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

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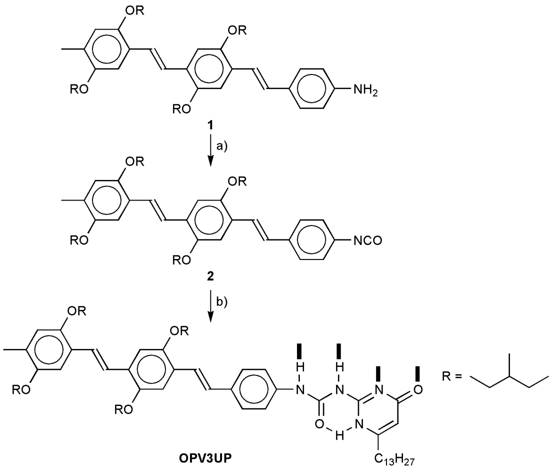
Direct self-assembly of π-conjugated oligomers *via* self-complementary quadruple hydrogen bonding is achieved and the first steps towards supramolecular polymers with functional side chains are described.

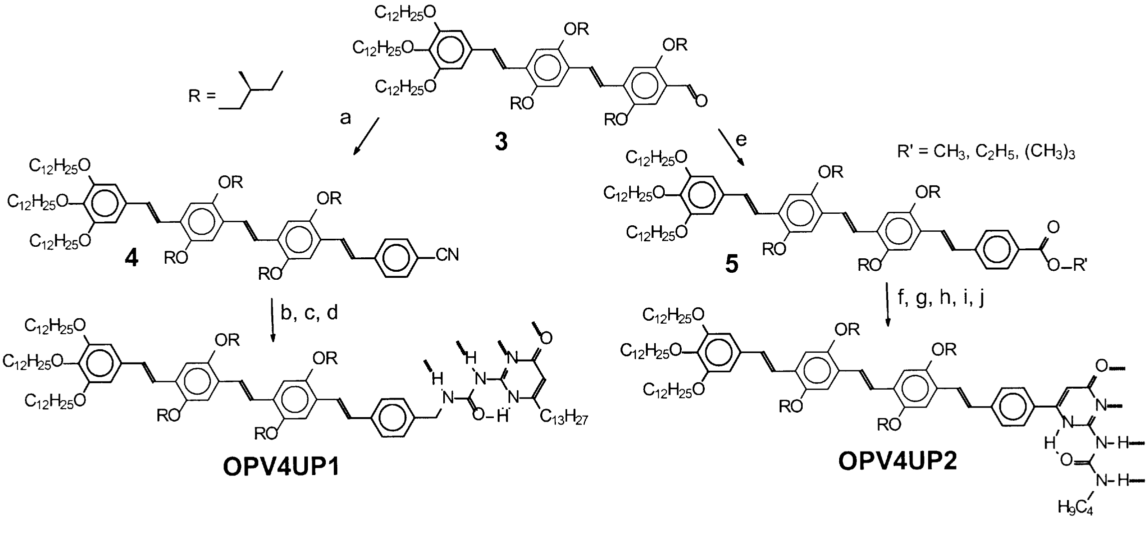
Conjugated polymers are investigated for a manifold of electronic semiconductor applications.[1] It is also widely accepted that well-defined oligomers will play a crucial role in the future advancement of π-conjugated materials, since their precise chemical structure and conjugation length stand for 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] spiro[6] and dendritic[7] 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 compound[10] 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*]-ureidopyrimidinone 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.



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

Compound **OPV3UP** was prepared starting from the amino functionalized oligomer. Using di-*tert*-butyl tricarbonate 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) $(NH_2)_2C{=}NH{\cdot}HCO_3$, EtOH, 90%; (j) n-$C_4H_9NCO$, pyridine, 90 °C.

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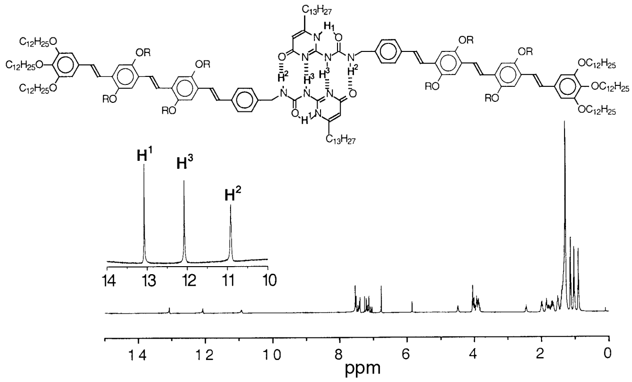

Fig. 1 ^{1}H-NMR spectra of **OPV4UP1** recorded in $CDCl_3$.

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}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 (λ_{max} = 409 nm) for the less extended π-conjugated **OPV3UP**. In the case of tetrameric oligophenylene vinylene, **OPV4UP1** and **OPV4UP2**, the absorption maxima are located at λ_{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 ($K_{dim} = 6 \times 10^7$ 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 ^{1}H and ^{13}C NMR, FT-IR, MALDI-TOF MS and elemental analyses. *Selected data*: for **OPV3UP**: δ_{N-H} ($CDCl_3$) 12.91, 12.35, 12.11, MALDI-TOF MS (MW = 974.68) *m/z* = 974.77 [M]$^+$, elemental analyses C, 74.46 (75.11), H, 9.28 (9.30), N, 5.96 (5.74%); **OPV4UP1**: δ_{N-H} ($CDCl_3$) 13.06, 12.07, 10.89, MALDI-TOF MS (MW = 1629.28) *m/z* = 1629.89 [M]$^+$, elemental analyses C, 77.68 (77.35), H, 10.77 (10.39), N, 3.26 (3.44%); **OPV4UP2**: δ_{N-H} ($CDCl_3$) 13.91, 12.03, 10.29, MALDI-TOF MS (MW = 1490.24) *m/z* = 1490.09 [M]$^+$, elemental analyses C, 75.99 (76.60), H, 9.58 (10.00), N, 3.45 (3.80%); calculated values in parenthesis.

1 R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. C. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Logdlund and W. R. Salaneck, *Nature*, 1999, **397**, 121.
2 R. E. Martin and F. Diederich, *Angew. Chem., Int. Ed.*, 1999, **38**, 1350.
3 J. M. Tour, *Chem. Rev.*, 1996, **84**, 303.
4 Z. Hu, J. L. Atwood and M. P. Cava, *J. Org. Chem.*, 1994, **59**, 8071; K. P. Baldwin, R. S. Simons, J. Rose, P. Zimmerman, D. M. Hercules, C. A. Tessier and W. J. Youngs, *J. Chem. Soc., Chem. Commun.*, 1994, 1257; C. J. Walter and J. K. M. Sanders, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 217; J. Zhang, D. J. Pesak, J. L. Ludwick and J. S. Moore, *J. Am. Chem. Soc.*, 1994, **116**, 4227.
5 Z. Wu, S. Lee and J. S. Moore, *J. Am. Chem. Soc.*, 1992, **114**, 8730.
6 J. M. Tour, R. Wu and J. S. Schumm, *J. Am. Chem. Soc.*, 1991, **113**, 7065; R. Wu, J. S Schumm, D. L. Pearson and J. M. Tour, *J. Org. Chem.*, 1996, **61**, 6906; J. Salbeck, F. Weissörtel and J. Bauer, *Macromol. Symp.*, 1997, **125**, 121.
7 Z. Xu and J. S. Moore, *Angew. Chem., Int. Ed.*, 1993, **32**, 1354.
8 D. Goldhaber-Gordon, M. S. Montemerlo, J. C. Love, G. J. Opiteck and J. C. Ellenbogen, *Proceedings of the IEEE*, 1997, **85**, 521; D. L. Pearson, L. Jones III, J. S. Schumm and J. M. Tour, *Synth. Met.*, 1997, **84**, 303.
9 F. S. Schoonbeek, J. H. van Esch, B. Wegewijs, D. B. A. Rep, M. P. de Haas, T. M. Klapwijk, R. M. Kellog and B. L. Feringa, *Angew. Chem., Int. Ed.*, 1999, **38**, 1393.
10 F. Würthner, C. Thalacker and A. Sautter, *Adv. Mater.*, 1999, **11**, 754.
11 J. L. Sessler, C. T. Brown, D. O'Conner, S. L. Springs, R. Wang, M. Sathiosatham and T. Hirose, *J. Org. Chem.*, 1998, **63**, 7370.
12 R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe and E. W. Meijer, *Science*, 1997, **278**, 1601; B. J. B. Folmer, R. P. Sijbesma, R. M. Versteegen, J. A. J. van der Rijt and E. W. Meijer, *Adv. Mater.*, 2000, **12**, 874; L. Brunsveld, B. J. B. Folmer and E. W. Meijer, *MRS Bull.*, 2000, **25**, 49; J. H. K. K. Hirschberg, F. H. Beijer, H. A. van Aert, P. C. M. M. Magusin, R. P. Sijbesma and E. W. Meijer, *Macromolecules*, 1999, **32**, 2696.
13 H. W. I. Peerlings and E. W. Meijer, *Tetrahedron Lett.*, 1999, **40**, 1021.
14 F. H. Beijer, R. P. Sijbesma, H. Kooijman, A. L. Spek and E. W. Meijer, *J. Am. Chem. Soc.*, 1998, **120**, 6761.
15 S. H. M. Söntjens, R. P. Sijbesma, M. H. P. van Genderen and E. W. Meijer, *J. Am. Chem. Soc.*, in press.
16 See *e.g.* E. Peeters, M. P. T. Christiaans, H. F. M. Schoo, H. P. J. M. Dekkers and E. W. Meijer, *J. Am. Chem. Soc.*, 1997, **119**, 9909; B. M. W. Langeweld-Voss, D. Beljone, Z. Shuai, R. A. J. Janssen, S. C. J. Meskers, E. W. Meijer and J.-L. Brédas, *Adv. Mater.*, 1998, **10**, 1343.

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