

Quadruple hydrogen bonded oligo(*p*-phenylene vinylene) dimers

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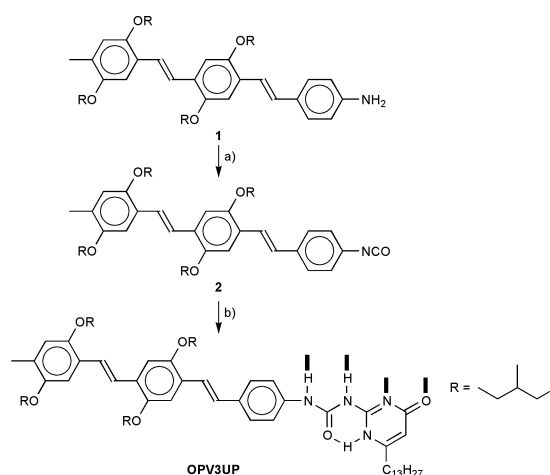
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Direct self-assembly of π -conjugated oligomers via self-complementary quadruple hydrogen bonding is achieved and the first steps towards supramolecular polymers with functional side chains are described.

Conjugated polymers are investigated for a manifold of electronic semiconductor applications.¹ It is also widely accepted that well-defined oligomers will play a crucial role in the future advancement of π -conjugated materials, since their precise chemical structure and conjugation length stand for defined functional properties and facilitate enhanced control over their supramolecular architecture.^{2,3} Synthetic efforts have been mainly directed towards the synthesis of extended linear conjugated oligomers of length of 5–10 nm, but cyclic,⁴ bicyclic,⁵ spiro⁶ and dendritic⁷ structures have also been reported. Further, different π -conjugated functionalities have been combined in a large number of well-defined donor–acceptor molecules. The major challenge is now to obtain control of the supramolecular ordering over length scales extending into the macroscopic regime.⁸ Only a few examples have been reported on spatial organization of functional π -conjugated entities by making use of hydrogen bonding motifs. Self-assembled fibers of mono and bisthiophene bisurea compounds have been reported and showed efficient charge transport within these fibers.⁹ Superstructure formation of π -conjugated materials has also been obtained by hydrogen bonding complexation of perylene bisimide derivatives with a ditopic melamine compound¹⁰ and with chlorine singlet excited-state electron donor and a naphthalene bisimide acceptor.¹¹

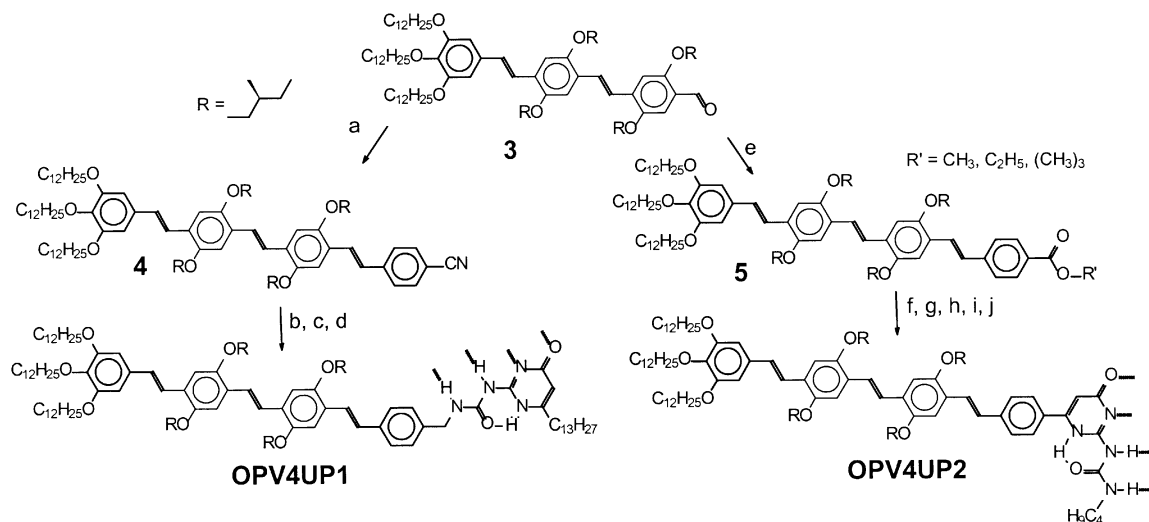
Recently, we have reported supramolecular polymers which exhibit real macroscopic polymeric properties.¹² These polymeric systems are based on the strong dimerization of quadruple hydrogen-bonding self-complementary 2-ureido-4[1*H*]-ureido-



Scheme 1 Synthesis of **OPV3UP**. (a) di-*tert*-butyl tricarbonatate, CH_2Cl_2 , 100%; (b) 6-tridecylisocytosine, pyridine, 90 °C, 26%.

pyrimidinone units. These recent developments pave the way to combine the specific electronic and optical properties of conjugated oligomers with the material properties of polymers, by incorporating well-defined π -conjugated moieties in these supramolecular polymeric assemblies. Here we report on the synthesis of the ureidopyrimidinone derivatives **OPV3UP**, **OPV4UP1** and **OPV4UP2** (depicted in Schemes 1 and 2) and on their supramolecular ordering.

Compound **OPV3UP** was prepared starting from the amino functionalized oligomer. Using di-*tert*-butyl tricarbonatate the amine functionality was quantitatively converted to the isocyanate **2**.¹³ Reaction of **2** with 1.5 eq. of 6-tridecylisocytosine



Scheme 2 Synthesis of **OPV4UP1** and **OPV4UP2**. (a) diethyl 4-cyanobenzylphosphonate, *t*-BuOK, DMF, 91%; (b) LiAlH_4 , Et_2O , 93%; (c) COCl_2 , toluene, 100 °C, 100%; (d) 6-tridecylisocytosine, pyridine, 90 °C, 52%; (e) diethyl 4-(methylbenzoate)phosphonate, *t*-BuOK, DMF, THF; (f) KOH, EtOH, 80 °C, 100%; (g) COCl_2 , CH_2Cl_2 , DMF, 100%; (h) MgCl_2 , Et_3N , EtOAc, HCl aq., 30%; (i) $(\text{NH}_2)_2\text{C}=\text{NH}\cdot\text{HCO}_3$, EtOH, 90%; (j) $n\text{-C}_4\text{H}_9\text{NCO}$, pyridine, 90 °C.

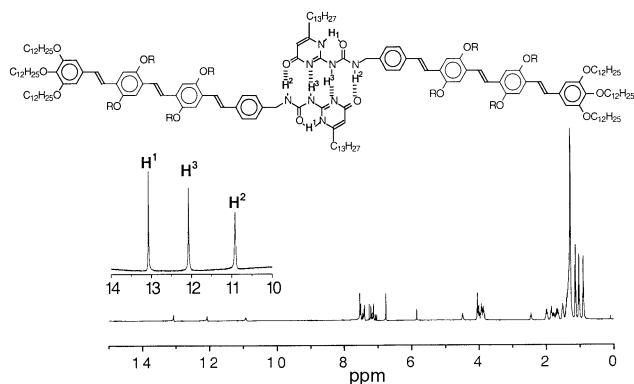


Fig. 1 $^1\text{H-NMR}$ spectra of **OPV4UP1** recorded in CDCl_3 .

in anhydrous pyridine at 90°C afforded **OPV3UP** in 26% yield after column chromatography. The low yield of **OPV3UP** is probably due to the relatively low reactivity of aromatic isocyanates. Therefore, benzylic isocyanates were used for the preparation of **OPV4UP1**. To obtain the benzylic isocyanate, aldehyde **3** was allowed to react with diethyl 4-cyanobenzylphosphonate in a Wittig–Horner reaction to give the nitrile compound in 91% yield. The nitrile functionality was subsequently reduced using LAH to afford the benzylic amine. The pure compound was isolated after work-up and precipitation in 93% yield. The amine derivative was reacted with phosgene in refluxing toluene to give the isocyanate. Reaction of the latter with 6-tridecylisocytosine in anhydrous pyridine at 90°C gave **OPV4UP1** in 52% yield. In order to obtain full conjugation between the OPV and hydrogen bonding unit, **OPV4UP2** was synthesized. Reaction of aldehyde **3** with diethyl 4-(methylbenzoate)phosphonate in a Wittig–Horner reaction afforded a mixture of esters **5**. Saponification of these esters gave quantitatively the acid, which was quantitatively converted to the acid chloride using oxalylchloride in DCM and DMF. The β -ketoester was obtained in 30% yield by reaction of the acid chloride with potassium ethylmalonate in presence of triethylamine and magnesium chloride. Reaction of the β -ketoester with guanidinium carbonate yielded quantitatively the isocytosine. The desired compound **OPV4UP2** was finally obtained in 90% yield by reaction of the isocytosine and *n*-butylisocyanate in anhydrous pyridine at 90°C .

All the compounds **OPV3UP**, **OPV4UP1** and **OPV4UP2** were fully characterized.[†] These π -conjugated oligomers form quadruple hydrogen bonded **DDAA**-dimers in solution as is evident from the $^1\text{H-NMR}$ spectra (Fig. 1). The large downfield shift for the N–H protons gives direct evidence for the involvement of these protons in strong hydrogen bonding.¹⁴ The electronic absorption spectra recorded in CHCl_3 solution display a weak band in the visible spectral region ($\lambda_{\text{max}} = 409\text{ nm}$) for the less extended π -conjugated **OPV3UP**. In the case of tetrameric oligophenylene vinylene, **OPV4UP1** and **OPV4UP2**, the absorption maxima are located at $\lambda_{\text{max}} = 431$ and 446 nm , respectively. The red shift of the absorption maxima of **OPV4UP2** indicates conjugation between the OPV segment and the hydrogen bonding unit. In addition, in dilute CHCl_3 solution (*ca.* 10^{-5} M) these hydrogen bonded species are present in dimeric form since the association constant of the ureidopyrimidinone units is extremely high ($K_{\text{dim}} = 6 \times 10^7\text{ M}^{-1}$ in CHCl_3 solutions).¹⁵ In dodecane solution, both the dimers of **OPV4UP1** and **OPV4UP2** aggregate into larger architectures and circular dichroism (CD) spectroscopy shows an exciton coupling of the π - π^* transition in this solvent. In other words, the side-chain chirality is expressed at the supramolecular level.¹⁶ In the bulk, the two trialkoxybenzene capped dimers are liquid crystalline, but investigation concerning their detailed structure is in progress.

In conclusion, directed self-assembly of π -conjugated oligomers *via* self-complementary quadruple hydrogen bonding has been achieved. It opens new possibilities for the design of electronically active supramolecular materials in which the specific properties of well-defined oligomers can be combined with the material properties of polymers.

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Notes and references

[†] Full synthetic details will be given elsewhere. All new compounds were authenticated by ^1H and ^{13}C NMR, FT-IR, MALDI-TOF MS and elemental analyses. *Selected data:* for **OPV3UP**: $\delta_{\text{N-H}}$ (CDCl_3) 12.91, 12.35, 12.11, MALDI-TOF MS (MW = 974.68) $m/z = 974.77$ [$\text{M}]^+$, elemental analyses C, 74.46 (75.11), H, 9.28 (9.30), N, 5.96 (5.74%); **OPV4UP1**: $\delta_{\text{N-H}}$ (CDCl_3) 13.06, 12.07, 10.89, MALDI-TOF MS (MW = 1629.28) $m/z = 1629.89$ [$\text{M}]^+$, elemental analyses C, 77.68 (77.35), H, 10.77 (10.39), N, 3.26 (3.44%); **OPV4UP2**: $\delta_{\text{N-H}}$ (CDCl_3) 13.91, 12.03, 10.29, MALDI-TOF MS (MW = 1490.24) $m/z = 1490.09$ [$\text{M}]^+$, elemental analyses C, 75.99 (76.60), H, 9.58 (10.00), N, 3.45 (3.80%); calculated values in parenthesis.

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