ChemComm

Mass spectrometric evidence for aggregation of a substituted sexithiophene

A. F. M. Kilbinger,[a] H. J. Cooper,[b] L. A. McDonnell,[b] W. J. Feast,*[a] P. J. Derrick,*[b] A. P. H. J. Schenning[c] and E. W. Meijer[c]

[a] *IRC in Polymer Science and Technology, University of Durham, Durham, UK DH1 3LE. E-mail: wj.feast@durham.ac.uk*
[b] *Institute of Mass Spectrometry and Department of Chemistry, University of Warwick, Coventry, UK CV4 7AL*
[c] *Laboratory of Macromolecular and Organic Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands*

Received (in Cambridge) 9th December 1999, Accepted 7th February 2000

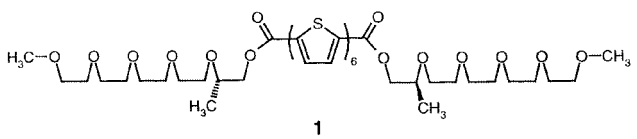
Nanospray FT-ICR mass spectroscopy provides unambiguous evidence for solvent-dependent aggregation of a substituted sexithiophene.

We report evidence for the solvent-dependent aggregation of an α,ω-disubstituted sexithiophene, obtained by nanospray Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry[1–6] of solutions of varying polarity. Electrospray ionisation (ESI),[3] of which nanospray[4–6] is a variant, has been used for studying aggregation of proteins.[7,8] In this work, we used FT-ICR coupled with ESI (nanospray) to probe aggregation of an oligomer; high resolution was important in order to resolve overlapping signals due to differently sized aggregates.

Aggregation in solution is well known for α-oligothiophenes and poly(thiophenes).[9–11] Evidence for aggregation of such chromophores has been deduced from shifts in UV–VIS spectra, quenching of photoluminescence, broadening of linewidths in NMR or observation of a circular dichroism spectrum for aggregates of chiral chromophores.[12,13] Whereas these techniques give indirect evidence for aggregation, we have established direct evidence for solvent-dependent aggregation by FT-ICR mass spectrometry.

We have established a synthesis for 2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′-sexithiophene-5,5⁗′-dicarboxylic acid (2*S*)-2-methyl-3,6,9,12,15-pentaoxahexadecyl ester **1** (Fig. 1) and UV (absorption and emission) and CD spectroscopic evidence for its temperature dependent chiral aggregation in solution.[13] Compound **1** appears to aggregate in polar protic solvents such as THF–water mixtures and to be molecularly dissolved in organic solvents such as pure THF or $CHCl_3$. We have used nanospray FT-ICR mass spectrometry to investigate **1** in THF and THF–water mixtures. The nanospray technique provided the possibility of ionising the oligomer **1**, and its suspected aggregates, without fragmentation.

Experiments were performed using nanospray on a Bruker BioApex FT-ICR mass spectrometer equipped with a shielded 9.4 T magnet (Magnex Scientific Ltd., Abingdon, UK), a 6 cm diameter cylindrical infinity cell and electrospray ionisation source (Analytica of Branford, Branford, USA).[14,15] Low capillary and skimmer potentials were used to minimise any possibility of the non-covalent bonds of the aggregate being disrupted in the source. Solutions were made up using THF and a polar solvent mixture (PSM) containing equal volumes of ammonium acetate solution (10 mM, pH 6.0) and methanol, and 2% v/v concentrated acetic acid.



1

Fig. 1 2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2⁗′:5⁗′-sexithiophene-5,5⁗′-dicarboxylic acid (2*S*)-2-methyl-3,6,9,12,15-pentaoxahexadecyl ester **1**.

In agreement with our previous observations from UV–VIS and photoluminescence spectroscopy, the results from nanospray FT-ICR indicated that **1** did not aggregate in predominantly aprotic solution. Fig. 2 shows the mass spectrum obtained from a solution of **1** in 90% THF–10% PSM. The neutral oligomer is designated as 6T in the spectrum. Intense signals due to the ammonium and sodium ion adducts of the monomeric compound can be seen in Fig. 2. The experimental isotope patterns matched the theoretical, confirming that each cluster of peaks represented a single species. The measured mass-to-charge (*m*/*z*) ratios agreed with those calculated to within 1 ppm in all cases (all-^{12}C $[6T+NH_4]^+$, measured mass 1096.2811 *cf.* calc. 1096.2802; all-^{12}C $[6T+Na]^+$, measured mass 1101.2342 *cf.* calc. 1101.2356). There was no evidence for aggregation. Nanospray from a more polar solution of **1**, (75% THF–25% PSM), again gave mainly monomeric ammonium and sodium ion adducts but also a weak signal due to the dimeric diammonium ion adduct (Fig. 3). Peaks from the doubly charged dimer can lie underneath those from the singly charged monomer or appear between the singly charged monomer peaks. Thus, the all-^{12}C monomer peak and the all-^{12}C dimer peak both theoretically fall at *m*/*z* 1096.2802. The one-^{13}C monomer peak falls at *m*/*z* 1097.2836 but the one-^{13}C dimer peak falls between these two peaks at *m*/*z* 1096.7822 and is detected as a weak peak. The spectrum (Fig. 3) establishes that the bonding in the dimer between the constituent monomers is non-covalent, because the measured mass of the dimer is exactly twice that of the monomer. If the bonding had been covalent, loss of two hydrogen atoms might have been expected; there is no possibility of simple addition dimerisation of **1**. In the case of loss of two hydrogen atoms, there would have been a detectable peak at *m*/*z* 1095.2724 due to the doubly-charged all-^{12}C dimer, there was no peak at this *m*/*z*.

The diammonium ion adduct of the tetramer (Fig. 4), the diammonium ion adduct of the pentamer (Fig. 5) and the

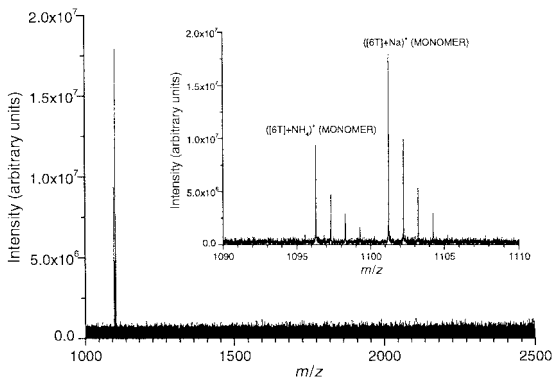


Fig. 2 Compound **1** (50 μM) in THF–PSM (90 : 10 v : v). Only monomeric species can be observed. The inset shows the isotope patterns of the ammonium adduct ion, $([6T]+NH_4)^+$ and of the sodium adduct ion, $([6T]+Na)^+$. 6T is a designation used for the neutral compound **1**.

DOI: 10.1039/a909686h

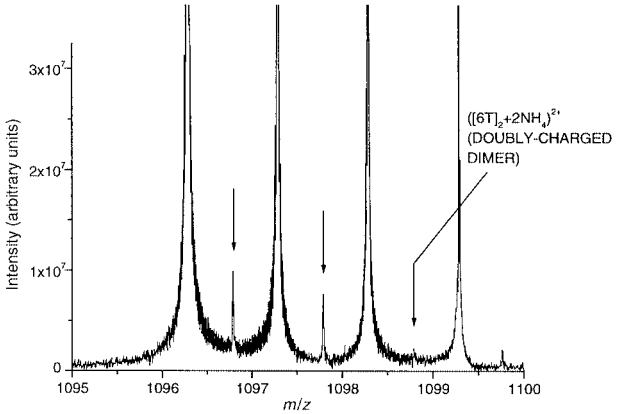


Fig. 3 Compound **1** (150 μM) in THF–PSM (75 : 25 v : v). The monomeric ammonium adduct ion (see also Fig. 2) and the dimeric diammonium adduct ion, $([6T]_2+2NH_4)^{2+}$ (see arrows) are observed.

triammonium ion adduct of the hexamer were observed when a solution of compound **1** in 50% THF–50% polar solvent mixture was investigated.

The diammonium adduct of the tetramer overlays the ammonium adduct of the dimer (Fig. 4). That the isotope distributions of the two ions were directly coincident indicates that the mass of the tetrameric species was exactly twice that of the dimer, *i.e.* bonding was non-covalent in the tetramer. The most intense peak in the isotope distribution of the diammonium pentamer adduct (Fig. 5) corresponds to the six-^{13}C species; the all-^{12}C isotopomer cannot be discerned in Fig. 5. The cluster of peaks shown in Fig. 6 represent isotopes of three species: the singly charged ammonium adduct of the dimer $([6T]_2+NH_4)^+$, the doubly-charged diammonium tetramer adduct

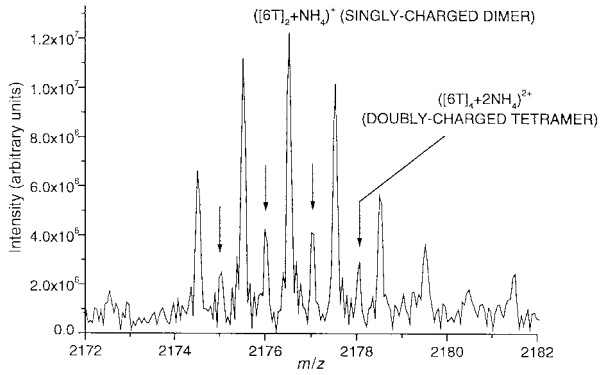


Fig. 4 Compound **1** (50 μM) in THF–PSM (50 : 50 v : v). Peaks due to the ammonium ion adduct of the dimer, $([6T]_2+NH_4)^+$, and the diammonium adduct ion of the tetramer, $([6T]_4+2NH_4)^{2+}$, are superimposed.

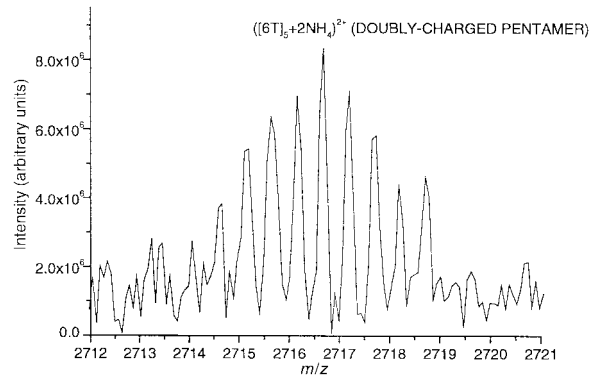


Fig. 5 Compound **1** (50 μM) in THF–PSM (50 : 50 v:v). Isotopic distribution of the diammonium adduct ion of the pentamer, $([6T]_5+2NH_4)^{2+}$.

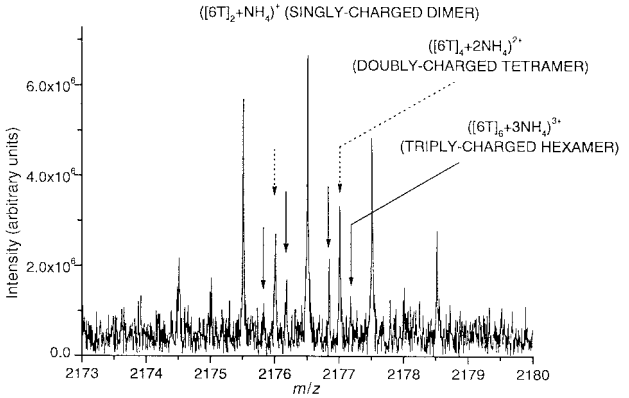


Fig. 6 Compound **1** (100 μM) in THF–PSM (50 : 50 v : v). Peaks due to the ammonium adduct ion of the dimer, $([6T]_2+NH_4)^+$, the diammonium adduct ion of the tetramer, $([6T]_4+2NH_4)^{2+}$ (dotted arrows) and the triammonium ion adduct of the hexamer, $([6T]_6+3NH_4)^{3+}$ (straight arrows) are overlaid.

$([6T]_4+2NH_4)^{2+}$ and the triply charged triammonium hexamer adduct $([6T]_6+3NH_4)^{3+}$.

The size of detectable aggregates is currently limited by the instrument configuration and the relationship between behaviour in solution and in the mass spectrometer source[16] is a matter for continuing study. However, we conclude that oligomeric aggregates of compound **1**, from the dimer to the hexamer have been observed by nanospray FT-ICR mass spectrometry when sprayed from polar solution, whereas the monomer alone was observed when sprayed from THF solution. Taken together these results constitute unambiguous evidence for the aggregation of **1** in solution, a process which intensifies with increasing solution polarity.

We thank Luc Brunsveld for the chiral penta(ethylene glycol), the European Commission Training and Mobility of Researchers Network SELOA (contract number ERBFMRX-CT960083) and the Royal Dutch Academy of Arts and Sciences. The FT-ICR laboratory at the University of Warwick is an EPSRC National Facility.

Notes and references

1 M. B. Comisarow and A. G. Marshall, *Chem. Phys. Lett.*, 1974, **25**, 282.
2 A. G. Marshall, M. B. Comisarow and G. Parisod, *J. Chem. Phys.*, 1979, **71**, 4434.
3 J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong and C. M. Whitehouse, *Science*, 1989, **246**, 64.
4 M. S. Wilm and M. Mann, *Int. J. Mass Spectrom., Ion Proc.*, 1994, **136**, 167.
5 M. S. Wilm and M. Mann, *Anal. Chem.*, 1996, **68**, 1.
6 R. Korner, M. Wilm, K. Morand, M. Schubert and M. Mann, *J. Am. Soc. Mass Spectrom.*, 1996, **7**, 150.
7 D. Lafitte, A. J. R. Heck, T. J. Hill, K. Jumel, S. E. Harding and P. J Derrick, *Eur. J. Biochem.*, 1999, **261**, 337.
8 A. A. Rostom and C. V. Robinson, *J. Am. Chem. Soc.*, 1999, **121**, 4718.
9 E. Ramos Lermo, B. M. W. Langeveld, R. A. J. Janssen and E. W. Meijer, *Chem. Commun.*, 1999, 791.
10 B. M. W. LangeveldVoss, M. P. T. Christiaans, R. A. J. Janssen and E. W. Meijer, *Macromolecules*, 1998, **31**, 6702.
11 G. Bidan, S. Guillerez and V. Sorokin, *Adv. Mater.*, 1996, **8**, 157.
12 B. M. V. LangeveldVoss, D. Beljonne, Z. Shuai, R. A. J. Janssen, S. C. J. Meskers, E. W. Meijer and J. L. Bredas, *Adv. Mater.*, 1998, **10**, 1343.
13 A. F. M. Kilbinger, A. P. H. J. Schenning, F. Goldoni, W. J. Feast and E. W. Meijer, *J. Am. Chem. Soc.*, 2000, in press.
14 A. J. R Heck and P. J. Derrick, *Anal. Chem.*, 1997, **69**, 3603.
15 H. Lavanant, P. J. Derrick, A. J. R. Heck and F. A. Mellon, *Anal. Biochem.*, 1998, **255**, 74.
16 S. M. Hunt, M. M. Sheil, M. Belov and P. J. Derrick, *Anal. Chem.*, 1998, **70**, 1812.

Communication a909686h