Supporting Information

Supramolecular chirality control via self-assembly of oligoaniline in the chemical oxidative polymerization process

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Experimental section

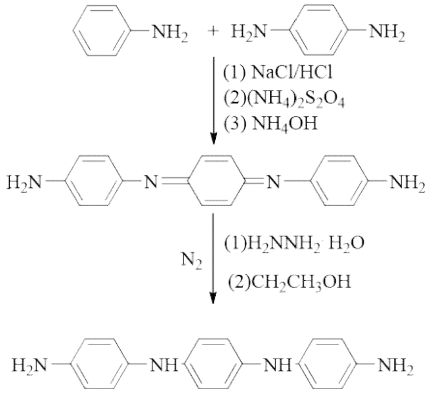
Synthesis of the oligomers:

1. Synthesis of oligomer b_2[S1]

0.86 g (8.0 mmol) of *p*-phenylenediamine was dissolved in a solution of 40 mL aqueous 1 M HCl. The solution was then cooled to about -5 °C in a NaCl-crushed ice bath. To this solution was added 1.8 g (8.0 mmol) of ammonium persulfate in one portion with stirring under air atmosphere. Then the reaction solution became dark brown and 1.5 mL (16.0 mmol) of doubly distilled aniline was added quickly. Several minutes later, a blue particle suspension was formed and the reaction mixture was stirred vigorously for additional 30 minutes. The solid product was collected by filtration through a Buchner funnel under a reduced pressure and was washed with 30 mL 1 M HCl followed by 80 mL distilled water. The product was then treated with 40 mL 1 M aqueous solution of

ammonium hydroxide for 1 to 2 h. The mixture was filtered under a reduced pressure and the remaining solid was washed with distilled water until the filtrate became neutral in pH. Upon drying at 50℃ overnight under vacuum, the product needed to be purified by column chromatography.

The trimer was reduced to the leucoemeraldine with hydrazine hydrate under nitrogen atmosphere by refluxing in ethanol. After filtration, the product was dried in dynamic vacuum for 24 hours. Finally, the product was purified by column chromatography.



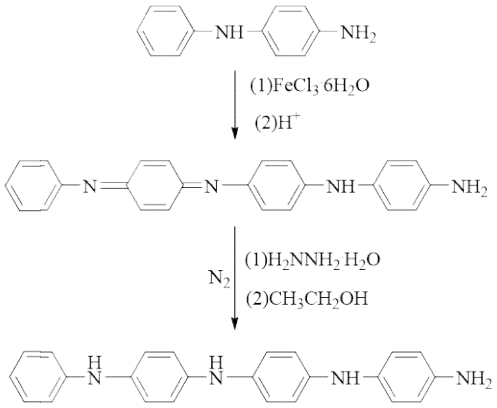
Scheme 1 Synthesis of aniline oligomer b_2

2. Synthesis of the oligomer a_3^{S2}

Ferric chloride hexahydrate (0.1 mol) was dissolved in 100 mL 0.1 M HCl at room temperature. The hydrochloride salt of N-phenyl-1,4-phenylenediamine (dimer, 0.1 mol) was suspended in 500 mL 0.1 M HCl in a 2000 mL beaker with strong mechanical stirring for 0.5 hour at room temperature. The ferric chloride solution was added to the dimer suspension, with strong stirring very quickly. The suspension was then stirred for 2 hours. After 2 hours filtration, the precipitate collected was transferred into 500 mL of 0.1 M HCl. The resulting suspension was stirred for 1 hour, and filtered through the same

Buchner funnel. This washing process was repeated 5 times. Alternatively, the precipitate could be separated and washed by centrifugation. The precipitate was dedoped by 0.l M ammonia hydroxide for 2 hours. The precipitate was dried in dynamic vacuum for 24 hours at room temperature.

The tetramer was reduced to the leucoemeraldine with hydrazine hydrate under nitrogen atmosphere by refluxing in ethanol. After filtration, the product was dried in dynamic vacuum for 24 hours. Finally, the product was purified by column chromatography.



Scheme 2 Synthesis of the oligomer a_3

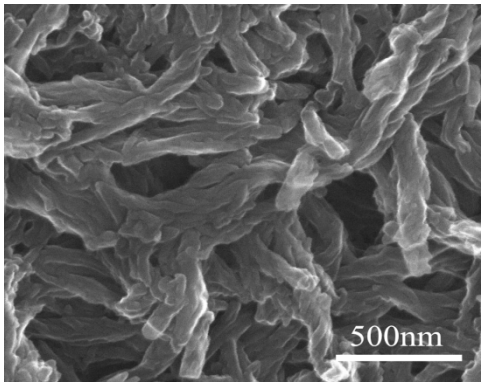


Figure 1. Morphologies of PANI synthesized with oligomer b_2

Supporting references

(S1) Y. Wei, C. C. Yang, T. Z. Ding, A one-step method to synthesize N, N′-bis (4′-aminophenyl)-1, 4-quinonenediimine and its derivatives, *Tetrahedron Letters* 37 (1996) 731-734.

(S2) W. J. Zhang, J. Feng, A. G. MacDiarmid, A. J. Epstein, Synthesis of oligomeric anilines, *Synthetic Metals* 84 (1997) 119–120.