**Supporting Information**

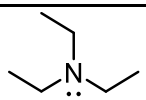
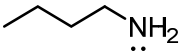
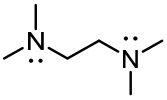
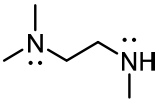
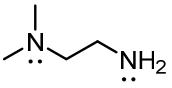
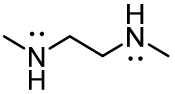
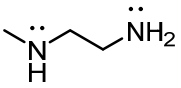
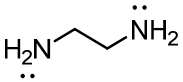
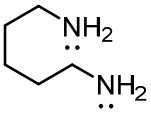
## The Mechanism of Dedoping PEDOT:PSS by Aliphatic Polyamines

Tom P. A. van der Pol,[†] Scott T. Keene,[§] Bart W. H. Saes,[†] Stefan C. J. Meskers,[†] Alberto Salleo, [§] Yoeri van de Burgt,*,[‡] and René A. J. Janssen*,[†]

[†]Department of Chemical Engineering and Chemistry and Institute for Complex Molecular Systems and [‡]Department of Mechanical Engineering and Institute for Complex Molecular Systems, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

[§]Department of Materials Science and Engineering, Stanford University, Stanford, California 94305, United States

**Table S1.** The electrical ratio ($R_E$) and optical ratio ($R_O$) of dedoping with all tested compounds. For these compounds, their full name is given as well as the acronym and the structural formula. The shade of green denotes the degree of dedoping. The temperature at which the maximum dedoping capacity is obtained is given.

| Compound | Acronym | Structural formula | $R_E$ | $R_O$ | $T$ (°C) |
|---|---|---|---|---|---|
| triethylamine | TEA |  | 4.5 | 1.27 | 25 |
| *n*-butylamine | n-BA |  | $1.6\times10^1$ | 2.02 | 50 |
| *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethanediamine | TeMEDA |  | $5.5\times10^2$ | 5.13 | 50 |
| *N*,*N*,*N*′-trimethyl-1,2-ethanediamine | TrMEDA |  | $4.7\times10^2$ | 2.99 | 25 |
| *N*,*N*-dimethyl-1,2-ethanediamine | 1,1-DMEDA |  | $3.7\times10^2$ | 4.14 | 50 |
| *N*,*N*′-dimethyl-1,2-ethanediamine | 1,2-DMEDA |  | $1.4\times10^4$ | 5.87 | 90 |
| *N*-methyl-1,2-ethanediamine | MEDA |  | $3.2\times10^6$ | 7.78 | 90 |
| 1,2-ethanediamine | EDA |  | $1.1\times10^6$ | 27.4 | 50-90 |
| 1,5-pentanediamine | Cadaverine |  | $3.1\times10^6$ | 7.32 | 120 |

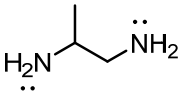
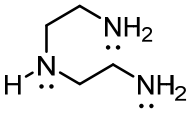
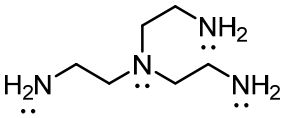
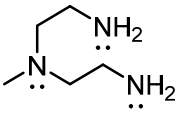
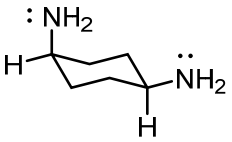
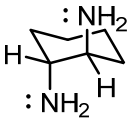
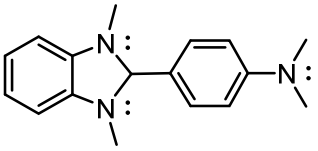
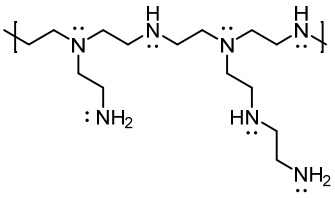
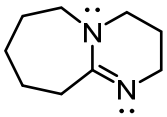
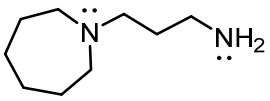
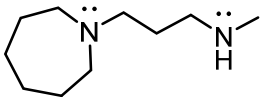
| | | | | | |
|---|---|---|---|---|---|
| 1,2-propanediamine | 1,2-PDA |  | $1.1\times10^{6}$ | 9.63 | 25-50 |
| *N*-(2-aminoethyl)-1,2-ethanediamine | DETA |  | $5.9\times10^{6}$ | 25.4 | 120 |
| *N*,*N*-bis(2-aminoethyl)-1,2-ethanediamine | T-AEA |  | $1.5\times10^{9}$ | 29.7 | 120 |
| *N*-(2-aminoethyl)-*N*-methyl-1,2-ethanediamine | DEMTA |  | $1.8\times10^{5}$ | 33.8 | 95 |
| cis-1,4-cyclohexanediamine | c-1,4-DACH |  | $8.1\times10^{2}$ | 3.71 | 90 |
| trans-1,2-cyclohexanediamine | t-1,2-DACH |  | $1.4\times10^{2}$ | 3.93 | 90-120 |
| *p*-phenylenediamine | PPD |  | 3.6 | 5.01 | 25 |
| 4-(1,3-dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl)phenyl)dimethylamine | N-DMBI |  | 3.9 | 2.97 | 25 |
| branched poly(ethyleneimine) | PEI |  | $4.4\times10^{4}$ | 7.03 | 80 |
| 1,8-diazabicyclo(5.4.0) undec-7-ene | DBU |  | $7.5\times10^{7}$ | 18.7 | 90-120 |
| 3-(azepan-1-yl)propan-1-amine | APA |  | $3.9\times10^{4}$ | 6.36 | 90-120 |
| 3-(azepan-1-yl)-*N*-methylpropan-1-amine | AMPA |  | $1.9\times10^{1}$ | 3.81 | 90-120 |

**Table S2.** List of suppliers and purity of the employed amines. The purity is left blank if not specified by the supplier.

| Compound | Supplier | Purity |
|---|---|---|
| triethylamine | Sigma Aldrich | >99.5% |
| *n*-butylamine | Acros Organics | 99+% |
| *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethanediamine | Sigma Aldrich | ~99% |
| *N*,*N*,*N*′-trimethyl-1,2-ethanediamine | Acros organics | 97% |
| *N*,*N*-dimethyl-1,2-ethanediamine | Aldrich | ≥98% |
| *N*,*N*′-dimethyl-1,2-ethanediamine | Aldrich | 99% |
| *N*-methyl-1,2-ethanediamine | TCI Chem. | |
| 1,2-ethanediamine | Acros Organics | 99+% |
| 1,5-pentanediamine | Sigma Aldrich | 95% |
| 1,2-propanediamine | Sigma Aldrich | 99% |
| *N*-(2-aminoethyl)-1,2-ethanediamine | Sigma Aldrich | 99% |
| *N*,*N*-bis(2-aminoethyl)-1,2-ethanediamine | Fluka | 98% |
| *N*-(2-aminoethyl)-*N*-methyl-1,2-ethanediamine | TCI-EP | |
| cis-1,4-cyclohexanediamine | TCI | |
| trans-1,2-cyclohexanediamine | Combi Blocks | 98% |
| *p*-phenylenediamine | Sigma | |
| 4-(1,3-dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl)phenyl) dimethylamine | Aldrich | 98% |
| branched poly(ethyleneimine) $M_w$ 700 (GPC) | Aldrich | |
| 1,8-diazabicyclo(5.4.0)undec-7-ene | Acros Organics | 98% |

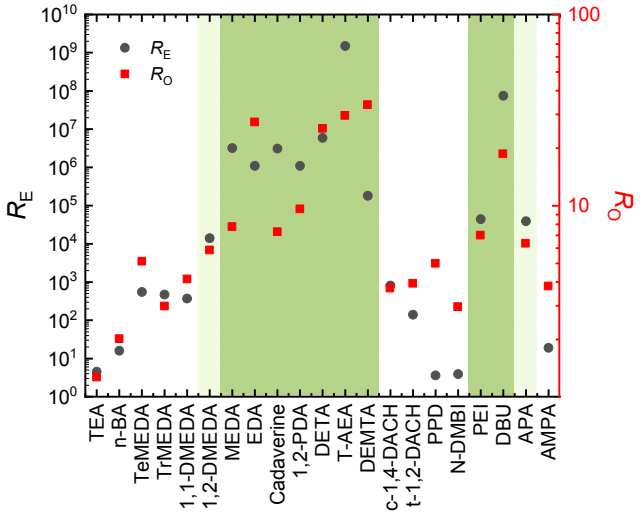



**Figure S1.** The $R_E$ and $R_O$ of all tested compounds displayed in a graph for visual aid. Strong and mild dedopants are colored dark-green and light-green respectively.

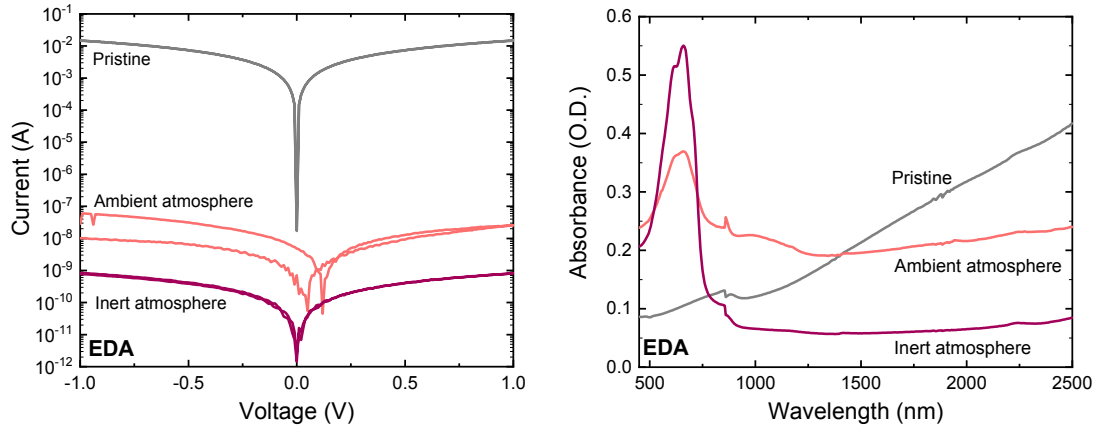



**Figure S2.** (a) Semi-logarithmic *I-V* characteristics and (b) UV-vis-NIR spectra of pristine and dedoped PEDOT:PSS layers using EDA as dedopant under ambient and $N_2$ atmosphere.

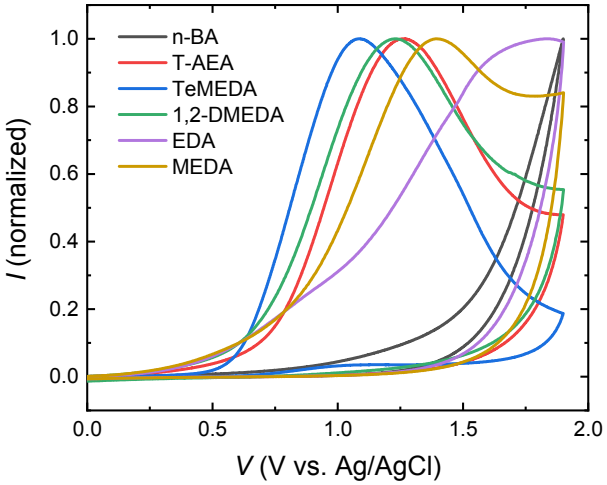



**Figure S3.** Cyclic voltammograms for selected amines.

**Table S3.** Oxidation potentials of selected amines from cyclic voltammetry (Figure S3).

| Amine | Oxidation Onset (V) | Peak (V) |
|---|---|---|
| n-BA | 1.55 | N/A |
| T-AEA | 0.70 | 1.26 |
| TeMEDA | 0.61 | 1.08 |
| 1,2-DMEDA | 0.68 | 1.23 |
| EDA | 0.84 | 1.84 |
| MEDA | 0.80 | 1.39 |

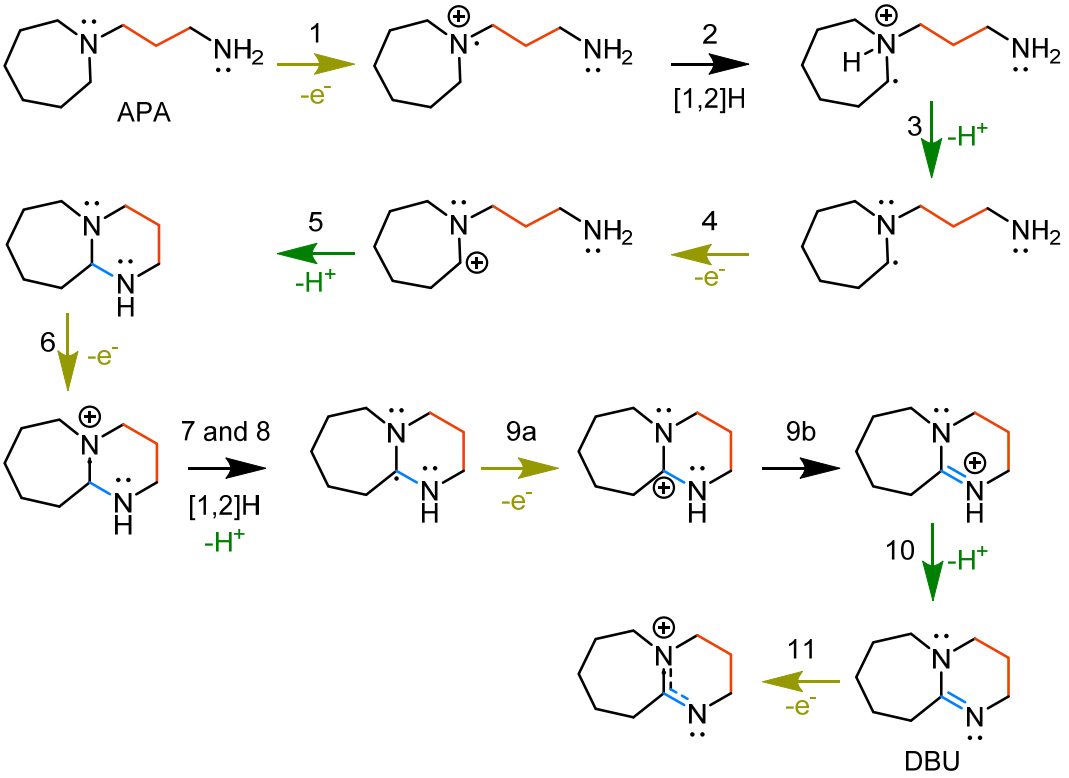



**Figure S4.** Chain of reactions for the oxidation of APA as derived from the mechanism.

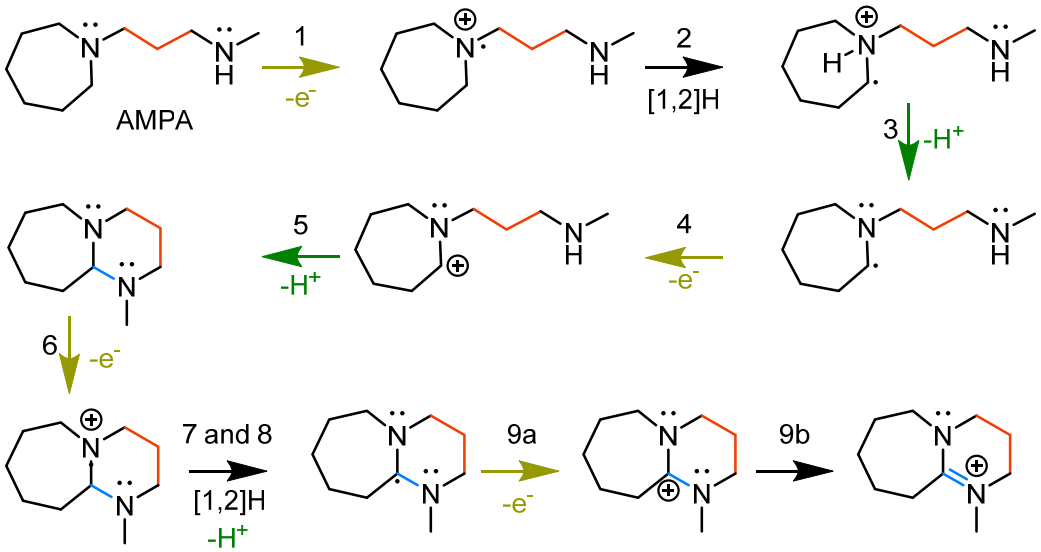



**Figure S5.** Chain of reactions for the oxidation of AMPA as derived from the mechanism.

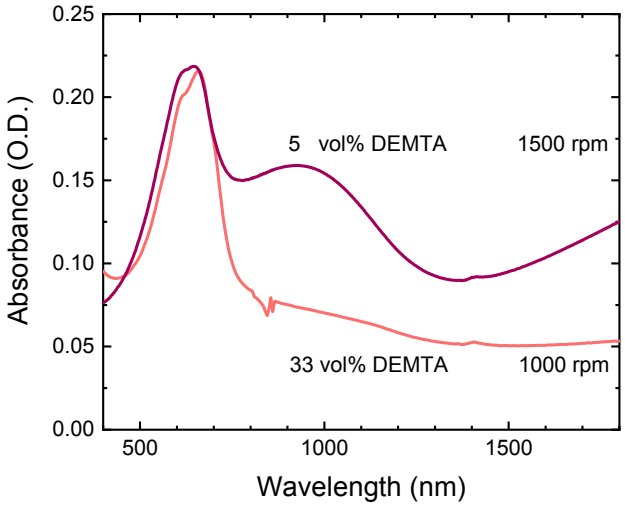



**Figure S6.** The absorbance spectra of layers of PEDOT:PSS spin-coated from a dispersions of aqueous PEDOT:PSS/EG/DEMTA in 0.63:0.03:0.33 and 0.90:0.05:0.05 (v/v/v)) spin coated at 1000 and 1500 rpm respectively.

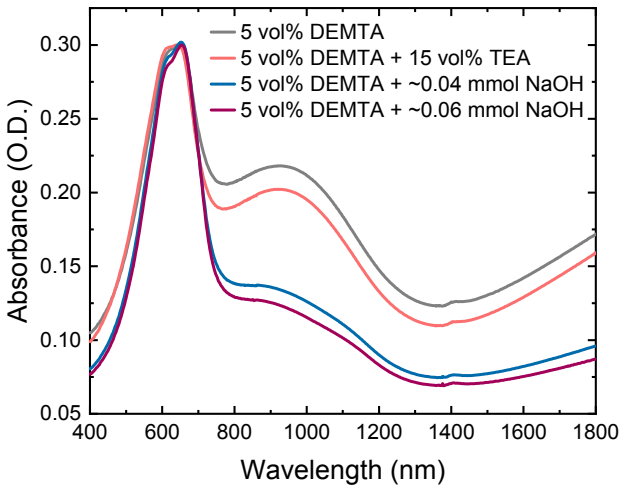



**Figure S7.** UV-vis-NIR absorption spectra of PEDOT:PSS layers spin-coated from dispersions of PEDOT:PSS with 5 vol% DEMTA (1 mL total volume), without or with additional base added. Spectra were normalized at $A = 0.3$.