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Acetylenic scaffolding on solid support: poly(triacetylene)-derived oligomers by Sonogashira and Cadiot–Chodkiewicz-type cross-coupling reactions†

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We report the first synthesis of poly(triacetylene)-derived oligomers by Pd(0)-catalysed Sonogashira and Cadiot– Chodkiewicz-type cross-coupling reactions on solid support. Oligo(phenylene triacetylene)s, members of a new class of linearly π -conjugated oligomers with all-carbon backbones, feature very high fluorescence intensities.

Investigations of monodisperse π -conjugated oligomers of precise length and constitution provide specific information about the structural, electronic and optical properties of their polydisperse polymeric counterparts.¹ Fluorescent conjugated oligomers are explored for incorporation into organic electroluminescent devices.² Recently, the testing of rigid conjugated oligomers as molecular wire components in nanoelectronics devices has attracted particular interest.³ With the extensive development of solid-phase organic synthesis in the 1990s,⁴ monodisperse molecular wires, in particular oligothiophenes⁵ and oligo(phenylene ethynylene)s^{2,6} are increasingly being prepared on polymeric support, taking advantage of versatile oligomeric length control and facilitated workup and purification protocols.

Here we describe the first polymer-supported synthesis of poly(triacetylene)⁷-derived monodisperse oligomers using Pd(0)-catalysed Sonogashira⁸ and Cadiot–Chodkiewicz-type⁹ cross-couplings as key steps in the construction of the acetylenic scaffolds. Whereas the former has found abundant application in the solid-phase synthesis of oligo(phenylene ethynylene)s,^{2,6} only one report has appeared on Cadiot–Chodkiewicz couplings on solid support.¹⁰ With the oligo(phenylene triacetylene)s **1–4**, we report the first members of a new family of stable, highly fluorescent molecular wires.



For our investigations, we chose the Merrifield resin¹¹ (chloromethylated polystyrene, 0.4 mmol Cl g⁻¹ resin) as solid support in combination with a triazene linker. 1-Aryltriazene linkers are well known for their compatibility with Pd(0)-catalysed coupling reactions^{2,6} and for their facile cleavage from the resin.^{12,13} The evaluation of possible linkers in preliminary liquid-phase studies revealed, in our hands, substantial advantages of the benzyloxyethyl derivative **5**^{6c} over the benzyl derivative **6**,^{2,6a,b} in terms of cleavage efficiency and yield. Therefore, we used the resin-linker combination **7**, for which elemental analysis revealed an iodide loading of ≈ 0.2 mmol g⁻¹ resin.



Attachment of mono-deprotected diethynylethene (DEE, (E)-hex-3-ene-1,5-diyne) **8**^{14a} to the resin-bound linker by Sonogashira coupling proceeded smoothly and provided the polymer-supported alkyne **9** (Scheme 1). Subsequent cleavage from the support with MeI^{2,6a-c} gave the (phenylene triacetylene) monomer **1** in excellent yield (83% starting from **8**). ‡ All cleavage reactions in this study required 24 h at 120 °C in agreement with previous reports¹⁵ that electron-withdrawing groups in the *para*-position (such as the DEE moiety in **9**)¹⁶ slow down the conversion to the aryl iodide.

After protodesilylation of **9**, the resulting polymersupported, terminally deprotected alkyne was subjected to Pd(0)-catalysed Cadiot–Chodkiewicz cross-coupling with **10**,^{14b} which was followed by cleavage of the products from the solid support with MeI. Under all experimental conditions, which were optimised in a systematic way while carefully excluding O_2 , a mixture of three products was obtained, namely the desired cross-coupled DEE dimer **11**, homo-coupled DEE dimer **12** and uncoupled monomer **13**. [†] The highest cross-coupling yield (**11**: 37%, **12**: 10% and **13**: 2%) was obtained using 5.0 equiv. of **10** and 0.2 equiv. of [Pd₂(dba)₃] in the absence of CuI at 45 °C.

Starting from 1, on the other hand, repetitive cycles of protodesilylation, followed by Pd(0)-catalysed Sonogashira cross-coupling, allowed the efficient modular construction of the oligo(phenylene triacetylene)s 2–4 on solid phase (Scheme 2). Purification of the products, cleaved from the solid support with MeI, was readily accomplished by column chromatography (SiO₂, hexane–CH₂Cl₂ mixtures as eluent), and the pure oligomers were obtained in quantities of 100–200 mg. The reduced yields of the higher oligomers 3 and 4 were not due to less efficient cross-coupling on the polymeric support but rather to their increasing insolubility which affected the workup. Such problems should be readily avoided in future work by introducing alkyl side chains on the phenyl moieties.

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[†] Electronic supplementary information (ESI) available: typical procedures for the reactions on solid phase and physical as well as spectral data of compound **2**. See http://www.rsc.org/suppdata/ob/b2/b210184j/



Scheme 1 Pd(0)-catalysed Cadiot–Chodkiewicz cross-coupling on solid phase. *Reagents and conditions:* (i) $[Pd_2(dba)_3]$ (dba = dibenzylidene acetone), CuI, PPh₃, Et₃N, 70 °C, 20 h; (ii) MeI, 120 °C, 24 h, 83% (2 steps); (iii) NaOH, THF–MeOH, 70 °C, 3 h; (iv) $[Pd_2(dba)_3]$, CuI, LiI, C₆H₆, 1,2,2,5,5-pentamethylpiperidine (PMP), 45 °C, 24 h; (v) MeI, 120 °C, 24 h, 37% (11), 10% (12), 2% (13).



Scheme 2 Synthesis of oligo(phenylene triacetylene)s by Pd(0)-catalysed Sonogashira cross-coupling on solid phase. *Reagents and conditions:* (i) NaOH, THF–MeOH, 70 °C, 3 h; (ii) 1, $[Pd_2(dba)_3]$, CuI, PPh₃, Et₃N, 70 °C, 24 h; (iii) MeI, 120 °C, 24 h.

Table 1Electronic absorption and emission data for the oligo-
(phenylene triacetylene)s 1-4 in CHCl3 at r.t.

	Absorption $\frac{1}{2} \sqrt{nm^{a}}$	Emission	
Compound	$(\varepsilon/\mathrm{M}^{-1}\mathrm{cm}^{-1})^{b}$	$\lambda_{\rm max}/{\rm nm}^{c}$	${oldsymbol{\Phi}_{ extsf{F}}}^{d}$
1	337 (41100)	364	0.01
2	360 (54200)	414	0.24
3	381 (97800)	436	0.69
4	384 (122000)	444	0.60

^{*a*} Longest-wavelength absorption maximum. ^{*b*} Molar extinction coefficient. ^{*c*} Fluorescence emission maximum. ^{*d*} Fluorescence quantum yield, determined by using anthracene ($\Phi_{\rm F} = 0.33$) as reference compound.¹⁷

The UV/VIS spectral data of the novel oligo(phenylene triacetylene)s 1–4 in CHCl₃ are depicted in Fig. 1. The longest wavelength absorption maxima are shifted bathochromically with increasing oligomeric length, from $\lambda_{max} = 337$ (1) to 384 (4) nm, and the corresponding molar extinction coefficients also increase in the same direction, reaching $\varepsilon = 122000 \text{ M}^{-1} \text{ cm}^{-1}$ for tetramer 4 (Table 1). Saturation of the optical properties is

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not yet observed, *i.e.* the effective conjugation length ^{1b} of oligo(phenylene triacetylene)s involves more than 40 conjugated carbon atoms. Interestingly, dimer 2 and, in particular, trimer 3 and tetramer 4 display strong fluorescence emission with the highest quantum yield, ¹⁷ $\Phi_{\rm F} = 0.69$, being measured for trimer 3. This strong luminescence is in sharp contrast to the poor emitting behaviour of the corresponding oligo(triacetylene) oligomers, with the dimer and trimer being only weakly fluorescent ($\Phi_{\rm F} = 0.01$)¹⁶ and the tetramer not emitting at all. The high fluorescence quantum yields of 2–4 are quite remarkable in view of their terminal iodine substituents which should promote intersystem crossing to the corresponding triplet excited state. Investigations of the electroluminescence properties of 3 and 4 are underway.

In conclusion, we accomplished the first synthesis of oligo(triacetylene)-related oligomers by Pd(0)-catalysed acetylenic scaffolding on solid phase. Whereas optimal conditions for polymer-supported Cadiot–Chodkiewicz-type coupling reactions still remain to be found, Sonogashira cross-coupling proceeded smoothly and led rapidly to the new oligo(phenylene triacetylene) oligomers 1–4 featuring intense longest-wavelength absorption bands and, most interestingly, a dramatically



Fig. 1 UV/VIS spectra of oligo(phenylene triacetylene)s 1–4 recorded in $CHCl_3$ at r.t.

enhanced fluorescence emission as compared to the corresponding oligo(triacetylene)s.

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Notes and references

[‡] All new compounds were fully characterised by IR, UV/VIS, ¹H and ¹³C NMR, mass spectrometry and microanalysis. Overall yields for the products obtained after cleavage from the resin refer to the iodide loading of the polymer-bound aryltriazene 7. In the optimisation of the Pd(0)-catalysed Cadiot–Chodkiewicz coupling, only side product 13 was isolated in pure form, whereas the yields of 11 and 12, which could hardly be separated, were determined by calibrated HPLC. For full characterisation, 11 and 12 were independently prepared by liquid-phase synthesis. Electronic supplementary information (ESI) includes typical procedures for the reactions on solid phase and physical as well as spectral data of compound 2.

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