

## Supporting Information

# A MILD, COPPER CATALYZED ROUTE TO CONDUCTING POLYANILINE

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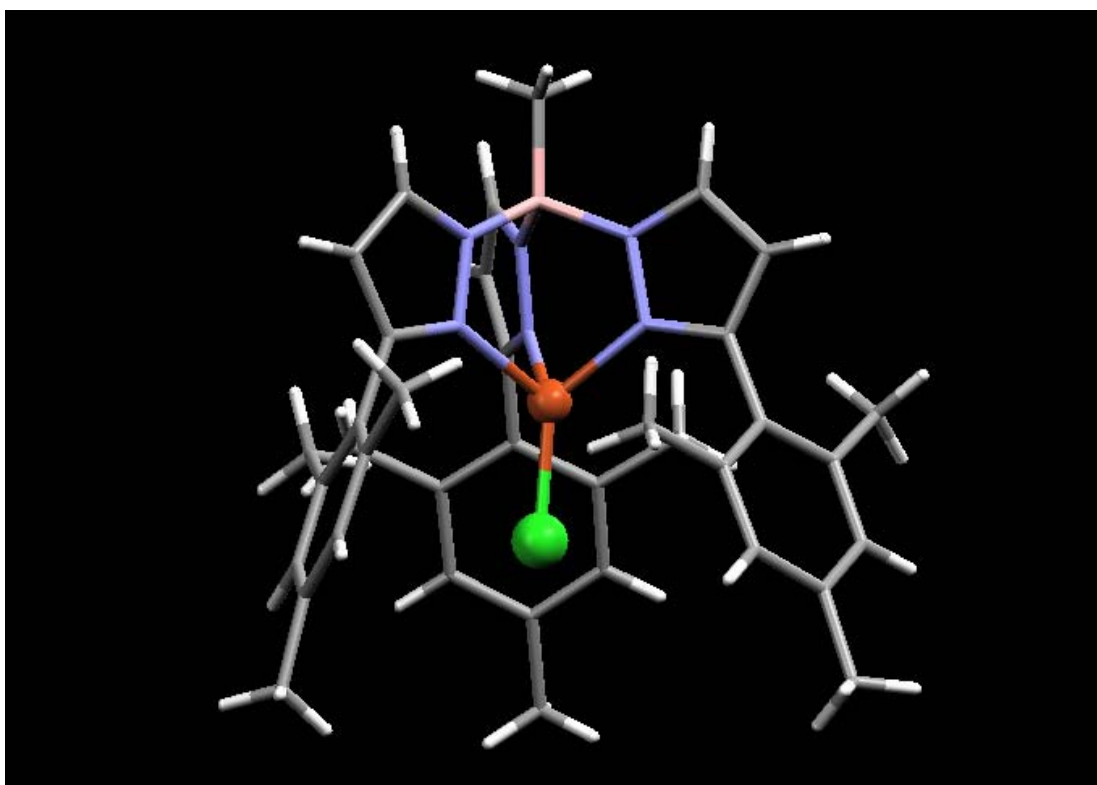
## EXPERIMENTAL

### *Preparation of [MeB(3-(Mes)Pz)<sub>3</sub>]CuCl*

To a solution of CuCl<sub>2</sub>•2H<sub>2</sub>O (0.511g, 3.00 mmol) in a dichloromethane/acetone (40 mL/15 mL) solvent mixture was added [MeB(3-(Mes)Pz)<sub>3</sub>]Tl (2.358 g, 3.00 mmol) dissolved in dichloromethane (40 mL). The mixture turned reddish brown and a solid precipitated. After stirring the reaction for 2 hours, the solvent was removed using a rotary evaporator and the residue was extracted with dichloromethane. Upon evaporation of dichloromethane under reduced pressure, 2.1 g of reddish brown crude product was obtained which was recrystallized from dichloromethane/heptane at 25 °C to give a deep

red crystalline product (1.353 g, 66% yield). Mp: 255~257 °C. FT-IR (KBr,  $\text{cm}^{-1}$ ): 3141, 2952, 2920, 2856, 1614, 1484, 1354, 1179, 1019, 849, 778, 687. UV-Visible [dichloromethane,  $\lambda_{\text{max}}$  nm ( $\epsilon$   $\text{cm}^{-1} \text{M}^{-1}$ ): 228 (6368), 393 (321). Elemental analysis for  $\text{C}_{37}\text{H}_{42}\text{N}_6\text{BCuCl}$ : Calculated: C 65.30%; H 6.22%; N 12.35%. Experimental: C% 65.16; H 6.60%; N, 12.34%. The X-ray crystal structure of  $[\text{MeB}(3\text{-(Mes)Pz})_3]\text{CuCl}$  was also determined (**Figure S1**). The CCDC 293122 contains the supplementary crystallographic data for  $[\text{MeB}(3\text{-(Mes)Pz})_3]\text{CuCl}\cdot\text{CH}_2\text{Cl}_2$ . These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK).

**Figure S1:** X-ray crystal structure of  $[\text{MeB}(3\text{-(Mes)Pz})_3]\text{CuCl}$ .



### ***Preparation of polyaniline***

*N*-phenyl-1,4-phenylenediamine (0.921 g, 5.0 mmol) was added to a mixture of HCl (0.50 g, 36.5% HCl, 5.0 mmol), acetonitrile (18 mL) and H<sub>2</sub>O (18 mL) under a nitrogen atmosphere and stirred for 10 min. The oxidant H<sub>2</sub>O<sub>2</sub> (0.855 g, 30% H<sub>2</sub>O<sub>2</sub> solution, 7.5 mmol) was added to this mixture. The resulting mixture was then added to the catalyst [MeB(3-(Mes)Pz)<sub>3</sub>]CuCl (0.170 g, 0.25 mmol) dissolved in a minimum amount of 1:1 CH<sub>3</sub>CN/H<sub>2</sub>O. The solution was stirred for 24 hr under N<sub>2</sub> at room temperature. A dark precipitate was formed. This precipitate was separated by filtration and washed with MeOH (3×30 mL), dilute HCl (0.1 M, 3×30 mL), and CHCl<sub>3</sub> (3×30 mL), and dried under reduced pressure to obtain PANI (51% yield).

Following the standard procedure described above, several samples of polyaniline were prepared by taking different proportions of the dimer:catalyst:H<sub>2</sub>O<sub>2</sub>:HCl ratios in 1:1 CH<sub>3</sub>CN:H<sub>2</sub>O mixture at different temperatures in order to optimize the system. The dark precipitates obtained are all soluble only in *N*-methylpyrrolidinone (NMP) giving violet solutions which upon addition of an NMP solution containing camphor sulfonic acid turn greenish. Another experiment was carried out in which the addition of acid is deliberately avoided during the polymer synthesis but the product obtained was finally acidified with 1 mol/L HCl(aq) or 1 mol/L camphor sulfonic acid in NMP. A controlled reactions were also done (i) without using any copper catalyst, and (ii) by using CuCl<sub>2</sub> in place of [MeB(3-(Mes)Pz)<sub>3</sub>]CuCl. The reaction without a copper catalyst produced only a trace amount of a solid after 24 hrs.

The PANI samples obtained were characterized by UV-visible spectroscopy (JASCO UV-530), FT-IR spectroscopy (JASCO FT-IR-410), cyclic voltammetry (CH

Instruments Electrochemical Analyzer, Texas, USA), Electrochemical Impedance Spectroscopy (CH Instruments Electrochemical Analyzer, Texas, USA) and by bulk conductivity measurements using the standard four-point probe method.

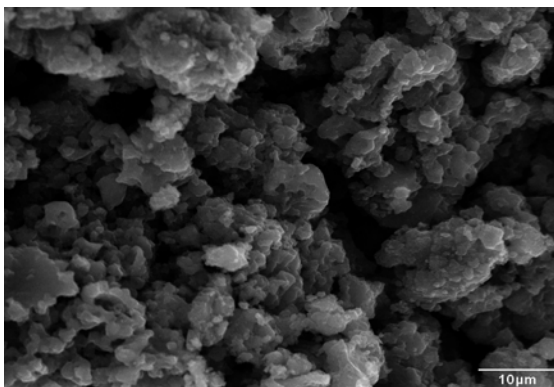
The UV-visible spectra of the samples were recorded using NMP solutions of the samples. The acidified samples were prepared by adding required quantities of camphor sulfonic acid dissolved in NMP to the samples to have 1:1.5 molar ratio of monomer unit:acid. The reference used was NMP. The FT-IR spectra were recorded by preparing polyaniline-KBr pellets using 1:20 mass ratio of polyaniline:KBr. Both as-prepared polyaniline and those acidified with HCl followed by drying under ambient laboratory conditions were used for FT-IR measurements.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopic (EIS) studies of as-prepared and acidified polyaniline samples were performed as follows. The samples were dissolved in a minimum amount of NMP to give a concentrated solution and a drop of this solution was placed carefully on the Pt tip of the Pt disc electrode (CH Instruments  $r = 1$  mm) and allowed to dry. When the drop is completely dry another drop was placed and again allowed to dry under ambient laboratory conditions. Due to the low volatility of NMP it took about two days for complete dryness to achieve and to have uniformly coated polymer attached to the Pt surface. The CV and EIS studies were performed using three-electrode configuration in one-compartment cell. The background electrolyte is a dry nitrogen purged acetonitrile solution containing 0.05 M tetrabutylammonium tetrafluoroborate (TBATFB). The reference electrode used is non-aqueous  $\text{Ag(s)}/\text{Ag}^+(\text{acetonitrile}, \text{TBATFB})$  and the counter electrode is a Pt wire sealed

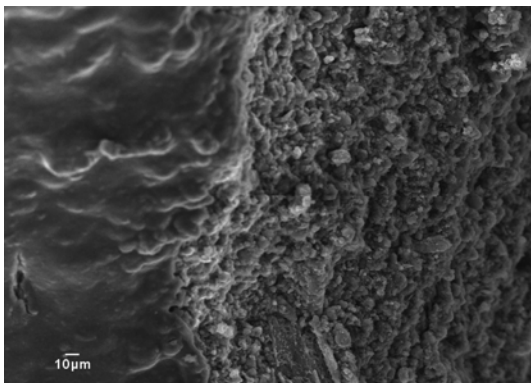
in kel-F (CH Instruments). The potentials are quoted with respect to the standard hydrogen gas electrode ( $E = 0$  V at 298 K).

Samples for bulk conductivity measurements were prepared as follows: 0.50 g of PANI sample was placed in 12 mL of 1 M HCl and stirred for 12 hrs. The solid was then separated by filtration, rinsed with 10 mL of H<sub>2</sub>O and air dried for 24 hr and pellets were made using about 0.1 g of sample and a IR Pellet maker.

**Figure S2:** A scanning electron micrographs of polyaniline (PANI) samples prepared under different conditions showing (a) open, mushroom structure (at lower temperature with only a slight excess of  $\text{H}_2\text{O}_2$ ) and (b) more compact fibril structure (at higher temperature using excess  $\text{H}_2\text{O}_2$ )

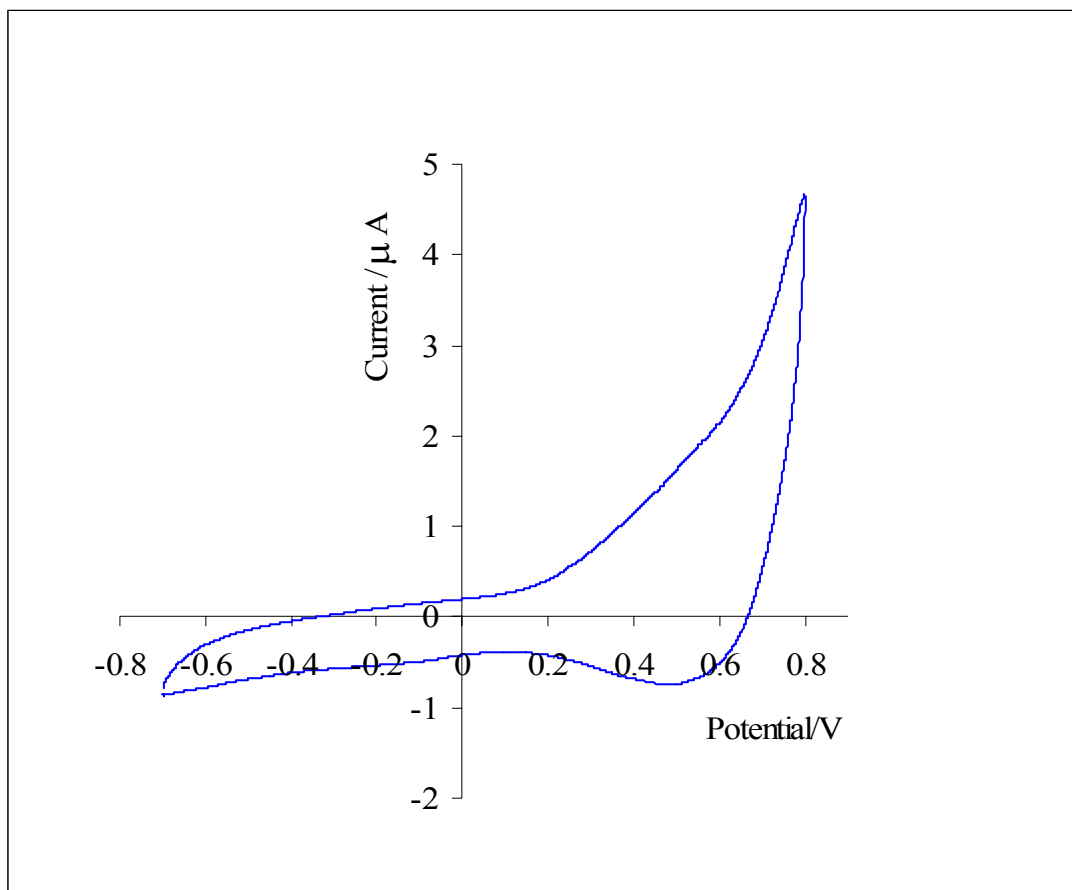


a) SEM (x 1600) of PANI produced at 20°C using dimer:catalyst: $\text{H}_2\text{O}_2$ :HCl mole ratio of 1:0.05:1.5:1

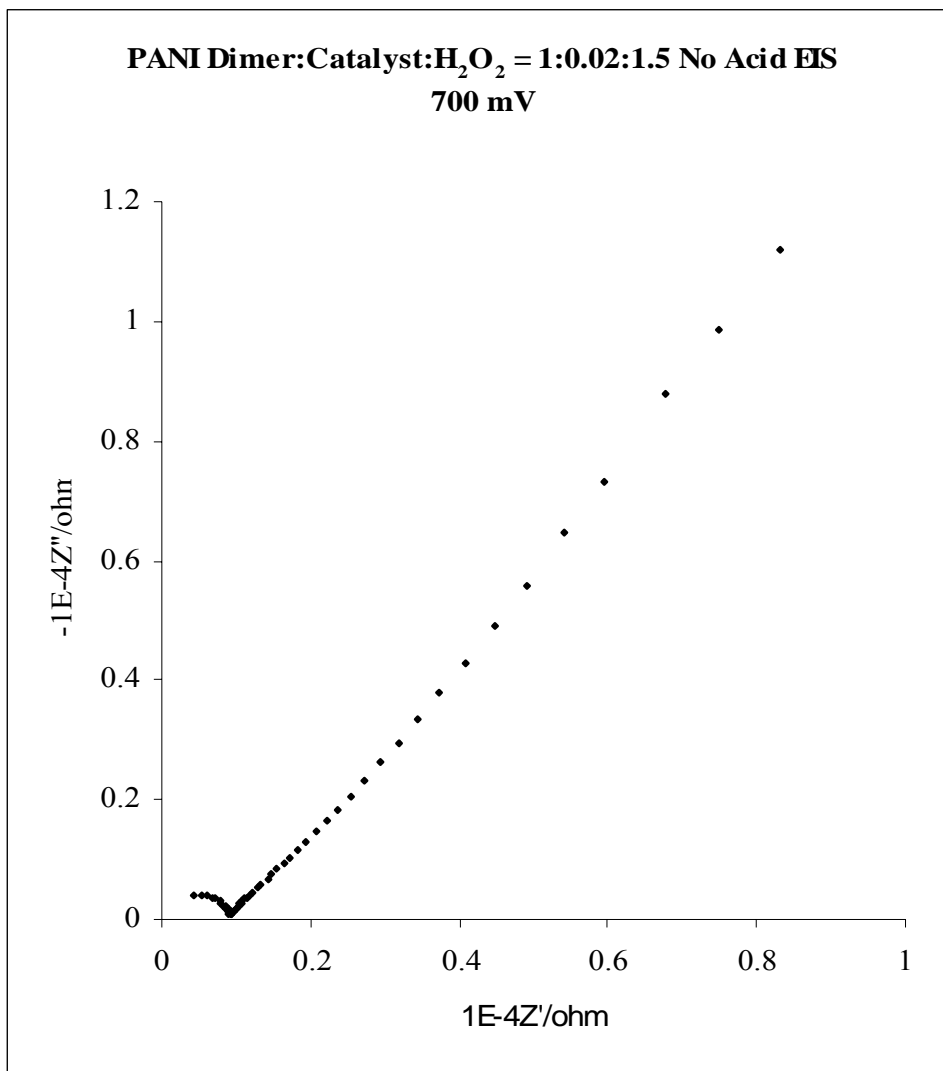


(b) SEM (x 300) of PANI produced at 40°C using dimer:catalyst: $\text{H}_2\text{O}_2$ :HCl mole ratio of 1:0.05:10:1

**Figure S3:** Cyclic voltammogram at  $20 \text{ mV s}^{-1}$  of polyaniline sample prepared *without acid* (i.e., dimer:catalyst:H<sub>2</sub>O<sub>2</sub>:HCl mole ratio of 1:0.02:1.5:0), and acidified with camphor sulfonic acid after the preparation, on Pt disc electrode in 0.05 mol/L tetrabutylammonium tetrafluoroborate background electrolyte.



**Figure S4:** The Electrochemical Impedance Spectra at 700 mV for the PANI Sample prepared using dimer:catalyst:H<sub>2</sub>O<sub>2</sub> = 1:0.02:1.5 with no HCl present during preparation but acidified with camphor sulfonic acid after the synthesis.





**Figure S5:** The Electrochemical Impedance Spectra at various DC potentials for the PANI Sample prepared using dimer:catalyst:H<sub>2</sub>O<sub>2</sub> = 1:0.02:1.5 with no HCl present during preparation but acidified with camphor sulfonic acid after the synthesis.

