionalized ropyrenes were systematically characterized by means of UV/Vis–NIR and photoluminescence spectroscopy showing a bathochromic shift of 80 nm per naphthalene unit and a nearly linear increase of the extinction coefficients. Cyclic voltammograms and DFT calculations identify them as electron-rich dyes and show a narrowing of the electrochemically determined HOMO–LUMO gap and lower oxidation potentials for the higher homologues.

Polyaromatic hydrocarbons (PAHs) offer a huge variety of applications related to their unique (opto-)electronic properties, for example in materials for organic electronics and photovoltaics.[1] Studies elucidating structure–property relations gave rise to the synthesis of nanographenes with defined structures and tailored properties.[2] Especially the edge structure and width determine their electronic properties (band structure).[3] The family of poly-perinaphthalenes (rylenes, see Figure 1b), also known as 5-armchair graphene nanoribbons (5-AGNRs), is a broadly studied class of PAHs.[4] Compared to other GNRs their simple structure, broad spectral light absorbance,[5] and singlet fission properties,[6] as well as length-dependent band gap sizes[7] were motivation for recent years.[17–20] Terropyrenes, for example, the unsubstituted stem system[23] or bent varieties for cyclophane syntheses,[24] are rare in literature. All published strategies required multi-step organic syntheses, especially for accessing the higher homologues, terropyrenes.[22,25,26] Key of the synthesis route reported by Chalifoux and co-workers are iterative extensions of aromatic systems using two- or tetrafold alkynylated precursors in acid-mediated,[25,26] or InCl₃-catalyzed benzannulations.[25]

Inspired by the modular construction principle of higher rylene diimide dyes[11,13,15] and the novel reductive functionalization approaches for naphthalene diimide (NTCDI)[28] and perylene diimide (PTCDI)[29,30] in our group and in the group of Miyake, we intended to reductively access higher homologue ropyrenes. The precursors 2, 3, 11, and 12 of the final peropyrenes, teropyrenes, and quarterropyrenes are synthesized in analogy to the modular synthesis of soluble, liquid crystalline dihydroxy-ropyrene-quinoines reported by Buffet and Bock (Scheme 1).[31] Peropyrenequinone 2 was directly reduced and silylated, reacting with Zn as reducing agent in the presence of trimethylsilylethyl chloride to the orange air sensitive peropyrene silyl ether 4. Zinc turned out to be the best reducing agent. It is readily available, non-toxic, and processable even under non-inert conditions. For reductive silylation of the smaller dihydroxy pyrenequinone 2 we could introduce four trisopropylsilyl groups, leading to highly soluble pyrene-tetrasilyl ether 5 in rather poor yield. Next,
we turned our attention to the application of a similar reduction protocol to obtain the higher homologues of 2, terropyrenequinone 11 and quarterropyrenequinone 12.

11 and 12 were synthesized in a facile two-step protocol starting with bis-boronic acid pinacol esters 6 and 7 together with peri-brominated hydroxyphenalenone 8 under standard Suzuki–Miyaura coupling conditions in a 1:2 ratio. The resulting ter- and quarternaphthyls 9 and 10 could be isolated as inseparable isomer mixture (see SI) by a simple precipitation due to protonation with diluted acetic acid and subsequent washing with methanol. Non-planar 9 and 10 were heated in a CsOH melt for three hours to 280 °C in a Ni-crucible on air until the gas evolution ceased. We chose CsOH as base because of the improved intercalation and interaction capabilities of caesium cations with intermediately formed aromatic anions. 11 and 12 were isolated as insoluble dark blue solids that were directly used for further transformations.

Surprisingly, 11 and 12 reacted under similar conditions as 2 with zinc and trialkylsilyl chlorides in dioxane despite their insolubility at 100 °C. The resulting silylated products were soluble since their capability of π–π stacking is reduced due to the sterically demanding silyl groups. Hence, a similar terropyrene-trimethylsilylether 13, as a higher homologue to 4, could be isolated as purple-red solid. After activating triisopropylsilyl chloride with imidazole, a reductive silylation of 11 and even 12 yielded the air stable terropyrene-trisopropyl silylether 14 and royal blue colored quarterropyrene-trisopropylsilyl 15 with superior solubility, high purity, however low yields. Both 14 and 15 could be isolated by column chromatography with dichloromethane. We further synthesized a congener of 15 with n-butyl groups in both terminal positions and TMS groups (S4) in order to improve the solubility, but the solubilizing effect of non-bulky butyl groups was not significantly more effective. Unfortunately, all attempts to synthesize a higher homologue penterropyrene were not successful so far, since the corresponding penterropyrene-quinone was too insoluble for further transformations.

The good solubility of our silylated rylenes 4, 13, and 15 in chlorinated solvents made it possible to obtain X-ray diffractional single crystals via slow gas phase diffusion of n-pentane (Figure 2). Trimethylsilyl ethers 4 and 13 crystallize in the monoclinic space group P2₁/c with π–π stacking pairs (dπ–π = 3.30 Å (4) and 3.64 Å (13)) of molecules oriented in a herringbone arrangement for 13. Quarterropyrene 15 crystallizes in the monoclinic spacegroup P2₁/n being the first investigated quarterropyrene in the crystalline state to the best of our knowledge. Its bulkier TIPS groups do not prevent the face-to-face π–π stacking interactions in the solid state...
Figure S7. Typical for rylene dyes,\textsuperscript{11,13} the absorption spectra of a) pyrene silylethers and b) cyclovoltammograms of both quarter-luminescence spectroscopy as well as cyclovoltammetry. The absorption maxima ($\lambda_{\text{max}}$) and extinction coefficients ($\varepsilon$) increase nearly linearly with each additional naphthalene unit [a bathochromic shift of about 80 nm and an increase of the extinction coefficient from $\varepsilon = 24500 \text{ Lmol}^{-1}\text{s}^{-1}$ for 5 to $\varepsilon = 128200 \text{ Lmol}^{-1}\text{s}^{-1}$ for 15 (Figure 3a)] with extinction coefficients in slightly smaller magnitudes compared to the related rylene diimides.\textsuperscript{11,13} All four compounds showed nearly no concentration-dependent absorption maxima (see Figure S2–S6). TD-DFT (see Figure S13) supports the trend also regarding the oscillator strengths of the $\lambda_{\text{max}}$ transitions. The mirrored emission spectra reveal a similar trend with Stokes shifts of around 15 nm. 4, 13, and 15 show strong vibronic progressions indicating, together with the narrow Stokes shift, small reorganization energies.\textsuperscript{34} A broadening of the bands can be observed for the higher homologues. Measured fluorescence quantum yields ($\phi_{\text{FL}}$, see SI) were only moderately high in case of 4 (0.30), lower for 13 (0.08) and 14 (0.06), and undetectably low in 4 and 15 with bulky rotating TIPS groups most likely deactivating the fluorescence through reorganization energy loss. The predictable evolution of optical properties can also be rationalized with the Kohn–Sham molecular orbitals of the HOMO and LUMO for 4, 5, 13, and 15, being of similar modular symmetry (Figure 3d). The frontier molecular orbital energies were experimentally assigned using cyclic voltammetry (Figure 3c). The electron-rich dyes 4, 5, 14, and 15 show two pronounced and quasi-reversible oxidation potential waves, whereas only 14 shows one and 15 shows two not fully reversible reduction potential waves within the electrochemical window of dichloromethane. In comparison to reported arylated pero- and teropyrenes, 5 and 14 show lower oxidation potentials and are therefore more electron-rich.\textsuperscript{29} Additionally, a narrowing of the electrochemically determined HOMO–LUMO gap with the growing π-system could be observed. The experimental HOMO energies were referenced to the vacuum energy level of the ferrocene/ferrocenium redox couple (−4.8 eV\textsuperscript{35} see Figure S8–S12) and the LUMO energy was accessed with the help of the optical HOMO–LUMO gap (determined from the intersection wavelength of normalized UV/Vis and PL spectra\textsuperscript{36}). Both experiment and theory show an energy gap ($E_g$) narrowing from $E_g = 3.02 \text{ eV}$ (theory 3.48 eV) for pyrene 5 to 1.93 eV (theory 1.96 eV) to 15, respectively (see Table 1). This is indicated by higher HOMO and lower LUMO energies (from experimentally −5.01 eV (HOMO) and −2.04 eV (LUMO) of 5 to −4.62 eV (HOMO) and −2.73 eV (LUMO) for 15), with theoretical values supporting the observed trends. In comparison with arylated rylene s, silylether substitution leads to higher HOMO levels.\textsuperscript{29}

The high HOMO value of 15 and also the existence of a non-zero baseline in the NIR region of the UV/Vis spectrum gave rise to the assumption that minor amounts of the oxidation product [15\textsuperscript{+}] are present after column chromatography with dichloromethane, also observed for other electron-rich PAHs and resulting from traces of acid in the presence of air.\textsuperscript{37} In order to study the oxidation product of 15, we added the oxidant nitrosyl tetrafluoroborate (NOBF\textsubscript{4}) in a UV/Vis–NIR titration experiment. Upon addition of excess (10 equiv) of NOBF\textsubscript{4} a gradual color change from blue to turquoise green and broad NIR absorption bands appearing at 820 and 1050 nm (Figure 4) were observed. Addition of...
more than 10 equiv NOBF_4 had no further effect. Using 1H NMR, the formation of a paramagnetic compound could be observed by the absence of distinct signals. TD-DFT calculations (see SI, Figure S15) of [15] describe the novel band at 1050 nm as SOMO–LUMO transition.

In summary, we report a facile and efficient access to the higher homologues of peropyrene by a modular and scalable synthetic bottom-up approach with a reductive aromatization by Zn/R_3SiCl as a key step towards functionalized, soluble, and easily isolable electron-rich rylene silylethers. Supported by comprehensive experimental spectroscopy and spectrometry, the influence of the enlargement by naphthalene units on the HOMO–LUMO gap was rationalized by spectroscopy, CV, and DFT calculations. As OSiR_3 groups can be converted to OTf functionalities for further transformations, we are convinced that our new synthesis strategy allows an efficient general synthetic entry into novel functionalized PAHs for high-performance organic electronic materials.

Supporting Information available: Additional experimental details, NMR spectra, CV/DPV measurements, UV/Vis and TD-DFT spectroscopy, cartesian coordinates of calculated structures (XYZ), and XRD data. The CIF files of the presented structures are provided.

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