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Pyridine-Capped, Oligomeric (*o*-Phenyleneethynylene)s

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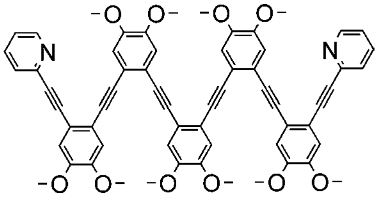
ABSTRACT



The synthesis, optical properties, and solid-state structures of a series of *o*-(aryleneethynylene) oligomers containing three to seven aryl units is described. The main chain in all examples is composed of between one and five 4,5-dimethoxybenzene rings which are capped on each end by 2-pyridyl rings. These oligomers demonstrate pH-dependent emission and absorption spectra. Single crystals were obtained from the aryleneethynylenes containing three to five arene rings. These single crystals were investigated by X-ray diffraction.

Aryleneethynylenes[1,2] (AE) constitute a class of molecules in which arene units are connected by alkynyl linkers. In most aryleneethynylenes, benzene rings are used as the arene of choice, perhaps due to simplicity and commercial access to the starting materials. The first AEs reported were the cyclic trimers and hexamers[3−6] and not linear oligomers. Linear oligomers of the para and meta type were synthesized[7−13] for their potential application in molecular electronics and to study solvent-driven folding processes in conjugated oligomers.

The first linear *o*-oligo-PEs were synthesized by Grubbs and Kratz,[14] but despite their interesting thermal behavior and their unusual helical structures in the solid state, they have attracted less attention than their meta or para counterparts.

Anderson[15] has utilized kinked PEs in which ortho linkages were present, as active materials for LEDs. Donor−acceptor *o*-PEs were investigated by Nicoud[16] et al. as NLO-type materials and showed interesting properties.

Recently, Tew et al.[17] have reported alkoxy substituted *o*-PEs (trimer to hexamer) and have performed a theoretical study[18] of their helix formation. The "floppiness" of the

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o-PEs should give rise to a multitude of different conformations in solution and several conformations in the solid state. The compound **1**[19,20] and its parent[21,22] (without the methoxy groups) are suitable ligands for transition metals as they can coordinate in a *trans*-spanning fashion, forming monomeric complexes, or be the bridging part of a metal−organic coordination polymer. We present the synthesis and the structural characterization of the pyridine end-capped *o*-PEs **1**−**4** (Figure 1), which are potentially attractive as active layers in light emitting diodes and as building blocks for larger metal organic solid-state polymers.

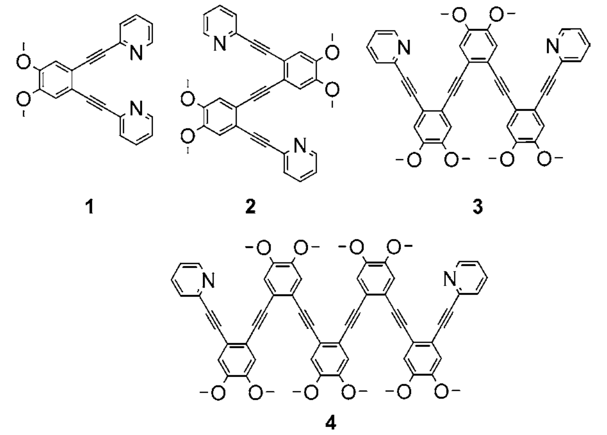
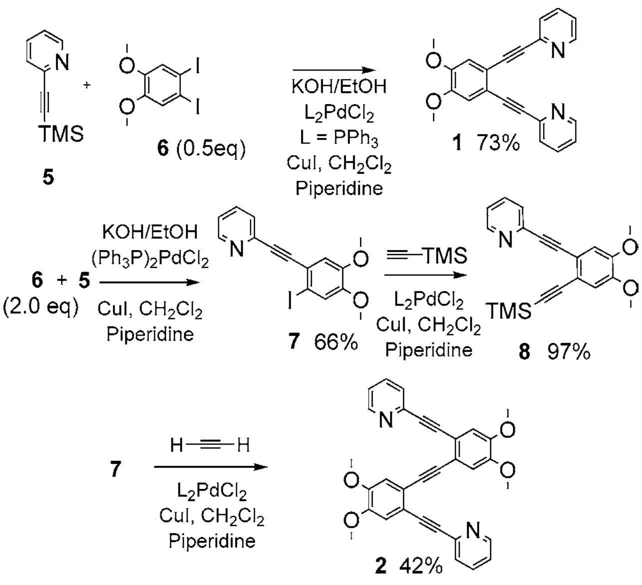


Figure 1. Synthesized oligomers.

The synthesis begins with the in situ deprotection and coupling reaction of 2-trimethylsilylethynylpyridine (**5**) with the diiodo compound **6**, using 0.5 equiv of **6** (Scheme 1). The TMS group of **5** is cleaved in situ,[23] with coupling, by the addition of KOH in ethanol to the reaction mixture. The Pd catalyst is not affected by the presence of hydroxide ions. This reaction yields **1** in a 73% yield. Using the same reactants, but with an excess of **6**, the monocoupled compound, **7**, is isolated in a 66% yield.

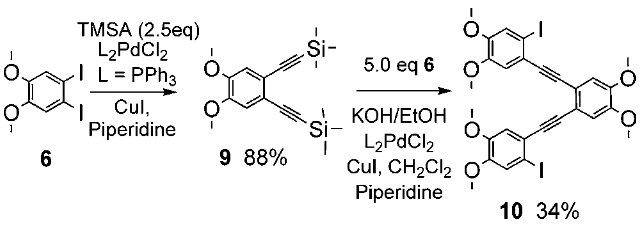
Scheme 1



Alkynylation of **7** with TMS-acetylene yields the unsymmetrical diyne, **8**, in 97% yield; **8** is a building block in the synthesis of longer oligomers. The oligomer **2** is synthesized by treating **7** with acetylene gas under Sonogashira[24] conditions to yield **2** in a 42% yield.

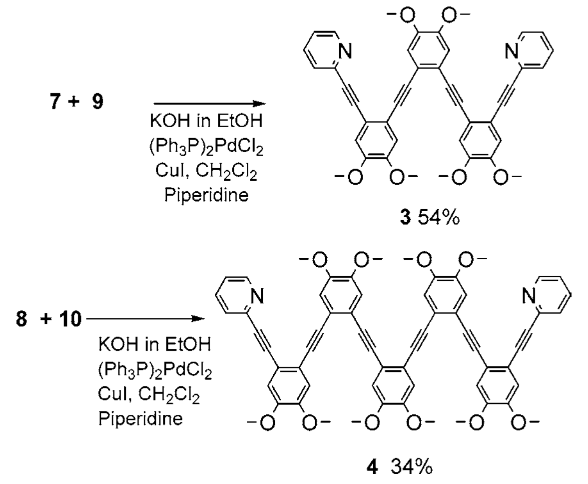
The synthesis of the other necessary building blocks for the creation of **3** and **4** begins with the Pd-catalyzed reaction of **6** with 2.5 equiv of TMS-acetylene to yield **9** in 88% yield (Scheme 2). The diyne **9** is treated with an excess of the diiodide **6** under in situ deprotection conditions to yield the diiodide **10** in 34% yield. Other products from this reaction are longer oligomers.

Scheme 2



The synthesis of **3** and **4** is shown in Scheme 3. The dialkynyl compound **9** is deprotected and coupled in situ to the monosubstituted iodide **7**, in a similar fashion as in the previous couplings, to give **3** in a 54% yield. The oligomer

Scheme 3



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4 is created from the diiodide **10** by reacting it with the unsymmetrical alkyne **8** (34% yield) under standard Pd catalysis.

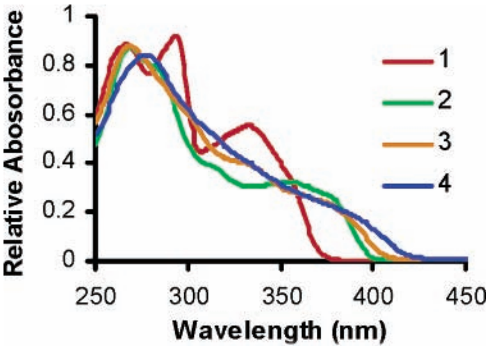

Figure 2. Absorbance of oligomers **1**−**4** in chloroform.

Table 1. Optical and Photophysical Data of **1**−**4**

	$\lambda_{max,abs}$ (nm)	$\lambda_{max,\ abs}$ + TFA (nm)	$\lambda_{max,em}$ (nm)	Φ_{sol} (%)
1	263, 294, 324	285, 318, 389	396, thin film: 508	36
2	268, 352	282, 322, 406	416, thin film: 538	28
3	265	291, 336	430, thin film: 542	28
4	272	276, 378	436, thin film: Nd	35

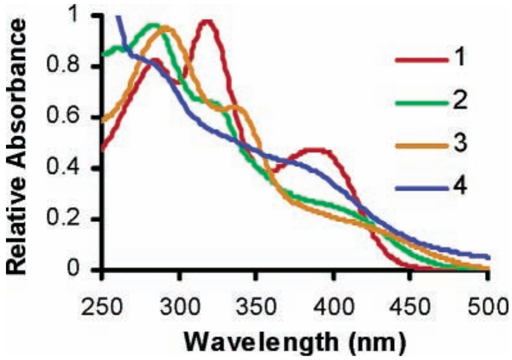

Figure 3. Absorbance of oligomers **1**−**4** in chloroform upon addition of TFA.

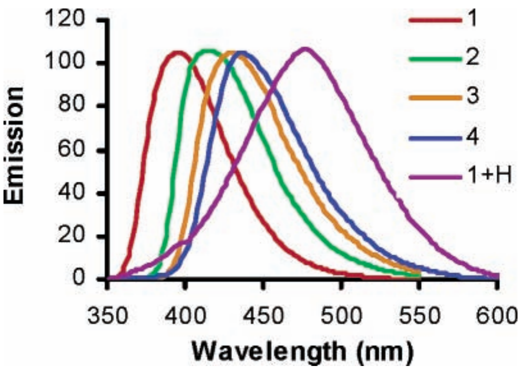

Figure 4. Emission of oligomers **1**−**4** in chloroform and emission of **1** in the presence of trifluoroacetic acid.

The UV−vis spectra of **1**−**4** in dilute solution are shown in Figure 2 and Table 1. With increasing length, λ_{max} is shifted from 324 to 408 nm. While the absorption of the trimer is well structured, the absorptions of the higher oligomers become broader, shoulder-like, and less defined. We trace this behavior back to the conformational freedom of these floppy molecules. The larger the oligomer, the more conformational freedom it has. As a consequence, an increase in length leads to broadening of the absorption spectra. The addition of trifluoroacetic acid to dilute solutions of **1**−**4** (Figure 3) leads to a significant bathochromic shift in their

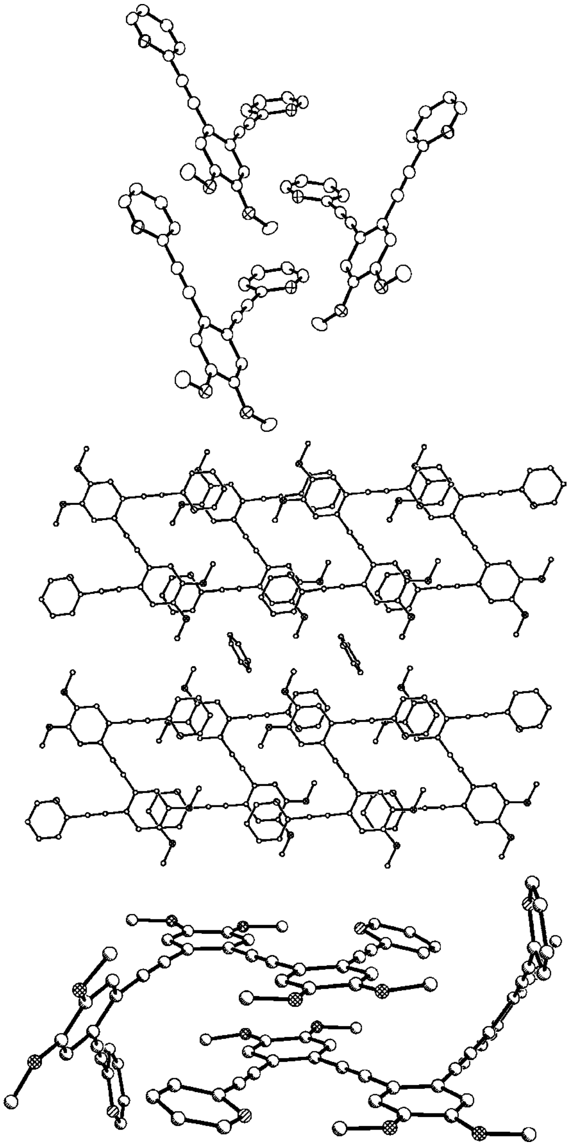

Figure 5. Ball and stick plot of the packing of the **1** (top), **2** (middle), and **3** (bottom) in the solid state.

UV−vis spectra, a consequence of the protonation of the pyridine bases. This shift is most distinct in the case of **1** and leads to further broadening of the UV−vis features in **2**−**4**. All of the oligomers are emissive, and contrary to the absorption spectra, the emission spectra do not broaden upon going from the oligomer **1** to the oligomer **4** (Figure 4). A similar behavior is observed in the case of linear PEs and was explained by the planarization of the oligomers in the excited state. We can construe that planarization in the lowest excited state will drive the oligomers into a zigzag type planar structure from which emission is observed.[8] The quantum yield of the emission for **1**−**4** is significant and in the range from 28 to 36% but lower than that of the corresponding linear PEs.

Upon addition of TFA the fluorescence of the oligomers is quenched, with the exception of the fluorescence of **1**, which shifts from 396 to 478 nm, i.e., from purple to yellow. This may be a charge-transfer effect. Oligomers **1**−**4** are flexible and could in principle attain any conformation ranging from planar to twisted and/or helical. While most of the conformations will be attained in solution, in the solid state one or several conformations should be preferred. The parent *o*-phenyleneethynylenes have been investigated by Grubbs and Kratz,[14] and the resulting solid-state structures were helical. It was of interest to see in how far the presence of the methoxy groups and the pyridine units would make a difference in the solid-state organization.

Figure 5 shows the structures of **1**−**3** in the solid state. The oligomers **1** and **3** crystallized without solvent, while **2** cocrystallizes with one molecule of pyridine. The bond lengths and bond angles are inconspicuous in all oligomers. In the cocrystal of **2** the oligomer is virtually planar, with strong and short $\pi-\pi$ interactions between the arene units, while in the cases of **1** and **3** the conjugated backbones are twisted out of plane. While **2** is planar and **1** is twisted, the pentamer **3** forms a dimer in the solid state that looks almost like a collapsed box, with the 90-degree twisted pyridine units as its side walls. Our substituted oligomers seem to be inclined toward either a planar or twisted conformation, but do not show a helical packing in the solid state.

In conclusion we have synthesized a series of pyridine-terminated *o*-aryleneethynylene oligomers (**1**−**4**). We have examined their photophysics in solution and their structures in the solid state. The oligomers are emissive in solution and in the solid state, but only the **1** is fluorescent after addition of trifluoroacetic acid. The structures of **1**−**3** were determined by single-crystal X-ray diffraction. Contrary to the hydrocarbon oligomers investigated by Grubbs and Kratz,[14] **1**−**3** do not form helical structures; instead, either planar (**2**) or intermediate (**3**) arrangements are preferred in the solid state. At the moment, we are investigating the use of **1**−**4** as active layers in organic LEDs.

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Supporting Information Available: Detailed descriptions of experimental procedures, NMR data, and X-ray crystallographic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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