The different electronic natures displayed by the alkylthio groups in simple and higher conjugated aniline systems†

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Received 4th July 2006, Accepted 12th July 2006
First published as an Advance Article on the web 8th August 2006
DOI: 10.1039/b609506b

Systematic studies based on ^{1}H NMR and ^{13}C NMR indicated that the alkylthio group behaves as a weak electron-withdrawing group in a simple aniline system like 2-butylthioaniline, while the same alkylthio group clearly acted as a resonance electron-donating group in higher conjugated aniline trimer systems, like butylthio-substituted PDA (mono-PDA) and dibutylthio-substituted PDA (2,6-diPDA). The formation of 2,6-diPDA as the major byproduct during the preparation of mono-PDA from PDI and butane-1-thiol provided additional support for the resonance electron donating nature of the butylthio group in these aniline trimer systems. Furthermore, CV studies also clearly indicated that the redox potential $E°$ (*vs.* SCE) of the aniline trimer systems decreased with the increase in the number of butylthio groups, further confirming the electron-donating nature of the butylthio group in these higher conjugated trimer systems.

Introduction

Among the conducting polymers, polyaniline (Pan) has gained widespread attention due to its excellent stability in air, low cost, and great opportunities for application.[1–3] However, just like other conducting polymers, the application potential of Pan is seriously limited due to its poor solution processibility. Although the solubility problem can be eased by incorporating alkyl and alkoxy groups on polymer backbones based on modified aniline monomers, the alkyl- and alkoxy-substituted polyanilines obtained however suffered a severe loss in conductivity by *ca.* 1 to 7 orders of magnitude,[4] which has long been attributed by the community to arise from the steric effects associated with the substituent group. On the contrary, we believe it is probably caused by the increased numbers of nonconjugated backbone linkage defects (1,3-ring linkage) due to the electronic directing influences of the -R and -OR groups on the formation of backbone linkage.[4c] Such an adverse electronic influence was even more severe in the case of 2-butylthioaniline, and seemed to even prevent it from forming its own homopolymer. The copolymers prepared from aniline and 2-butylthioaniline, *via* the conventional oxidative copolymerization (OCP) method, containing only ~32 mol% of the butylthio group already showed a much poorer conductivity (10^{-5} S cm^{-1})[4c] than the homopolymer of butoxyaniline (10^{-3} S cm^{-1}).[4d] On the other hand, the butylthio-substituted polyaniline (Pan-SBu) prepared *via* our previously reported concurrent reduction and substitution (CRS) method (*via* post-functionalization directly on the existing Pan backbones) had not only gained greatly improved solution processibility but also retained the high conducting nature of the unsubstituted Pan.[4a] We further found out that the introduction of even bulkier groups, such as octylthio and dodecylthio, *via* this new CRS method to Pan did not lower the conductivity as it would otherwise be expected; instead these Pan-SR gained even higher conductivity (7–10 S cm^{-1})[5] than the parent Pan (1–5 S cm^{-1}).[6] Since both Pan-SR and Pan have exactly the same backbone structure, we had attributed the improved conducting nature of Pan-SR (*vs.* Pan) to the electron-donating contribution of the alkylthio groups, which helps increase the electron density of the backbone and results in higher conductivity. The increased backbone electron density in this case has been partly supported by our previous CV and UV studies, showing the lowered oxidation potentials and red-shifted absorption wavelength in Pan-SBu as compared with its parent unsubstituted Pan. Therefore, to clearly understand the electronic behaviour of the SBu group in the aromatic aniline systems, we carried out a systematic investigation with a series of simple and conjugated aniline model compounds and tried to analyse them with unambiguous spectral characterisations using various NMR experiments.

Results and discussion

In our continuous efforts to strive for even more rigorous spectroscopic evidence to show that the electron density of the phenyl rings is indeed enhanced by the butylthio substituent, we have prepared the butylthio-substituted aniline monomer, *i.e.*, 2-butylthioaniline, *via* selective S-alkylation of 2-aminobenzenethiol by butyl bromide in a THF medium using sodium hydride as the base and used it for detailed NMR studies. Based on its ^{1}H NMR spectrum and an NOE experiment, we have unambiguously assigned the NMR peaks and the results are summarized in Fig. 1.

The results however indicated that the incorporation of the butylthio group into aniline does not help to increase the electron density of the phenyl ring, instead it make its *ortho* proton (*i.e.*, one of the *meta* protons to the amino group) shift downfield from δ 7.00 to δ 7.21; whereas all the four phenyl protons of its alkoxy analogues, *e.g.*, 2-methoxyaniline, were found to be shifted upfield to the range of δ 6.7–6.8. The NMR results indicate the

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† Electronic supplementary information (ESI) available: ^{1}H, ^{13}C and 2D HETCOR spectra of mono-PDA and 2,6-diPDA. See DOI: 10.1039/b609506b

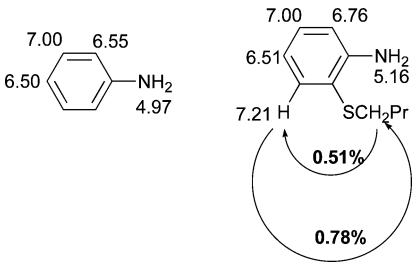


Fig. 1 The ^{1}H NMR chemical shift values (δ ppm) of aniline and 2-butylthioaniline and the NOE result for 2-butylthioaniline in DMSO-d_6.

butylthio group of 2-butylthioaniline prefers to act as an electron withdrawing substituent rather than electron releasing substituent.

Such electron withdrawing nature of alkylthio groups in the model compounds was also clearly demonstrated by their ^{13}C NMR data. The ^{13}C NMR chemical shifts were unambiguously assigned using 2D NMR (HETCOR) experiments and the results are summarized in Fig. 2. The results clearly showed that the chemical shift value of the carbon *ortho* to the SBu group was shifted downfield from δ 128.8 in aniline (which is its *meta* carbon) to δ 134.5 in 2-butylthioaniline.

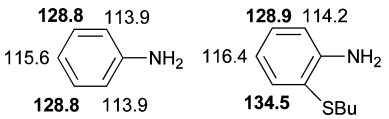
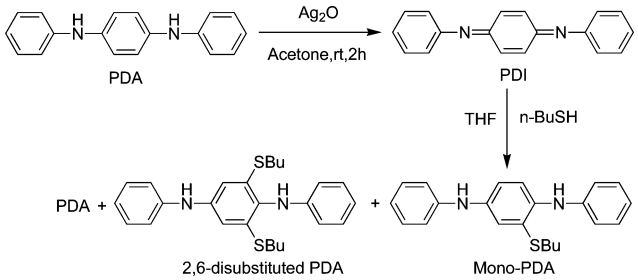


Fig. 2 The ^{13}C NMR chemical shift values (δ ppm) of aniline and 2-butylthioaniline in DMSO-d_6.

The electronic behaviour of the alkylthio group in the simple aniline system seems to contradict the observations in our polymer (Pan-SBu) systems. We rationalized that this may be due to the energy mismatching of the atomic orbitals for the 2nd and 3rd period elements (*i.e.*, carbon and sulfur) which hinders the electron donating resonance of the alkylthio group to the aromatic ring. Additionally, the ring electrons may also delocalize into the vacant 3d orbital of sulfur, making the alkylthio group slightly electron withdrawing. We felt that the difference in the electronic influence of the alkylthio groups between the monomer and polymer systems may be caused by the obvious difference in their conjugation lengths. Because, in general, as the conjugation length increases, the band gap becomes smaller due to the rising of the energy level of the HOMO and the lowering of the energy level of the LUMO.[2] The polarizability of the electron cloud of the backbone would also increase with the conjugation degree. We believe that both the lowering of the LUMO level and the increased polarizability in the polymer systems should help facilitate the electron-donating resonance of the alkylthio group. As conjugation interaction plays an important role in lowering the LUMO and increasing the polarizability, it would be more appropriate to examine the electronic nature of the alkylthio group based on an aniline system with a moderate conjugation length. Therefore, an aniline trimer with a butylthio substituent seems to be the ideal candidate, because it is a minimum redox unit of polyaniline and it is still simple enough for unambiguous spectroscopic characterisation. The trimer molecule PDA (*i.e.*, *N*,*N*′-diphenyl-1,4-phenylenediamine) with a butylthio-substituent was thus prepared by the CRS method as shown in Scheme 1. Interestingly, along with the mono-substituted PDA, some disubstituted PDA and PDA were also formed. NMR studies were performed to understand the electronic nature of the butylthio groups in both mono-PDA and disubstituted PDA.



Scheme 1 CRS reaction of PDI with butane-1-thiol.

The structure of the mono-PDA was unambiguously characterized using the NMR studies. For the mono-PDA, the proton signals for the center ring *B* (Fig. 3) can be clearly distinguished from those protons of the terminal rings *A* and *C* based on the splitting patterns of the protons and their integration intensity. The two correlated sets of *ortho*-, *meta*-, and *para*-proton signals associated with either ring *A* or *C* were clearly identified using homodecoupling experiments. NOE experiments were further performed to unambiguously assign the proton sets for rings *A* and *C*. The two non-equivalent NH proton signals are identified using deuterium exchange experiments. The NOE results and the final assignments are summarized in Fig. 3. The ^{1}H NMR results clearly demonstrate that the butylthio substituent shifts ring *A* more upfield than ring *C*, probably due to the resonance electron donating nature of the butylthio group. To further confirm this hypothesis, the ^{13}C NMR of mono-PDA was recorded and the results are presented in Fig. 4; the assignments were based on the HETCOR experiments. The results indeed confirmed that ring *A* is shifted more upfield than ring *C*. It is also interesting to note that the *ortho* carbon (δ 117.1) and *para* carbon (δ 115.4) to the SBu group in the central phenyl ring comes very much more upfield than the *meta* carbon (δ 124.9).

The fact that ^{1}H, ^{13}C chemical shifts of mono-PDA (a secondary aniline system) come relatively downfield compared to those of aniline (a primary aniline), can be attributed to the difference in their chemical structures. For a more appropriate comparison,

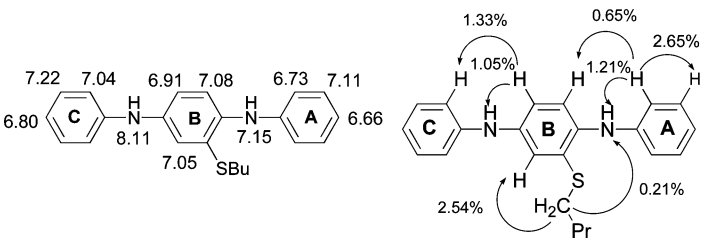


Fig. 3 The NOE results of mono-PDA and its peak assignments.

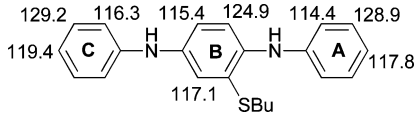


Fig. 4 The ^{13}C NMR chemical shift values (δ ppm) of mono-PDA in DMSO-d_6.

another secondary aniline, *i.e.*, diphenylamine was used as a model compound and studied with ^{1}H, ^{13}C and HETCOR NMR experiments and the results are given in Fig. 5. It is interesting to note that the chemical shifts (both ^{1}H and ^{13}C) of diphenylamine are almost identical with the chemical shifts of ring *C* of mono-PDA while those of ring *A* of mono PDA are shifted more upfield.

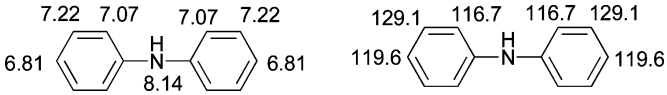


Fig. 5 The ^{1}H and ^{13}C NMR chemical shift values (δ ppm) of diphenylamine in DMSO-d_6.

Similarly, the disubstituted PDA (formed in ~10% yield) was also characterized using the deuterium exchange, homodecoupling, HOMOCOSY and NOE experiments. Interestingly, the ^{1}H NMR spectrum of the disubstituted PDA indicated that it is not as symmetrically substituted as would be expected for 2,5- or 2,3-disubstituted PDA's. Two sets of *ortho*-, *meta*-, and *para*-proton signals corresponding to the two nonequivalent terminal phenyl rings *A′* and *C′* plus one singlet peak associated with the two equivalent protons of the central phenyl ring *B′* were observed. The ^{1}H NMR results suggested that it is a 2,6-disubstituted PDA (2,6-diPDA)[7] (Fig. 6). Furthermore, the two NH peaks (δ 7.03 and δ 8.29) were clearly identified by the deuterium exchange experiment. Based on the homodecoupling experiments, the proton sets that are associated with either of the two terminal phenyl rings *A′* or *C′* were identified. NOE experiments were carried out to further confirm the actual physical location of the SBu group in relation to the *A′* and *C′* rings (Fig. 6). The NOE results clearly demonstrated that substitutions of SBu groups make the ring *A′* appear more upfield shifted than ring *C′*.

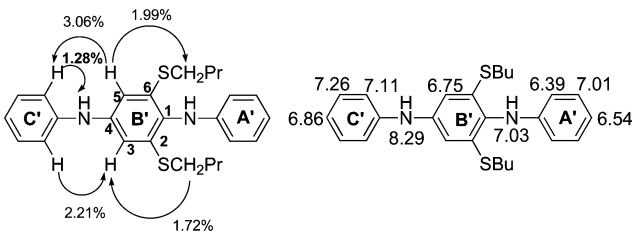


Fig. 6 The NOE results of 2,6-diPDA and its peak assignments.

The same conclusion can also be obtained from the ^{13}C NMR results of 2,6-diPDA as summarized in Fig. 7. Once again, the assignments were done using HETCOR experiments. The results clearly showed that the *B′* and *A′* rings of 2,6-diPDA are both further shifted upfield from the corresponding *B* and *A* rings of mono-PDA, due to the contribution of one additional electron-donating butylthio group.

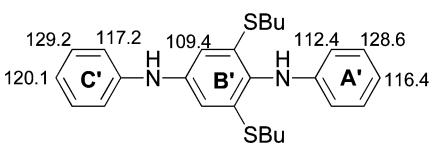


Fig. 7 The ^{13}C NMR chemical shift values (δ ppm) of 2,6-diPDA in DMSO-d_6.

Furthermore, the ^{1}H and ^{13}C NMR results of mono-PDA and 2,6-diPDA were then compared with those of unsubstituted PDA (Fig. 8) to better understand the substituent effect of SBu on the aromatic ring. The ^{1}H and ^{13}C chemical shift values clearly show the upfield trends for ring *A* and *A′* of mono-PDA and 2,6-diPDA compared to that of the unsubstituted PDA.

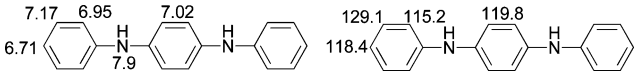


Fig. 8 The ^{1}H and ^{13}C NMR chemical shift values (δ ppm) of unsubstituted PDA in DMSO-d_6.

All the above NMR results of both mono-PDA and disubstituted PDA clearly prove that the phenylamino group (ring *A* or *A′*) at the *ortho* position (a conjugated position) to the butylthio group comes more upfield than the phenylamino group at the *meta* position (a non-conjugated position) as illustrated in Fig. 9. As expected, in the aniline systems with moderate conjugation length, such as mono-PDA and 2,6-diPDA, the butylthio groups act as an electron releasing substituent, unlike that in the simple aniline system of 2-butylthioaniline.

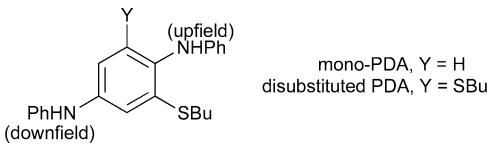


Fig. 9 The upfield and downfield phenylamino groups in the mono-PDA and 2,6-diPDA.

Further study indicated that the formation of disubstituted PDA was mainly caused by the reoxidation of the mono-PDA by unsubstituted PDI (*i.e.*, *N*,*N′*-diphenyl-1,4-phenylenediimine) to form mono-PDI (*i.e.*, butylthio-substituted PDI) (Fig. 10) which then underwent the subsequent second CRS reaction and resulted in the disubstituted PDA. Interestingly, the preferential formation of the 2,6-diPDA also sheds evidence for the electron releasing nature of the butylthio group in these trimer systems.

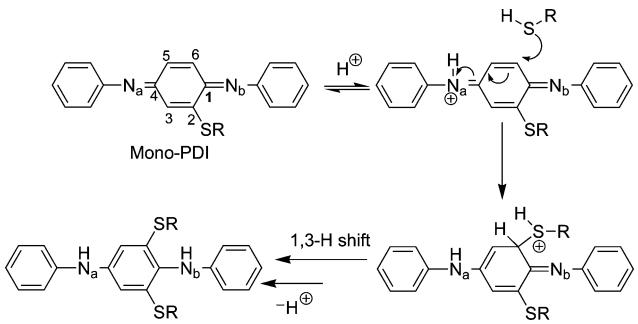


Fig. 10 Plausible mechanism for the preferential formation of 2,6-diPDA.

For the mono-PDI, the basicity of its N_a will be preferentially increased due to the resonance delocalization of the lone pair electrons on sulfur, thereby allowing it to be preferentially protonated over its counterpart N_b which then makes the C6 position more susceptible towards nucleophilic attack by butane-1-thiol and thus results in the formation of the 2,6-diPDA (Fig. 10).

The hypothetical redox reaction between butylthio-substituted mono-PDA and PDI to form butylthio-substituted mono-PDI and PDA (Fig. 11) has been confirmed by our control experiments based on monitoring the ^{1}H NMR of an equimolar mixture of mono-PDA and PDI in d_8-THF or DMSO-d_6. The results showed that the redox reaction in d_8-THF (at room temperature) reached its equilibrium position after *ca.* 6 h and yielded 75% of mono-PDI and PDA. While in DMSO-d_6 the reaction rates were much slower at room temperature (25 °C) and 40 °C, forming only 32% and 40% of mono-PDI respectively at 6 h. When the reaction temperature was raised to 70 °C, a similar final equilibrium position as in d_8-THF was easily attained within 2 h.

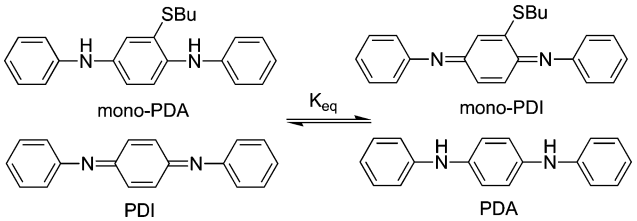


Fig. 11 The redox reaction between mono-PDA and PDI.

For the sake of easier comparison, the ^{1}H NMR spectra of the individual reactants (PDI and mono-PDA) and the products (PDA and mono-PDI) are given in Fig. 12. Due to the presence of *E*/*Z* isomers associated with the two PDI compounds, their NMR signals [Fig. 12(a), (d)] are more complicated than their corresponding PDA compounds [Fig. 12(c), (b)]. The complete assignment for PDI has been already reported in the literature.[8] For simplicity, only the chemical shift ranges associated with the α proton (-SCH_2) and the terminal methyl proton (-CH_3) of the butylthio group are presented in Fig. 13. The equilibrium constant of this reaction was measured to be about equal to or greater than 9, suggesting that the mono-PDA is more readily oxidized than PDA, possibly due to the presence of the butylthio group which

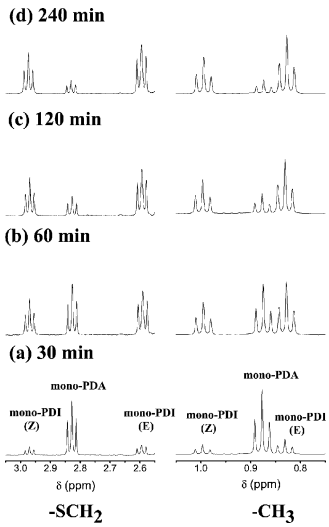


Fig. 13 The ^{1}H NMR monitoring of the redox reaction between PDI and mono-PDA in DMSO-d_6 at 70 °C.

increases the electron density of the trimer through its resonance electron donating effect.

Such electron donating nature of butylthio group in the trimer systems was also confirmed by our CV studies (Fig. 14), showing that the oxidation potential values $E°$ (*vs.* SCE) of PDA's decrease as the number of butylthio groups increases: PDA (0.389 V) > mono-PDA (0.346 V) > 2,6-diPDA (0.196 V).

Similar electronic behaviour has also been observed for other alkylthio-substituted trimers, which were prepared *via* the same CRS reaction in THF between PDI and other functionalized alkanethiols like 2-mercaptoethanol, 4-mercaptobutanol, mercaptopropanesulfonic acid sodium salt, and thiophenol.[9] Interestingly, in addition to the corresponding mono-PDA as the major product, a 10–20% of the 2,6-disubstituted PDA was always observed as the sole or predominant disubstituted product in

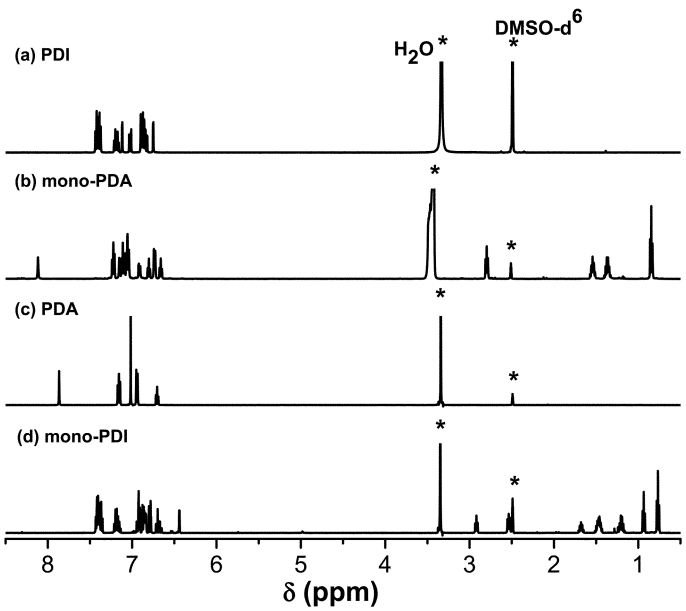


Fig. 12 The ^{1}H NMR spectra of (a) PDI, (b) mono-PDA, (c) PDA, and (d) mono-PDI in DMSO-d_6.

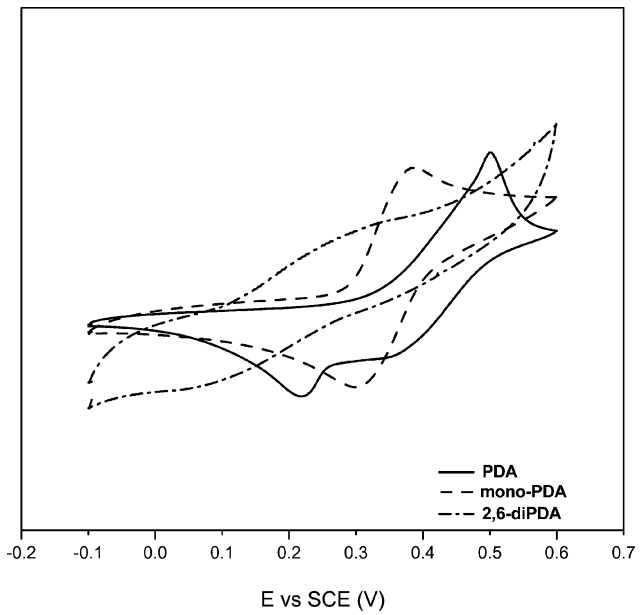


Fig. 14 The CV results of PDA, mono-PDA and 2,6-dPDA in an aqueous solution (pH = 1.3) containing 0.05 M TsOH.

all these cases, suggesting that the electron donating nature of these alkylthio groups are also effectively functioning in these moderately conjugated aniline trimer systems.

Conclusions

In conclusion, although the alkylthio group displayed a weak electron withdrawing effect in the aniline monomer systems, it however clearly showed a resonance electron-donating effect in the higher conjugated aniline trimer as well as in the polymer systems. Such interesting reversing electron behaviour may provide a vital clue to the possible polymerization mechanism. During the copolymerization course between aniline and 2-butylthioaniline, if the 2-butylthioaniline monomer attaches to the tail of the growing polymer chain (*i.e.*, the phenyl ring end), the butylthio group then becomes part of a higher conjugated system and starts behaving as a resonance electron donating group. When this reversal in electronic behaviour occurs, the butylthio group may begin to compete much more significantly with the amino group for directing the subsequent polymer chain linkage positions, leading to the formation of significant amounts of the non-conjugated (*i.e.*, 1,3-ring linkage) defect structures and resulting in poorly conductive copolymers.

Experimental

The thiols were purchased from Aldrich and used as such. PDA was obtained from Aldrich. ACS grade tetrahydrofuran refluxed and distilled over benzophenone–sodium and HPLC grade methanol were used for the reactions. NMR spectra were studied using Varian Unity Inova 500 MHz and Bruker Avance DMX 600 MHz. HRMS were recorded with the Thermo Finnigan Model MAT 95 XL. LRMS was measured by TRIO 2000 Micromass.

Synthesis of 2-butylthioaniline

To a stirred solution of 2-aminobenzenethiol (5 mmol, 0.63 g) in 20 mL of THF was added sodium hydride (5 mmol, 0.113 g), and the contents were stirred at room temperature for 1 h. The reaction was monitored by TLC and after the disappearance of the starting material, the solvent was removed under reduced pressure and the residue was dissolved in chloroform and washed with water (2 × 20 mL). The chloroform layer was dried over anhydrous $MgSO_4$ and the solvent removed under reduced pressure to yield 0.83 g of 2-butylthioaniline in 92% yield. ^{1}H NMR (500 MHz, DMSO-d_6, TMS as standard): δ 7.21 (dd, 1H, J = 7.5 Hz, 1.5 Hz), 7.00 (td, 1H, J = 7.6 Hz, 1.8 Hz), 6.76 (dd, 1H, J = 8 Hz, 1.5 Hz), 6.51 (td, 1H, J = 7.3 Hz, 1.6 Hz), 5.16 (s, 2H, NH_2), 2.70 (t, 2H, J = 7.0 Hz), 1.45 (quint, 2H, J = 7.4 Hz), 1.35 (sextet, 2H, J = 7.3 Hz), 0.84 (t, 3H, J = 7.3 Hz); ^{13}C NMR (125 MHz, DMSO-d_6 at δ 39.5 as standard): δ 149.1 (C), 134.5 (CH), 128.9 (CH), 116.4 (CH), 116.1 (C), 114.2 (CH), 33.0 (CH_2), 31.1 (CH_2), 21.1 (CH_2), 13.5 (CH_3).

Synthesis of PDI

N,*N*′-Diphenyl-1,4-phenylenediamine (1 g, 3.84 mmol) was dissolved in 75 mL of acetone and stirred at room temperature. To this stirred solution was added silver oxide (1.33 g, 5.76 mmol) in portions. The color of the solution changed from black to orange color. After stirring for 1 h, the product precipitated as an orange solid, which was collected and then recrystallized in cyclohexane. Yield: 0.94 g, 95% (a mixture of *E*/*Z* isomers). ^{1}H NMR (500 MHz, DMSO-d_6, TMS as standard): δ 7.42 (t, *E*, 4H, J = 7.75 Hz), 7.39 (t, *Z*, 4H, J = 8.5 Hz), 7.19 (t, *E*, 2H, J = 7.0 Hz), 7.17 (t, *Z*, 2H, J = 7.5 Hz), 7.12 (d, *Z*, 2H, J = 1.5 Hz), 7.02 (dd, *E*, 2H, J = 10.5 Hz, 2.0 Hz), 6.89 (d, *E*, 4H, J = 7.5 Hz), 6.86 (d, *Z*, 4H, J = 7.75 Hz), 6.83 (dd, *E*, 2H, J = 10.0 Hz, 2.5 Hz), 6.75 (d, *Z*, 2H, J = 2.5 Hz); ^{13}C NMR (125 MHz, DMSO-d_6 at δ 39.5 as standard): δ 157.86 (C), 157.81 (C), 149.8 (C), 149.7 (C), 137.7 (CH), 136.4 (CH), 129.12 (CH), 129.08 (CH), 125.3 (CH), 125.07 (CH), 125.03 (CH), 124.3 (CH), 120.4 (CH), 120.2 (CH). Exact mass: 258.1157; LRMS (EI-MS) 258 $[M]^+$.

Synthesis of mono-PDA and 2,6-diPDA

Butane-1-thiol (5 mmol, 0.44 g, 0.51 mL) dissolved in 25 mL of degassed tetrahydrofuran was taken in a flame dried three neck round bottomed flask equipped with an addition funnel, condenser, and a rubber septum. The system was air exchanged with nitrogen three times. To this system was then added dropwise a solution of PDI (5 mmol, 1.29 g) dissolved in 25 mL of degassed tetrahydrofuran. The contents were stirred at rt under nitrogen for 6 h. As the reaction proceeded, the orange color of the imine disappeared and a pale yellow color was seen. The reaction was monitored by TLC (eluant: 10% EA in hexane). After the complete disappearance of the starting materials the solvent was removed under reduced pressure using rotary evaporator. The crude product was purified by column chromatography using hexane followed by 4% EA in hexane as the eluants. Mono-PDA was obtained as a major product in 74% yield (1.21 g). The 2,6-diPDA was obtained in 10% yield (0.22 g). PDA, the fully reduced amine was obtained in 11% yield (0.14 g).

^{1}H and ^{13}C NMR of mono-PDA

^{1}H NMR (500 MHz, DMSO-d_6, TMS as standard): δ 8.11 (s, 1H, NH), 7.22 (t, 2H, J = 8.0 Hz), 7.15 (s, 1H, NH), 7.11 (t, 2H, J = 7.8 Hz), 7.08 (d, 1H, J = 8.5 Hz), 7.05 (d, 1H, J = 2.5 Hz), 7.04 (d, 2H, J = 7.8 Hz), 6.91 (dd, 1H, J = 8.3 Hz, 2.5 Hz), 6.80 (t, 1H, J = 7.2 Hz), 6.73 (d, 2H, J = 8.0 Hz), 6.66 (t, 1H, J = 7.0 Hz), 2.80 (t, 2H, J = 7.5 Hz), 1.54 (quint, 2H, J = 7.5 Hz), 1.37 (sextet, 2H, J = 7.4 Hz), 0.85 (t, 3H, J = 7.5 Hz); ^{13}C NMR (125 MHz, DMSO-d_6 at δ 39.5 as standard): δ 13.55 (CH_3), 21.5 (CH_2), 30.6 (CH_2), 31.2 (CH_2), 114.4 (CH), 115.4 (CH), 116.3 (CH), 117.1 (CH), 117.8 (CH), 119.4 (CH), 124.9 (CH), 128.9 (CH), 129.2 (CH), 132.7 (C), 133.1 (C), 139.8 (C), 143.9 (C), 146.5 (C). Exact mass: 348.1660; LRMS (EI-MS) 348 $[M]^+$.

^{1}H and ^{13}C NMR of 2,6-diPDA

^{1}H NMR (500 MHz, DMSO-d_6, TMS as standard): δ 8.29 (s, 1H, NH), 7.26 (t, 2H, J = 8.0 Hz), 7.11 (d, 2H, J = 7.5 Hz), 7.03 (s, 1H, NH), 7.01 (t, 2H, J = 7.5 Hz), 6.86 (t, 1H, J = 7.25 Hz), 6.75 (s, 2H), 6.54 (t, 1H, J = 7.0 Hz), 6.39 (d, 2H, J = 7.5 Hz), 2.74 (t, 4H, J = 7.25 Hz), 1.52 (quint, 4H, J = 7.6 Hz), 1.34 (sextet, 4H, J = 7.5 Hz), 0.85 (t, 6H, J = 7.5 Hz); ^{13} C NMR (125 MHz, DMSO-d_6 at δ 39.5 as standard): δ 13.5 (CH_3), 21.5 (CH_2), 30.0 (CH_2), 30.3 (CH_2), 109.4 (CH), 112.4 (CH), 116.4 (CH), 117.2 (CH), 120.1 (CH), 126.3 (C), 128.6 (CH), 129.2 (CH), 139.7 (C), 142.6 (C), 143.0 (C), 147.0 (C). Exact mass: 436.2007; HRMS (EI-MS) 436.2012 $[M]^+$.

^{1}H and ^{13}C NMR of PDA

^{1}H NMR (500 MHz, DMSO-d_6, TMS as standard): δ 7.9 (s, 2H, NH), 7.17 (t, 4H, J = 8 Hz), 7.02 (s, 4H), 6.95 (d, 4H, J = 8 Hz), 6.71 (t, 2H, J = 7.25 Hz); ^{13} C NMR (δ 150 MHz, DMSO-d_6 at δ 39.5 as standard): δ 144.9 (C), 136.5 (C), 129.1 (CH), 119.8 (CH), 118.4 (CH), 115.2 (CH).

CV measurements for the PDA's

Cyclic voltammograms (CV) for the PDA compounds were measured with a potentiostat (CHI 605A) in a three-electrode electrochemical cell with an aqueous solution of 0.05M TsOH as electrolyte, using a platinum plate (0.5 cm × 0.5 cm) as the working electrode and a gold plate (1 cm × 4 cm) as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The redox potential ($E°$) were calculated as the average of the anodic and cathodic peak potentials.

Acknowledgements

The authors acknowledge NSC for funding this research program.

References

1 H. S. Nalwa, in *Handbook of Organic Conductive Molecules and Polymers*, John Wiley & Sons, Chichester and New York, 1997, vol. 1–4.
2 T. A. Skotheim, in *Handbook of Conducting Polymers*, Marcel Dekker, Inc., New York and Basel, 1986, vol. 1–2.
3 E. M. Genies, A. Boyle, M. Lapkowski and C. Tsintavis, *Synth. Met.*, 1990, **36**, 139.
4 (*a*) C. C. Han, S. P. Hong, K. F. Yang, M. Y. Bai, C. H. Lu and C. S. Huang, *Macromolecules*, 2001, **34**, 587; (*b*) References 2 and 3 in ref. 4*a*; (*c*) C. C. Han, K. F. Yang, S. P. Hong, A. Balasubramanian and Y. T. Lee, *J. Polym. Sci., Polym. Chem. Ed.*, 2005, **43**, 1767; (*d*) G. D'Aprano, M. Leclerc, G. Zotti and G. Schiavon, *Chem. Mater.*, 1995, **7**, 33.
5 C. C. Han, unpublished results.
6 M. Angelopoulos, G. E. Asturias, S. P. Ermer, A. Ray, E. M. Scherr and A. G. MacDiarmid, *Mol. Cryst. Liq. Cryst.*, 1988, **160**, 151.
7 In separate experiments, we have prepared 2,5- and 2,3-disubstituted PDA's and they showed a single set of phenyl and NH protons.
8 M. Sandberg and T. Hjertberg, *Synth. Met.*, 1987, **29**, E257.
9 MeOH is used for the reaction with mercaptopropanesulfonic acid sodium salt as it is insoluble in THF.

