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Synthesis of Novel Low-Bandgap Organic Semiconductors: Azulene-1,3-diyl-vinylene Oligomers

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Summary: Novel low-bandgap polyconjugated organic materials, oligo(azulene-1,3-diyl-vinylene)s, were prepared in a multistep synthesis starting from azulene. The key synthetic step was the olefin-metathesis-polycondensation of 1,3-diprop-1-en-1-ylazulene. Oligomeric products were isolated by column chromatography and characterized by mass-, ^{1}H-NMR- and UV-Vis-NIR spectroscopy.

Keywords: azulene; low bandgap; organic semiconductors

Introduction

Azulene is known for its low-energy electronic transition (last peak near 700 nm $\equiv$ 1.77 eV), which borders with the infrared spectral region. The motivation of the presented work was to prepare azulene-based organic semiconductors with an even lower energy transition than azulene, by extending its π-conjugated system. Semiconducting polymers are typically considered as "low-bandgap", if they display a bandgap value lower than 1.5 eV. The most investigated materials of this type are polythiophene derivatives with additional aromatic or heteroaromatic rings fused to the thiophene ring, as well as some other polythiophene derivatives (for a review see[1]). In analogy to 1,4-divinylbenzene and its derivatives, which can be condensed via olefin metathesis (acyclic diene metathesis, ADMET) to yield the polyconjugated 1,4-phenylene-vinylene oligomers,[2,3] a synthesis of divinylazulene derivatives and their subsequent metathesis polycondensation was developed. As the synthesized 1,3-divinylazulene showed a very strong tendency to radical polymerization, the stable 1,3-diprop-1-en-1-ylazulene was used as monomer instead and was shown to be very reactive in the metathesis polycondensation. In this contribution, first results concerning the preparation and optical properties of small azulene-vinylene oligomers, which show light absorption till photon energies of 1.4-1.3 eV, are presented.

Experimental Part

Chemicals

Azulene was donated by Prof. Dr. Klaus Hafner. All other chemicals were purchased from Merck, Darmstadt.

Monomer Synthesis

1,3-diprop-1-en-1-ylazulene ("Monomer") was synthesized according to Scheme 1 via repeated Vilsmeier formylation (in analogy to papers;[4,5] this azulene formylation method is used till today and a procedure based on it is described e.g. in[6]) and repeated standard Wittig reaction (the reagent being made in situ from ethyltriphenylphosphonium bromide suspended in THF).

Metathesis (ADMET) Polycondensation

The olefin-metathesis polycondensation of 1,3-diprop-1-en-1-ylazulene (Scheme 2) was performed at room temperature, at

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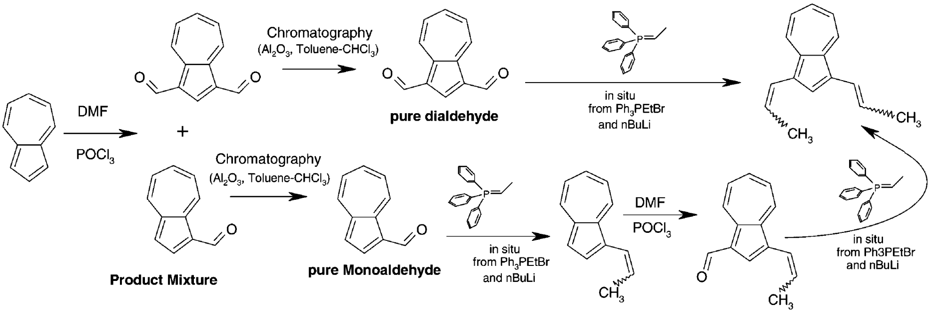


Scheme 1.
Synthetic routes to 1,3-diprop-1-en-1-ylazulene.

c(catalyst) = 10 mmol/L, and catalyst/monomer ratio 1/50 (see also[6]). The Schrock-type molybdenum alkylidene catalyst is depicted in Scheme 2. As solvent, hexane or toluene was used. The reaction was complete after ca. 20 min. The condensation products were separated by column chromatography (Al_2O_3, Hexane-Toluene).

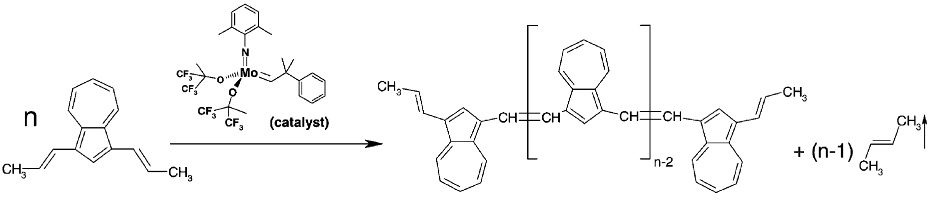
Characterization

MALDI-TOF-Mass spectra were recorded on a Biflex III spectrometer from Bruker (c = ca. 10^{-5} mol/L, Matrix 2,5-dihydroxybenzoic acid, external calibration). 500 MHz-^{1}H-NMR spectra were recorded on a Bruker DRX 500 spectrometer (c = ca. 2% in chloroform, internal standard: tetramethylsilane). The UV-Vis-NIR spectra were recorded on Perkin Elmer Lambda 35 spectrophotometer (c = ca. 10^{-5} mol/L; dissolved in chloroform, except azulene-vinylene trimer dissolved in cyclohexane).

Results and Discussion

Monomer Synthesis

An efficient synthesis of 1,3-diprop-1-en-1-ylazulene (“Monomer”) was developed: The formally shorter, two-step synthesis via azulene-1,3-dicarbaldehyde (Scheme 1 top) proved problematic on multigram (not 100 mg) scale, due to the labour-consuming chromatographic removal of monoaldehyde impurities from the dialdehyde. On the other hand, the formally longer path via azulene-1-carbaldehyde (Scheme 1 bottom) proved to be very efficient for large-scale syntheses, leading to short reaction times and high yields. Originally, a simpler monomer, 1,3-divinylazulene was synthesized in an



Scheme 2.
Olefin metathesis polycondensation of 1,3-diprop-1-en-1-ylazulene.

analogous way by the short route. However, its strong tendency to radical polymerization prevented its further use. 1,3-diprop-1-en-1-ylazulene was synthesized instead, and proved stable to radical polymerization, as well as highly reactive in olefin metathesis condensation (see below).

Metathesis Condensation and Product Isolation

The 1,3-diprop-1-en-1-ylazulene polycondensation (ADMET) proceeded fast (most of conversion occurring in the first minutes). Similarly to unsubstituted 1,4-phenylene-vinylene oligomers, the prepared oligomers also show a rapid decrease in solubility with increasing polymerization degree (P_n). Depending on the solvent used, the final molecular weight of the oligomers can be controlled: In pure hexane at room temperature, most of the product precipitates as Trimer, while from toluene at the same temperature products with $P_n > 5$ precipitate as the main fraction. Figure 1 shows a MALDI-TOF spectrum of a polycondensation mixture in toluene. The high oligomers are underestimated due to their poor solubility.

^{1}H-NMR Characterization of Azulene Derivatives

The high resolution, 500 MHz ^{1}H-NMR spectroscopy can be employed to give a direct proof of the structure of the azulene derivatives prepared. The assignment (shown for Dimer in Figure 2) was possible using the known chemical shifts and coupling constants of azulene protons and by comparing the spectra of the azulene derivatives prepared according to Scheme 1. The signal assignement for azulene, *Z,Z*-Monomer, *E,E*-Monomer and Dimer are given in Table 1. The spectrum of the Trimer is similar to the one of the Dimer, but more complex and less resolved; it is still to be fully assigned.

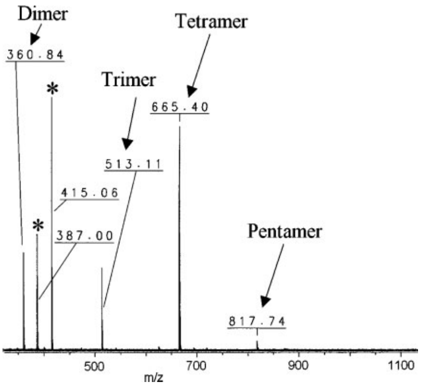


Figure 1.
MALDI-TOF mass spectrum of a productmixture of the 1,3-diprop-1-en-1-ylazulene metathesis condensation.

UV-Vis-NIR Spectra of the Azulene-Vinylene Oligomers

The UV-Vis-NIR spectra of azulene and its derivatives show two characteristic absorption regions (see Figure 3): the intense "UV-peaks" and the low-intensity (forbidden transition) "Vis-NIR-peak", which in some cases (concentrated solution, or bulk) also strongly contributes to the product color.

The long-wave (forbidden, "Vis-NIR") absorption is practically independent of P_n (see Figure 4 left): About the same shape and position of this peak were observed for Monomer, Dimer and Trimer. A strong red shift and broadening results if azulene is converted into the Monomer. This indicates that the "Vis-NIR" band is determined by the azulene ring and its directly neighboring π–conjugated substituents only. On the other hand, the "UV-Vis-peaks" show a strong dependence on P_n (see Figure 4 right): substantial red shift and intensity transfers are observed with increasing chain length. The difference between the Dimer and Trimer is much smaller than between the Monomer and Dimer, but remains strong if the colors of solutions, especially of concentrated ones, are observed. Generally, a fast convergence of colors in bulk as well as in solution is observed for the azulene-vinylene oligomers: Trimer and higher oligomers have a very similar appearance and solution color (but strongly different solubilities). The effective conjugation length hence seems to be a little more than 3 repeating units in the

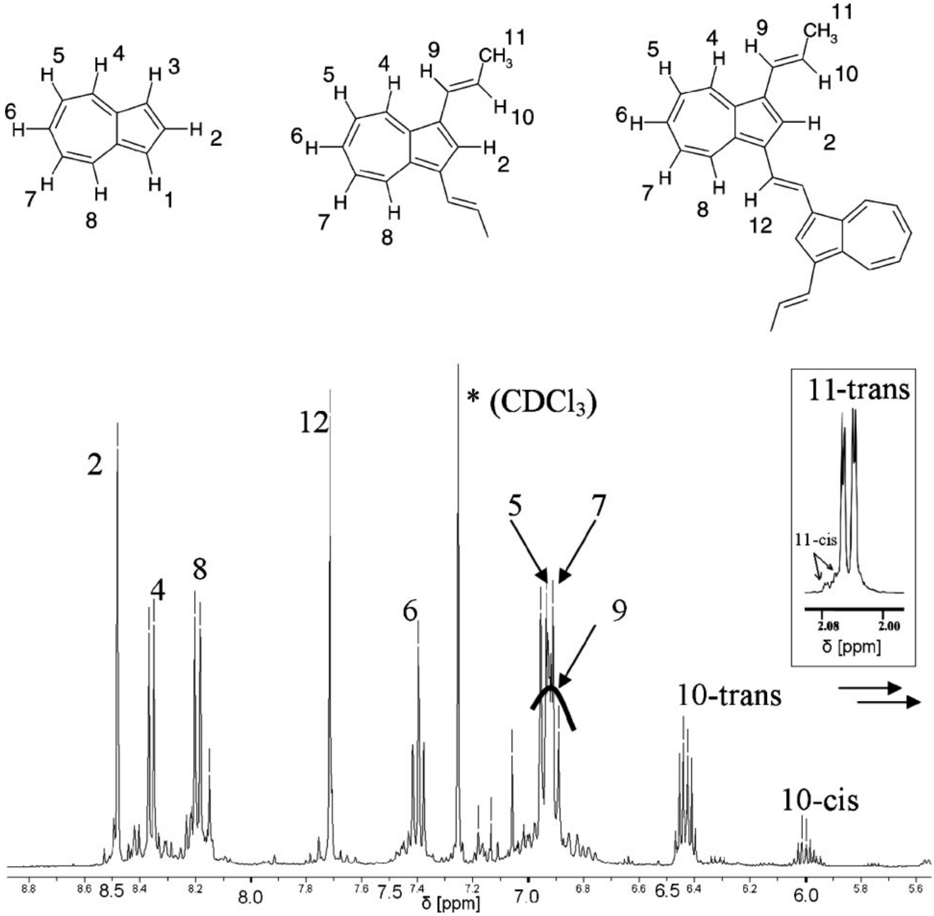


Figure 2.
Aromatic region of the 500 MHZ ^{1}H-NMR spectrum of the Dimer.

Table 1.
^{1}H-NMR chemical shifts (δ [ppm]) of Azulene, 1,3-diprop-1-en-1-ylazulene (Monomer) and of Dimer.

	Azulene	Monomer-*Z*,*Z*	Monomer-*E*, *E*	Dimer, (*E*, *E* end groups)
H-2	7.91 (t)	8.135 (s)	8.195 (s)	8.48 (s)
H-3	7.40 (d)	–	–	–
H-6	7.58 (t)	7.49 (t)	7.37 (t)	7.395 (t)
H-8/H-8, 4	8.346 (d)	8.236 (d)	8.187 (d)	8.19 (d)
H-4	–	–	–	8.36 (d)
H-7/H-7, 5	7.16 (t)	7.03 (t)	6.884 (t)	6.91 (t)
H-5	–	–	–	6.934 (t)
H-9	–	6.935 (dq)	6.901 (dq)	6.92 (dq)
H-10	–	5.89 (dq)	6.316 (dq)	6.43 (dq)
H-11	–	2.015 (dd)	1.98 (dd)	2.03 (dd)
H-12	–	–	–	7.71 (s)

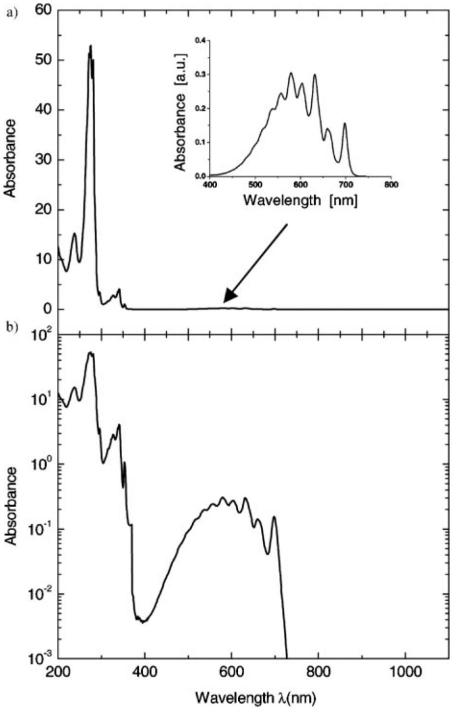


Figure 3.
UV-Vis-NIR spectrum of azulene normal (a) and logarithmic (b) scale.

unsubstituted poly(azulene-1,3-diyl-vinylene), similarly to unsubstituted PPV.

Conclusions

Novel low-bandgap azulene-1,3-diyl-vinylene oligomers were synthesized via olefin metathesis of 1,3-diprop-1-en-1-ylazulene. An efficient synthesis of the above monomer was developed, making multigram amounts accessible. The ''long-wave'' (Vis-NIR) electronic absorption peak in the Monomer, Dimer and Trimer shows about the same position and shape, and appears to be determined by the azulene ring and its directly neighboring π–conjugated substituents only. The "UV-peaks" of the investigated azulene derivatives show a strong red shift with increasing chain length (larger π–conjugated system), partly shifting into the visible region. The convergence of electrooptical properties of the unsubstituted azulene-vinylene oligomers seems to be achieved fast, as the UV-Vis-NIR spectra of Dimer and Trimer are already strongly similar.

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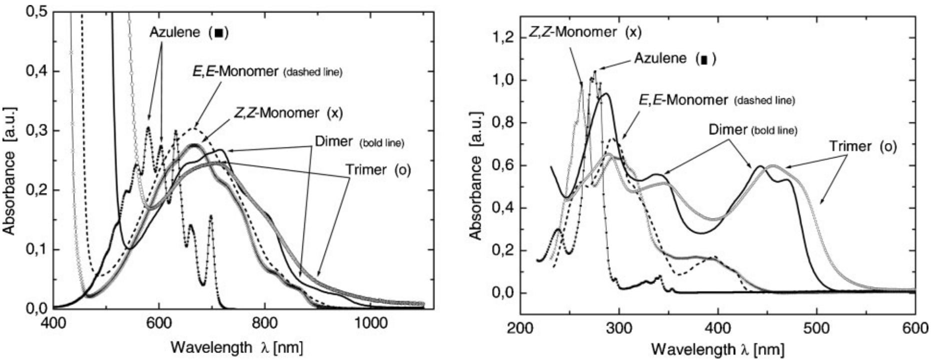

Figure 4.
Long-wave absorption band (left) and "UV-peaks"(right) of the azulene derivatives investigated.

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