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# PAPER

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# Block-like electroactive oligo(aniline)s: anisotropic structures with anisotropic function<sup>†</sup>

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A tetra(aniline)-alkyl diblock compound was designed, synthesized and fully characterized. By employing suitable conditions, doped, electroactive microstructures could be prepared. The microstructures were characterized in detail and their anisotropic conductivity measured for the first time.

### Introduction

Oligo(aniline)s are model compounds of the well-known conducting polymer poly(aniline) (PANI).<sup>1,2</sup> PANI has retained a high level of research interest owing to the ease of synthesis, high electrical conductivity,3 unique redox properties,4 excellent environmental stability, and potential for use in energy storage applications.<sup>5-9</sup> Oligo(aniline)s not only retain the advantageous properties of PANI,<sup>10</sup> but also exhibit much better processability than PANI, as these shorter functional analogues are soluble in most common organic solvents. These attractive properties prompted us to develop a new, single-step synthesis of a family of phenyl-capped tetra(aniline) (TANI) derivatives.<sup>11</sup> Not only does this strategy provide a facile route for modification of the electronic structure of tetra(aniline)s,11 but it also provides interesting materials for the preparation of oligo(aniline) bulk films,12 thin films,<sup>13</sup> and discrete self-assembled nanostructures.<sup>10</sup> It is therefore the expectation that these new synthetic developments will lead to a range of applications for oligo(aniline)s, including chemical sensors,14,15 gas-separation membranes,16 supercapacitors,<sup>17</sup> and artificial muscles (as already found for PANI).<sup>18</sup>

Block-like oligo(aniline)s have also attracted considerable scientific interest recently.<sup>19</sup> This interest mainly stems from the fact that the analogous high molecular weight materials, block copolymers, are very well known for (a) forming microphaseseparated nanostructures in the bulk, and (b) to self-assemble into various micellar structures in selective solvents due to the immiscibility between the different blocks. A number of blocklike systems have therefore been synthesized by attaching different types of functional groups to the amine terminus of the phenyl/amine-capped oligo(aniline)s.<sup>20–25</sup> For example, the attachment of different length alkyl chains has been reported for phenyl/amine-capped TANI (Ph/NH<sub>2</sub> TANI) *via* simple substitution reactions.<sup>26</sup> As the TANI blocks are rigid and the alkyl chains are flexible, the combinations are electroactive examples of rod-coil molecules.<sup>27</sup> These molecules can self-assemble into different nanostructures *via* competing interactions between the  $\pi$ - $\pi$  stacking of the rigid TANI conjugation blocks and the secondary interactions of the flexible alkyl blocks.<sup>27,28</sup>

Such oligo(aniline)-alkyl diblock materials are known to exhibit anisotropic conductive properties, yet in the published work to date, measurement and quantification of these properties have not been performed. Here we report our initial investigations into the anisotropic functionality of microstructure prepared from TANI-alkyl diblock systems. We describe the synthesis of amide-linked TANI-alkyl diblock (TANI-C8, Scheme 1), and the characterization of electroactive anisotropic microstructures derived from its doped form (using the inorganic acid HCl), TANI-C8(HCl)<sub>0.5</sub>. Finally, anisotropic conductivity was measured for block-like architectures from doped TANI-C8 structures for the first time.

### **Result and discussion**

### Design and synthesis

The **TANI-C8** molecular architecture was designed to incorporate both the rigid TANI functional moiety, presenting opportunities for extensive  $\pi$ - $\pi$  stacking interactions, and a flexible alkyl moiety, allowing hydrophobic interactions. Furthermore, the linking amide group also provides the possibility for

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<sup>&</sup>lt;sup>†</sup> Electronic supplementary information (ESI) available: Details of experimental conditions and characterization of **TANI-C8**, including synthesis of Ph/NH<sub>2</sub> TANI, IR data, TEM, XRD and SAED data. See DOI: 10.1039/c2jm32278a

<sup>‡</sup> These authors contributed equally to the work.



Scheme 1 Synthesis of TANI-C8 (EB).

hydrogen bonding, to further assist the formation of anisotropic structures. **TANI-C8** was synthesized by reaction of the emeraldine base (EB) of Ph/NH<sub>2</sub> TANI (prepared by a reported method<sup>29</sup>) with octanoyl chloride (Scheme 1). To avoid side reactions with its secondary amines, a slight excess of Ph/NH<sub>2</sub> TANI was employed. Upon completion of the reaction, the ether-soluble EB Ph/NH<sub>2</sub> TANI was removed by repeated washing with diethyl ether. This simple approach provides a synthetic route to TANI-alkyl diblock compounds complementary to the reported condensation between Ph/NH<sub>2</sub> TANI and alkyl carboxylic acids.<sup>28</sup>

### **Bulk material**

Fig. 1 shows the solid-state UV/Vis-NIR spectra of the **TANI-C8** in the undoped EB state and in the ES state after full doping with HCl acid (film cast from  $10^{-2}$  M ethanol solution). The EB state shows the two typical absorption maxima (at 322 and 595 nm), which are both ascribed to  $\pi$ - $\pi$ \* transitions of the benzenoid and



Fig. 1 UV/Vis-NIR of TANI-C8 in the undoped EB, and HCl-doped ES state.

quinoid units.<sup>11,28,30</sup> When **TANI-C8** was doped with HCl, the UV/Vis-NIR spectra showed peaks at 322, 418 and 846 nm, which is in good agreement with the previous report in the literature.<sup>31</sup> A free-carrier tail is visible in the NIR region, a feature characteristic of metallic conductive materials.<sup>30,32</sup> The HCl-doped ES state has a relatively weak localized polaron band starting from 726 nm, which indicates poor overlapping of the polarons, but still extends up to almost 2000 nm. The presence of two bands in the Vis-NIR region may be related to the presence of non-equivalent radical cations in the TANI chemical structure.

Wide-angle X-ray diffraction (WAXS) data for pure **TANI-C8** and after doping with HCl is shown in Fig. S1, (ESI<sup>†</sup>), and the resulting structures are discussed in more detail below.

IR spectroscopy was used to investigate the extent of hydrogen-bonding behaviour in the solid state for both the undoped TANI-C8 and doped TANI-C8(HCl)<sub>0.5</sub>. In order to ascertain the relevant IR vibration frequencies without any hydrogen bonding, IR spectra were recorded in dilute CCl<sub>4</sub> solutions (i.e., a solvent which does not participate in hydrogen bonding). These spectra show that, for the TANI-C8, no hydrogen bonding takes place with the amide C=O (1652 cm<sup>-1</sup>).<sup>33</sup> A very weak signal was detected at 3405 cm<sup>-1</sup> for the free amine N-H from the TANI backbone. Interestingly, for the doped TANI-C8(HCl)<sub>0.5</sub>, very weak hydrogen bonding to the amide C=O was detected, even in CCl<sub>4</sub>, as evidenced by the small shift to higher wave numbers (1657 cm<sup>-1</sup>) and appearance of a very weak band at 1602 cm<sup>-1</sup> for the C=O stretching vibration. This very weak splitting of the signal (originally found at 1652 cm<sup>-1</sup>) is an indication of very weak partial hydrogen bonding,<sup>34</sup> most probably from the interaction with the HCl dopant. A number of very weak signals were furthermore detected (in the range  $3219-3377 \text{ cm}^{-1}$ ), as well as at  $3400 \text{ cm}^{-1}$ (the latter for the free amine N-H stretching frequency of the TANI, see Table 1).

When solid-state IR data was recorded, surprisingly similar results were found. No clear indication of hydrogen bonding interactions with the C=O moiety was seen for the EB TANI-C8, as this band appeared at essentially the same wavenumber (1654 cm<sup>-1</sup>). Investigation of the higher amide and amine N-H stretching frequencies showed only very weak bands at 3378 and 3284 cm<sup>-1</sup>, respectively, indicative of hydrogen bonding.<sup>28</sup> The behaviour of TANI-C8(HCI)<sub>0.5</sub> in the solid state showed slightly increased hydrogen-bonding tendencies. This was reflected in the split of the C=O stretching frequency found at 1656 and 1600 cm<sup>-1</sup>, and the lowering of the amide and amine N-H stretching frequencies to 3369 and 3231 cm<sup>-1</sup> (very broad), respectively.

**Table 1** Summary of IR vibration frequencies  $(cm^{-1})$  in solution and the solid state for **TANI-C8** and **TANI-C8(HCI)**<sub>0.5</sub><sup>*a*</sup>

	TANI-C8 (CCl <sub>4</sub> )	TANI-C8(HCl) <sub>0.5</sub> (CCl <sub>4</sub> )	TANI-C8 Solid state	TANI-C8(HCl) <sub>0.5</sub> Solid state
C=0	1652	1657	1654	1656
		1602		1600
N–H (amide)			3378	3369
N–H (amine)	3405	3400 (v. weak)	3284	3231 (v.b.)
a 1				

 $v.b. = very broad, see ESI^{\dagger}$  for IR spectra.

c)

Absorption (a. u.)

Finally, bulk solid-state conductivity of thin pellets of TANI-C8 in the undoped EB state, as well as TANI-C8(HCl)<sub>0.5</sub> was measured using a standard 4-probe setup (see ESI<sup>†</sup> for details). Due to the high resistivity, we were unable to measure the conductivity of undoped TANI-C8 (i.e., non-conductive and lower than  $10^{-9}$  S cm<sup>-1</sup>), while the conductivity of the doped **TANI-C8(HCl)**<sub>0.5</sub> was extremely low at  $0.38 \times 10^{-6}$  S cm<sup>-1</sup>.

### Anisotropic microstructures: preparation and characterisation

With the bulk material characterised and conditions for doping established, we focussed our investigations on the production and characterization of anisotropic structures. Anisotropic microstructures were prepared by dissolving undoped TANI-C8 in a good solvent (THF), and slowly adding water as a poor solvent. By optimizing the ratio between the good and poor solvent, microstructures of undoped TANI-C8 were obtained. At low poor solvent ratio, no precipitate was observed. SEM images showed that only small irregular aggregates were formed. When the poor solvent ratio was increased to 80%, regular microplates were formed and deposited from the solution.

A low-magnification scanning electron microscopy (SEM) image is shown in Fig. 2a, displaying high concentrations of twodimensional microplates. A high-magnification SEM image of a typical microplate is shown in Fig. 2b. The microplate is parallelogram-shaped, with typical dimensions of  $4 \times 5 \,\mu$ m, and well-defined angles and sides.<sup>35</sup> The UV/Vis-NIR spectrum of the microplate film was recorded before (in the EB state) and after doping (in the ES state). Doping was performed by exposing the drop-cast microplates to HCl vapours over night in a closed environment. As shown in Fig. 2c, the EB state showed the two typical absorption peaks (at 318 and 597 nm), which are both ascribed to  $\pi - \pi^*$  transitions of the benzenoid and quinoid

units.<sup>11</sup> After doping, two absorption peaks at 423 and 960 nm were obtained, and are typical for the ES state.<sup>30</sup> The absorption peak in the near infra-red region can be assigned to a localized polaron band, which again indicates successful doping.<sup>30</sup> The presence of two bands in the Vis-NIR region may, as before, be related to the presence of non-equivalent radical cations in the anisotropic microstructures.

To investigate the arrangement of TANI-C8 molecules in the anisotropic microstructures, further structural characterization was carried out on the undoped microplates. Fig. 3a shows the transmission electron microscopy (TEM) image of a representative microplate. The selected-area electron diffraction (SAED) pattern obtained from the same microplate is shown in Fig. 3b. The highly crystalline nature of the microplates was confirmed by the SAED patterns obtained. The patterns show a *d*-spacing of 3.95 Å from the (020) reflection of the  $\pi$ - $\pi$  stacking direction (b-axis) and 5.9 Å from the (100) reflection of the edge-on stacking direction (a-axis).

Fig. 3c shows WAXS profiles of the microplates, with all major peaks indexed (see ESI, Table S1<sup>†</sup> for details of the indexation). It is possible to deduce from these results that the microplates have an orthorhombic crystalline structure with parameters of a = 5.9 Å, b = 7.9 Å, c = 30.2 Å (the calculated length of a fully stretched TANI-C8 molecules is ca. 3 nm). Fig. 3d shows a schematic illustration of the arrangement of TANI-C8 molecules in single crystalline microplates. We propose that the main chain is oriented along the direction of the thickness of the microplate (*c*-axis), while the *b*-axis and *a*-axis is laying on the substrate.

We propose that an interplay of non-covalent interactions lead to the formation of the observed microstructures: the formation of the microplate structure is ascribed to efficient  $\pi$ - $\pi$  interactions and the action of hydrogen bonding between the molecules. The  $\pi$ - $\pi$  interactions between the TANI backbones lead to the  $\pi$ -stacking along the *b*-axis, whereas the arrangement along the *a*-axis is the result of intermolecular hydrogen bonding between amide-amide and amine-imine groups (Fig. 3d, as confirmed by



Fig. 2 (a) Low and (b) high magnification SEM images of two dimensional undoped TANI-C8 microplates, (c) UV/Vis-NIR spectra of TANI-C8 microplates in the EB (undoped) state and the ES (HCl-doped) states.

800

TANI-C8(HCI)(ES)

Fig. 3 (a) TEM image and (b) SAED patterns of undoped TANI-C8 anisotropic microplates, (c) WAXS spectrum of undoped microplates (d) schematic illustration of TANI-C8 molecules arrangement in singlecrystalline microplates (the *ab*-plane is on the substrate).

400

5 1/nm

٢

b-axis



Fig. 4 Two dimensional anisotropic conductivity measurements of single-crystalline microplate structures. (a) AFM height image of a microplate after evaporating Au electrodes and its section analysis; (b) current–voltage (I-V) curve and the conductivity of different directions of the microplate.

the IR investigations and a recently published study by Kim and Park<sup>28</sup>). In addition, the incorporation of the alkyl chains aid tuning of the solubility and the degree of aggregation of the TANI moieties.

We then proceeded to prepare HCl-doped **TANI-C8** microplates by exposure to HCl vapour in an N<sub>2</sub> atmosphere, and investigated their structure and anisotropic conductive properties (Fig. 4). TEM, WAXS and SAED investigations showed that the doped anisotropic microplate structures were intact, single crystalline and possessing an orthorhombic crystalline structure with similar parameters as for the undoped structure (see ESI, Fig. S4 and Table S1<sup>†</sup>).

Electron transport studies on single-crystalline undoped TANI-C8 microplates were performed in order to determine the anisotropic functional properties. The microplates were spincoated from aqueous solution on Si substrates, which was capped with a layer of SiO<sub>2</sub>. Au electrodes (about 20 nm thick) were deposited on the microplates by thermal evaporation, using an organic ribbon as a shadow mask. The organic ribbon was then removed to obtain a conducting channel.<sup>36</sup> Fig. 4a shows the AFM height image of a Au top-contact device constructed from a single TANI-C8 microplate (thickness of the microplate ca. 100 nm). First, it was confirmed that the microplate in the non-doped EB state was indeed not conductive (see inset table, Fig. 4). The microplate was then doped with HCl (similar procedure as above) before conductivity measurements were performed again. Anisotropic conductivity was measured across two different directions of the microplate. Fig. 4b shows the anisotropic conductivity observed after doping. All of the I-V curves were linear and symmetrical, which indicated that contact resistance is negligible, *i.e.* the contact was ohmic in nature. The results show that the conductivity along the *a*-axis is  $6.8 \times 10^{-5} \text{ S} \cdot \text{cm}^{-1}$  and the conductivity along the  $\pi$ - $\pi$  stacking direction (*b*-axis) is significantly higher, at  $2.1 \times 10^{-4} \text{ S} \cdot \text{cm}^{-1}$  (even if lower when compared to other reports<sup>37,38</sup>). We tentatively ascribe this lower value to a combination of factors, including the possibility that doping was not uniform throughout the microstructure and the dilution of the electroactive structures with the alkyl tails within

such a confined environment. We are therefore currently

### Conclusions

A tetra(aniline)-alkyl diblock compound, **TANI-C8**, was synthesized and self-assembled into single-crystalline twodimensional microplates. The microplates showed anisotropic conductivity owing to the anisotropic arrangement of the **TANI-C8** molecules in the microstructures. This investigation provides further insight into methods to prepare two-dimensional structures of oligo(aniline) and showed its potential application in organic electronics.

### **Experimental section**

# Synthesis of *N*-(4-(4- (phenylamino)phenylamino) phenylamino)phenyl)octanamide

To a nitrogen-protected two-neck round-bottom flask equipped with a dropping funnel was charged tetraaniline (200.3 mg, 0.55 mmol, 1 eq.), triethylamine (253.0 mg, 346.6 µL, 2.5 mmol, 5 eq.) and anhydrous diethyl ether (60 mL). The solid was stirred while the flask was cooled to 0 °C in an ice bath. A portion octanoyl chloride (81.3 mg, 85.3 µL, 0.5 mmol, 0.9 eq.) in anhydrous diethyl ether (20 mL) was slowly added to the reaction flask through the dropping funnel under nitrogen protection. The ice bath was then removed and the mixture was allowed to react overnight. The precipitate was collected by centrifugation and washed with ether until complete removal of the starting tetraaniline was achieved, as monitored by TLC analysis. The solid was dissolved in DMF (25 mL) and treated with phenylhydrazine (54.1 mg, 0.5 mmol) for 2 h. The solution was then poured into deionised water (250 mL). The precipitate was collected by centrifugation to afford the product, in the leucoemeraldine base state, as a gray powder. (196.9 mg, 80%): 1H NMR (400 MHz, DMSO- $d_6$ , 25 °C)  $\delta = 9.61$  (s, 1H), 7.76 (s, 1H), 7.67 (s, 1H), 7.63 (s, 1H), 7.38 (d, 2H, J = 8.8 Hz), 7.14 (t, 2H, J = 7.9 Hz), 7.00–6.85 (m, 12H), 6.67 (t, 1H, J = 7.3 Hz), 2.23 (t, 2H, J = 7.3 Hz), 1.61-1.52 (m, 2H), 1.34-1.20 (m, 8H), 0.86(t, 3H, J = 6.5 Hz); <sup>13</sup>C NMR (100 MHz, DMSO-d<sub>6</sub>, 25 °C)  $\delta =$ 170.9, 146.0, 129.6, 121.2, 119.8, 118.8, 118.5, 118.0, 116.1, 115.1, 31.8, 29.2, 29.0, 25.9, 22.6, 14.5; IR (neat, cm<sup>-1</sup>): 3378, 3369, 3324, 2923, 2851, 1656, 1602, 1531, 1514, 1497, 1312, 1302, 1221, 1110, 817, 744, 694; anal. calcd for C<sub>32</sub>H<sub>36</sub>N<sub>4</sub>O: C, 78.01; H, 7.37; N, 11.37. Found: C, 78.65; H, 7.40; N, 11.35%. HRMS calcd for C32H36N4O: 492.2889. Found: 492.2897.

### Notes and references

- 1 Z. X. Wei and C. F. J. Faul, *Macromol. Rapid Commun.*, 2008, 29, 280–292.
- 2 F. L. Lu, F. Wudl, M. Nowak and A. J. Heeger, *J. Am. Chem. Soc.*, 1986, **108**, 8311–8313.
- 3 A. G. MacDiarmid, S. L. Mu, N. L. D. Somasiri and W. Q. Wu, *Mol. Cryst. Liq. Cryst.*, 1985, **121**, 187–190.
- 4 D. K. Moon, M. Ezuka, T. Maruyama, K. Osakada and T. Yamamoto, *Macromolecules*, 1993, **26**, 364–369.

- 5 D. Li, J. Huang and R. B. Kaner, Acc. Chem. Res., 2009, 42, 135-145.
- 6 J. J. Xu, K. Wang, S. Z. Zu, B. H. Han and Z. X. Wei, *ACS Nano*, 2010, **4**, 5019–5026.
- 7 F. Fusalba, P. Gouerec, D. Villers and D. Belanger, J. Electrochem. Soc., 2001, 148, A1–A6.
- 8 K. Wang, J. Huang and Z. Wei, J. Phys. Chem. C, 2010, 114, 8062– 8067.
- 9 D. Belanger, X. M. Ren, J. Davey, F. Uribe and S. Gottesfeld, *J. Electrochem. Soc.*, 2000, **147**, 2923–2929.
- 10 Y. Wang, H. D. Tran, L. Liao, X. Duan and R. B. Kaner, J. Am. Chem. Soc., 2010, 132, 10365–10373.
- 11 Z. Shao, P. Rannou, S. Sadki, N. Fey, D. M. Lindsay and C. F. J. Faul, *Chem.-Eur. J.*, 2011, **17**, 12512–12521.
- 12 Z. X. Wei, T. Laitinen, B. Smarsly, O. Ikkala and C. F. J. Faul, Angew. Chem., Int. Ed., 2005, 44, 751–756.
- 13 T. G. Dane, P. T. Cresswell, O. Bikondoa, G. E. Newby, T. Arnold, C. F. J. Faul and W. H. Briscoe, *Soft Matter*, 2012, 8, 2824– 2832.
- 14 S. Virji, J. Huang, R. B. Kaner and B. H. Weiller, *Nano Lett.*, 2004, 4, 491–496.
- 15 J. Huang, S. Virji, B. H. Weiller and R. B. Kaner, J. Am. Chem. Soc., 2003, 125, 314–315.
- 16 C. J. Weng, Y. S. Jhuo, K. Y. Huang, C. F. Feng, J. M. Yeh, Y. Wei and M. H. Tsai, *Macromolecules*, 2011, 44, 6067–6076.
- 17 Y. G. Wang, H. Q. Li and Y. Y. Xia, Adv. Mater., 2006, 18, 2619– 2623.
- 18 B. K. Gu, Y. A. Ismail, G. M. Spinks, S. I. Kim, I. So and S. J. Kim, *Chem. Mater.*, 2009, 21, 511–515.
- 19 C. U. Udeh, N. Fey and C. F. J. Faul, J. Mater. Chem., 2011, 21, 18137–18153.
- 20 T. Canteenwala, V. Anantharaj, S. V. Patil, M. Halder and L. Y. Chiang, J. Macromol. Sci., Part A: Pure Appl. Chem., 2002, A39, 1069–1083.

- 21 B. Dufour, P. Rannou, J. P. Travers, A. Pron, M. Zagorska, G. Korc, I. Kulszewicz-Bajer, S. Quillard and S. Lefrant, *Macromolecules*, 2002, **35**, 6112–6120.
- 22 C. Querner, P. Reiss, J. Bleuse and A. Pron, J. Am. Chem. Soc., 2004, 126, 11574–11582.
- 23 K. Buga, R. Pokrop, A. Majkowska, M. Zagorska, J. Planes, F. Genoud and A. Pron, J. Mater. Chem., 2006, 16, 2150–2164.
- 24 H. F. Wang, P. Guo and Y. C. Han, *Macromol. Rapid Commun.*, 2006, **27**, 63–68.
- 25 Z. Yang, X. Wang, Y. Yang, Y. Liao, Y. Wei and X. Xie, *Langmuir*, 2010, 26, 9386–9392.
- 26 C. Luo, W. Huang, H. Wang and Y. Han, J. Chem. Phys., 2007, 127, 244903–244911.
- 27 H. J. Kim, T. Kim and M. Lee, Acc. Chem. Res., 2011, 44, 72-82.
- 28 H. Kim and J. W. Park, J. Mater. Chem., 2010, 20, 1186-1191.
- 29 W. J. Zhang, J. Feng, A. G. MacDiarmid and A. J. Epstein, Synth. Met., 1997, 84, 119–120.
- 30 W. Wang and A. G. MacDiarmid, Synth. Met., 2002, 129, 199-205.
- 31 R. Chen and B. C. Benicewicz, Macromolecules, 2003, 36, 6333-6339.
- 32 A. P. Monkman and P. Adams, Synth. Met., 1991, 41, 627-633.
- 33 No signal was detected at 3440 cm<sup>-1</sup>, where the amide N-H stretching frequency is expected to appear.
- 34 F. Camerel and C. F. J. Faul, Chem. Commun., 2003, 1958-1959.
- 35 Some of the microstructures were broken into smaller species, or, in some areas, aggregated. This is ascribed to incomplete structure formation, breaking of formed structures during processing, and aggregation of the microstructures during the deposition and the post-processing procedures.
- 36 L. Jiang, J. Gao, E. Wang, H. Li, Z. Wang, W. Hu and L. Jiang, Adv. Mater., 2008, 20, 2735–2740.
- 37 A. G. MacDiarmid and A. J. Epstein, Synth. Met., 1995, 69, 85-92.
- 38 C. Y. Yang, M. Reghu, A. J. Heeger and Y. Cao, Synth. Met., 1996, 79, 27–32.