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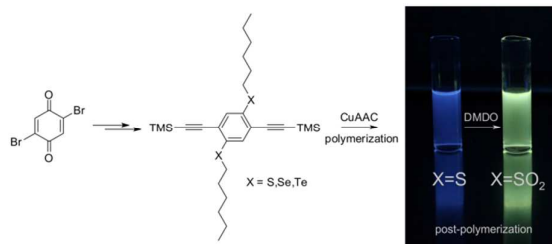
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Novel building blocks for functional organic materials have been synthesized,

subjected to polymerization and subsequently to post-polymerization modification.

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LETTER

Multigram Synthesis of Bis[(trimethylsilyl)ethynyl]benzenes suitable for Post-Polymerization Modification[†]

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Novel substituted bis[(trimethylsilyl)ethynyl]benzenes have been prepared as versatile building blocks for organic functional materials. The resulting effects of replacing sulfur by selenium and tellurium on photo-physical and electro-chemical properties have been examined. Polymerization via microwave-assisted Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) and subsequent post-polymerization modification by oxidation reveals the utility of the developed building blocks.

1,4-bis[(trimethylsilyl)ethynyl]-2,5-bis(hexyloxy)benzene (X = O) and the desilylated species 1,4-bis(ethynyl)-2,5-bis(hexyloxy) benzene are of current interest in the synthesis of a growing number of functional organic materials such as fluorescent polymers,[1] conjugated sensor materials,[2, 3] conducting metallopolymers[4] and special materials like shape-persistent macrocycles.[5] In terms of further applications, the two alkyne groups enable the functionalization by a variety of established reactions such as alkyne metathesis,[6, 7] Glaser coupling,[8] Sonogashira coupling,[9] azide-alkyne cycloaddition,[10] etc.

Despite the widespread utility of hexyloxy-substituted benzenes,[1-5] the synthesis of the sulfur, selenium and tellurium containing analogs **6a-c** has not been reported up to date. However, replacing the oxygen atom by these elements may significantly affect material properties, as reported for heterocyclic polymers polyfuran, -thiophene, -selenophene and -tellurophene. Whereas polyfuran has attracted less attention, polythiophenes are widely utilized due to

their conducting properties.[11] Replacing sulfur by selenium in polythiophenes results in reduced bandgaps and lower LUMO energy levels, leading to ambipolar charge transport properties.[12] In contrast, characteristics of polytellurophene are severely affected by Te-Te interactions, which are expected to result in strong interchain electronic coupling.[13]

We report on a straight-forward, comparatively cheap and scalable synthesis of novel sulfur, selenium and tellurium based analogs (**6a-c**) of 1,4-bis[(trimethylsilyl)-ethynyl]2,5-bis(hexyloxy)benzene. The introduction of these elements does not only impact material properties but also allows for a specific modification of photo-physical and electro-chemical characteristics by simple oxidation, which is demonstrated on the example of post-polymerization modification.

The discussion of the results is split into two subchapters: (1) the large-scale synthesis of novel building-blocks for functional organic polymers and (2) an exemplary application of the developed monomers in materials suitable for post-polymerization modification.

The synthetic pathway towards monomers **6a-c** is illustrated in Scheme 1. A multigram synthesis of 2,5-dibromobenzoquinone **3** from 1,4-dimethoxybenzene **1** was previously reported by López-Alvarado, et al.[14] Following this procedure, the synthesis of **3** could be achieved at 30 g scale (71%).

Nucleophilic addition[15] of TMS-acetylene applying *n*-BuLi resulted in an isomeric mixture of **4a** and **4b** (3:1 (cis/trans), not assigned) in good yield of 85% (20 g). Since both isomers are converted to **5** at similar rates in the subsequent reductive aromatization, a separation of the two isomers is not required. Nevertheless, the removal of impurities by filtration through a pad of silica and trituration in boiling *n*-hexane proved to be advantageous to avoid the cleavage of the TMS-group in the subsequent reduction step[15] to **5**, which was accomplished in good yields of 94% (12 g) using SnCl₂·2H₂O. The hexylthio-, hexylseleno- and hexyltelluro-groups were introduced by a lithium-halogen exchange and subsequent addition of either elemental sulfur or selenium and hexyl iodide to afford **6a** (2.5 g, 63%) and **6b** (1.7 g, 73%) or dihexyl ditelluride[16] to obtain **6c** (1.5 g, 53%).

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[†] Electronic supplementary information (ESI) for the synthesis and characterization of all synthesized compounds as well as crystal structures and Crystallographic Information Files (CIFs) for **6a**, **6b** and **6d** are available; See DOI: 10.1039/c000000x/
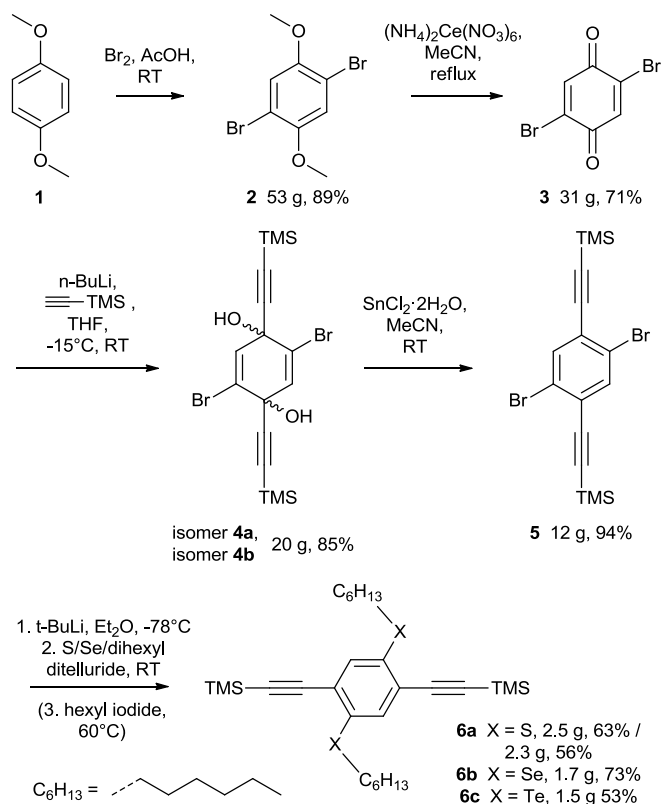
Scheme 1 Synthetic route towards monomers **6a-c**.

To ensure scalability, all steps toward **5** were carried out utilizing purification techniques such as extraction, crystallization, trituration and flash filtration through silica. **6a-c** were purified by column chromatography; however, exemplarily **6a** was alternatively purified by crystallization, resulting in only slightly lower yields (56% instead of 63%).

An alternative modification approach to the heteroatom exchange (S / Se / Te) represents the possibility to modify molecular properties by selective oxidation of these elements. This enables to directly convert the electron donating +M-substituent (e.g. alkylthio) to an electron accepting –M-substituent (e.g. sulfone), thus significantly influencing electro-chemical and photo-physical characteristics.

In order to evaluate convenient oxidation conditions the conversion of **6a** to sulfone **6d** was chosen as a model reaction (Scheme 2). Dimethyldioxirane (DMDO), a mild and versatile oxidation reagent, proved to be particularly advantageous with regard to purification, selectivity as well as efficiency (98%). With regard to applicability of this oxidation reagent, our group reported on a practical and efficient large-scale preparation of DMDO.[17]
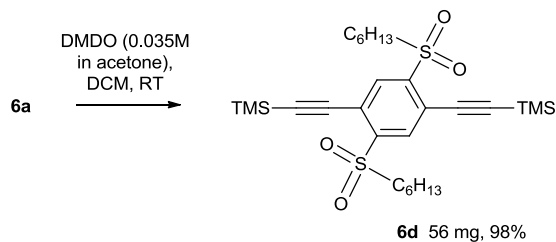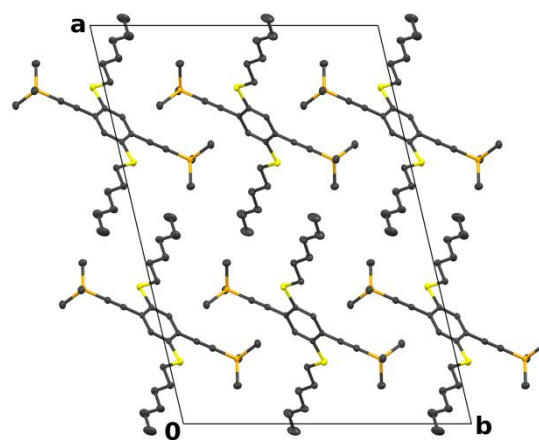

Scheme 2 General oxidation protocol towards **6d**.

Fig. 1 Crystal structure of **6a** viewed down [010]. C, S and Si atoms are represented by gray, yellow and orange ellipsoids drawn at 50% probability levels, respectively. H atoms were omitted for clarity.

Single crystals of **6a** and **6b** were obtained by solvent evaporation from *n*-hexane;[18] **6c** did not give suitable crystals. The crystal structure of **6a** is shown in Fig 1.

The crystal structures of **6a**[18] and **6b**[18] are isostructural and possess *C*2/*c* symmetry. One crystallographically unique molecule is located on a center of inversion. The hexyl chains extend in the plane of the benzene ring. Indeed, with the exception of the TMS groups the molecules are virtually flat: The largest distance of a non-H atom with the exception of the TMS-methyl groups to the least squares plane defined by the atoms of the π-conjugated core is 0.0958(13) Å (**6a**) and 0.121(3) Å (**6b**). The terminal atoms of the hexyl chain feature enlarged atomic displacement parameters, indicating static or dynamic disorder as expected for long alkyl chains. The molecules are arranged in a three dimensional network controlled solely by van-der-Waals interactions. As expected, the unit cell volume of **6b** is slightly larger than of **6a** (3164.8(8) vs. 3085.8(3) Å^3) due to the additional space required by the Se atom.[18]

6d[18] (crystals were grown by solvent evaporation from ethanol) crystallizes in space group *P*2$_1$/*c*. Although, like in **6a** and **6b**, the molecules are located on centers of inversion, **6d** is structurally unrelated to the former. Most notably, the hexyl chains in **6d** propagate nearly perpendicular to the plane of the benzene ring. They are located in pockets of the structure and the three terminal aliphatic C atoms feature disorder.

Electro-chemical and photo-physical properties of **6a-d** were probed by cyclic voltammetry (CV) as well as photometry (UV-vis absorption). CV revealed similar HOMO energy levels for compounds **6a** (-5.35 eV) and **6b** (-5.31 eV), whereas tellurium compound **6c** showed a significantly higher HOMO energy level of -5.08 eV. This fact is also indicated by decomposition of **6c** in DCM solution in contrast to **6a** and **6b**. DFT calculation performed did not reproduce the observed higher HOMO level for **6c**; however, a similar phenomenon for tellurium based compounds has been described in literature.[19]

UV-vis absorption spectra of **6a-c** are depicted in Fig 2 (right). The high wavelength absorption bands of **6a-c** are broad weak peaks, which are characteristic for n --> π* transitions. The bands below 320 nm are attributed to π --> π* transitions, given their spectral shape (vibronic structures) and intensity. The optical bandgaps were determined from the absorption on-sets (Table 1). Similar values for the optical bandgap have been observed for **6a** and **6b**, indicating
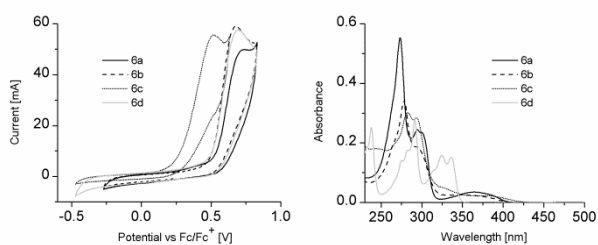
Fig. 2 CV charts of irreversible oxidation (left) and UV-vis absorption spectra (right) of **6a-d**.

Table 1 Photo-physical and electro-chemical data of **6a-d**.

	E_{ox} [V][a]	$\lambda_{on\text{-}set}$ [nm][b] / optical bandgap [eV]	HOMO level [eV][c]
6a	0.55	406 / 3.05	-5.35
6b	0.51	408 / 3.04	-5.31
6c	0.28	425 / 2.92	-5.08
6d	0.51	347 / 3.57	-5.31

[a] on-set potential vs Fc/Fc^+, [b] absorption on-set wavelength, [c] from CV on the premise that Fc/Fc^+ energy level is -4.80 eV.

only a minor influence of the S-Se exchange on photo-physical properties. In contrast, for compound **6c** a slightly reduced bandgap was observed.

The characterization of **6d** by CV and absorption measurements revealed minor influence on the HOMO energy levels (-5.31 eV), but significant changes in the absorption spectra with a blue-shift of the absorption on-set of ~60 nm / ~0.5 eV compared to **6a** (Fig 2). The marginal shift of the HOMO level indicates a minor conjugation between the heteroatom groups and the π-system of the benzene, which was also observed for the selenium derivative **6b**. The blue-shift in is explained by the elimination of the lone pair electrons and, thus, the lack of n --> π* transitions. The π --> π* transition of **6d** (320-350 nm) is red-shifted by ~30 nm compared to **6a**, indicating a reduced π - π* bandgap.

To outline the effect of selective oxidation on material properties post-polymerization modification[20] was chosen as a proof of concept (Scheme 3). Polymer **8** was obtained by microwave-assisted Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) polymerization of **6a** and **7**. The optimized procedure allows for an *in-situ* deprotection of **6a** and significantly reduces reaction times compared to conventional CuAAC polymerizations.[10]

The oxidation of **8** was performed in analogy to the model reaction towards **6d**. Indeed, post-polymerization modification was accomplished quantitatively yielding polymer **9** (conversion monitored by ^{1}H NMR spectroscopy). Since acetone is the only by-product of the oxidation using DMDO, **9** was simply purified by solvent evaporation.

GPC measurements of both **8** and **9** indicate no degradation of the polymers during oxidation. While the number average molecular weight slightly decreased from 3.6 kDa to 3.5 kDa, the weight average molecular weight increased from 7.2 kDa to 7.5 kDa. These variations are within the limitations of the chosen relative method for molecular weight determination.

The effects of post-polymerization modification were evaluated by absorption and fluorescence measurements for polymers **8** and **9**.
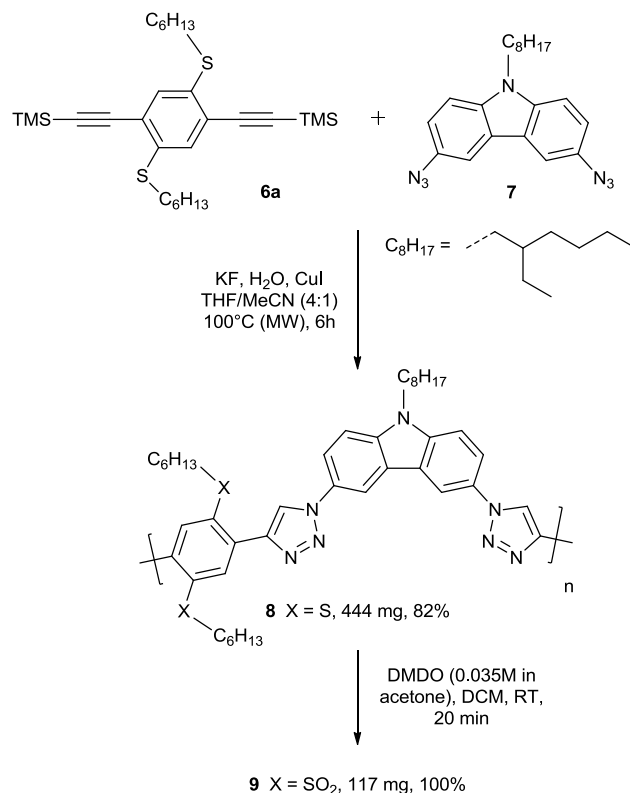
Scheme 3 Microwave-assisted CuAAC polymerization towards **8** and post-polymerization modification (oxidation) yielding **9**.

Despite the drastic structural and electronic modification, converting the electron donating into an electron withdrawing substituent, qualitatively similar absorption characteristics but reduced absorbance values were observed (Fig 3, left). In contrast, the fluorescence characteristics alter significantly shifting the emission maximum from 438 nm (**8**) to 516 nm (**9**). This severe red-shift of ~80 nm changes the emission color from blue to yellow (Fig 3, right) suggesting a variety of potential applications such as specific color tuning in the field of OLED, new strategies for device processing, etc. Further experimental and photo-physical investigations are currently performed to analyze this effect and to prove the general applicability of this approach. Determination of quantum yields using an Ulbricht sphere afforded similar values of 13% and 15% for polymers **8** and **9**, respectively.
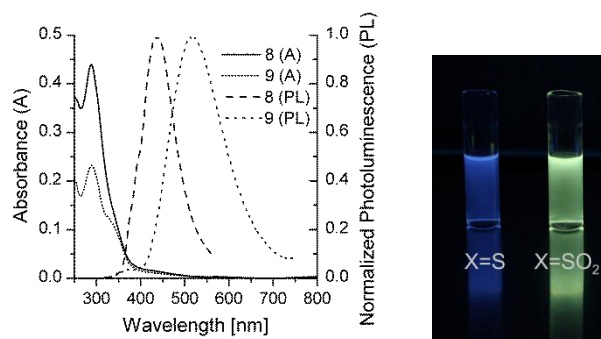

Fig. 3 UV-vis absorption and photoluminescence spectra of **8** (λ_{ex} = 288 nm) and **9** (λ_{ex} = 287 nm) (left), solutions of **8** (blue) and **9** (yellow) in DCM at λ_{ex} = 366 nm (right).

In conclusion, we have established a straight-forward, cheap and reliable synthesis of versatile building blocks 6a-c on (multi)gram-scale. An application of the developed building blocks potentially yields functional organic materials with entirely new properties compared to widely applied 1,4-bis[(trimethylsilyl)ethynyl]-2,5-bis(hexyloxy)benzene (X=O). Thus, microwave-assisted CuAAC polymerization of 6a and post-polymerization modification were demonstrated. The observed alteration of photo-physical properties by this simple oxidation procedure utilizing DMDO gives rise to several possible applications ranging from color tuning to post-processing modification of polymer layers.

Experimental section

General procedure towards 6a-c. 5 (1.0 eq) was dissolved in degassed dry Et_2O (0.1 M) under argon atmosphere in a pressure resistant glass vial. The solution was cooled to -78°C and t-BuLi (1.7 M in pentane, 4 eq) was slowly added. The resulting mixture stirred for 45 min at -78°C before allowing the solution to warm above 0°C. Sulfur, selenium or dihexyltelluride (2.1 eq) was then added and the yellow suspension was stirred for 3 h at room temperature / 60°C. If elemental reagents were used, hexyl iodide (2.2 eq) was additionally added and the suspension was stirred at 60°C overnight. The solution was poured on water and extracted three times with Et_2O. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The residue was purified by column chromatography (PE) or by crystallization from EtOH and following trituration in boiling EtOH. **Microwave-assisted CuAAC Polymerization.** Dialkyne **6a** (1.0 eq) and diazide **7** (1.0 eq) were weighed in into separate vials. CuI (10 mol%), KF (3.0 eq) and H_2O (8.0 eq) were added to **6a** and the vial was sealed and flushed with argon. **7** was dissolved in degassed THF/MeCN (4:1, 0.15 M) and added to the other reagents via a syringe. The reaction mixture was then heated to 100°C in the microwave-reactor for 6 h. The solution was added dropwise to methanol for precipitation and polymer **8** was collected by vacuum filtration.
Post-polymerization modification. Polymer **8** (1.0 eq) was dissolved in DCM (0.008 M). DMDO (0.035 M in acetone, 4.2 eq) was added dropwise and the solution stirred for 20 min at room temperature. Evaporation of the solvents yielded polymer **9**.

Acknowledgment

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