

Electronic Supplementary Information

Facile Approaching of Multi-colored Electrochromic Triarylamine-based Thermoset Epoxy with Tunable Intervalence Charge-Transfer Behavior

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Experimental Section

Materials

4,4'-Diamino-4"-methoxytriphenylamine (**1**) (mp: 148–149 °C) was synthesized by hydrazine Pd/C-catalyzed reduction of 4,4'-dinitro-4"-methoxytriphenylamine (mp: 206–209 °C) resulting from the condensation of *p*-anisidine with 4-fluoronitrobenzene in the presence of caesium fluoride according to a previously reported procedure.^{S1(a)} *N,N'*-Bis(4-aminophenyl)-*N,N'*-di(4-methoxyphenyl)-1,4-phenylenediamine (**2a**) (mp: 195–200 °C) was synthesized by hydrazine Pd/C-catalyzed reduction of *N,N'*-bis(4-nitrophenyl)-*N,N'*-di(4-methoxyphenyl)-1,4-phenylenediamine (mp: 231–232 °C) resulting from the potassium carbonate-mediated aromatic nucleophilic substitution reaction of 1,4-diiodobenzene with 4-methoxy-4'-nitrodiphenylamine according to a previously reported procedure.^{S1(b)} *N,N'*-Bis(4-aminophenyl)-*N,N'*-di(4-methoxyphenyl)-4,4'-biphenyldiamine (**2b**) (mp: 187–190 °C) was synthesized by hydrazine Pd/C-catalyzed reduction of *N,N'*-bis(4-nitrophenyl)-*N,N'*-di(4-methoxyphenyl)-4,4'-biphenyldiamine (mp: 201–203 °C) resulting from the potassium carbonate-mediated aromatic nucleophilic substitution reaction of 4,4'-diiodo-biphenyl with 4-methoxy-4'-nitrodiphenylamine according to a previously reported procedure.^{S1(c)} Tetrabutylammonium perchlorate (TBAP) (Acros) was recrystallized twice by ethyl acetate in a nitrogen atmosphere and then dried *in vacuo* prior to use. All other reagents were used as received from commercial sources.

Preparation of the Thermoset Epoxy Thick Films

The preparation of thermoset epoxy **I** was used as an example to illustrate the general synthetic route used to produce the thermoset epoxy thick films. A solution of the pre-epoxy polymer was prepared by dissolving 0.33 g (1.09 mmol; 1 eq) of diamine **1** and 1.62 g (4.36 mmol; 2 eq) of **DGEBA** in 1 mL of DMAc. The homogeneous solution was heated to 60 °C under nitrogen for 2 h. Next, dropping the solution into four molds which were made by release papers and heating in conventional oven under nitrogen atmosphere at 140 °C for 12 h to remove most of the solvent; then the semi-dried thick films were further dried *in vacuo* at 40 °C for 3 h, 170 °C for 1.5 h, and then 200 °C for 3 h. The thickness of the resulting films around 790-860 μm could be obtained and used for thermal analysis.

Preparation of the Thermoset Epoxy Thin Films

The preparation of epoxy **I** was used as an example to illustrate the general route used to produce the thermoset epoxy thin films. A solution of the pre-epoxy polymer was made by

dissolving 0.20 g (0.65 mmol; 1 eq) of diamine **1** and 0.97 g (2.60 mmol; 2 eq) of **DGEBA** in 5.8 mL of DMAc. The homogeneous solution was heated to 60 °C under nitrogen atmosphere for 2 h. After reacting, the solution was spin-coated onto indium tin oxide (ITO) glass substrate and cured under the program of 170 °C for 1.5 h, and then 200 °C for 3 h *in vacuo*. The obtained thin films were about 200-230 nm thick and were used for electrochemical and spectroelectrochemical tests.

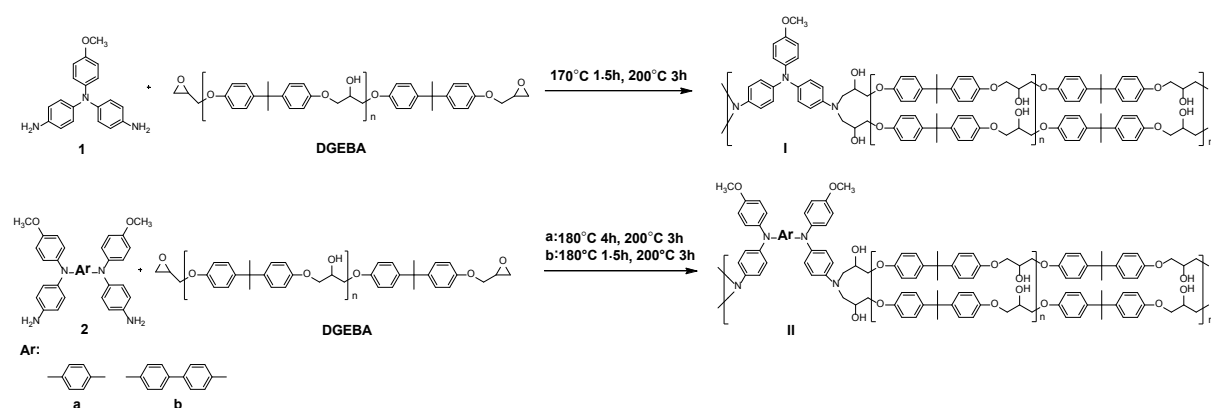
Measurements

Fourier transform infrared (FT-IR) spectra were recorded on a PerkinElmer Spectrum 100 Model FT-IR spectrometer. For temperature scanning, DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 10 °C/min and for isothermal scanning were at a scan rate of 30 °C/min to the certain temperature and then isothermal at the temperature in flowing nitrogen (20 cm³/min). Thermogravimetric analyses (TGA) were conducted with a PerkinElmer Pyris 1 TGA. Experiments were carried out on approximately 6-8 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm³/min) at a heating rate of 20 °C/min. Thermal Mechanical Analyzer (TMA) was conducted with a TA instrument TMA Q400. The TMA experiments were measured at a scan rate of 10 °C /min with a penetration probe under an applied constant load of 50mN. Dynamic mechanical thermal analysis (DMTA) was performed using a DMA 2980, TA Instruments (USA), at a heating rate of 3 °C min⁻¹ with a load frequency of 1 Hz in a tension mode in air. Electrochemistry was performed with a CH Instruments 612C electrochemical analyzer. Voltammograms were presented with the positive potential pointing to the left and with increasing anodic currents pointing downwards. Cyclic voltammetry (CV) was conducted with the use of a three-electrode cell in which ITO (the area of thermoset epoxy thin films were about 0.8 cm × 2.0 cm) was used as a working electrode. A platinum wire was used as an auxiliary electrode. All cell potentials were taken by using a homemade Ag/AgCl, KCl (sat.) reference electrode. Spectroelectrochemical experiments were carried out in a cell built from a 1 cm commercial UV-visible cuvette using Hewlett-Packard 8453 UV-Visible diode array and Hitachi U-4100 UV-Vis-NIR spectrophotometer. The ITO-coated glass slide was used as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl cell as the reference electrode. The thickness of the thermoset epoxy thin films was measured by alpha-step profilometer (Kosaka Lab., Surfcoorder ET3000, Japan).

Results and Discussion

Thermoset Epoxy Synthesis

The series of thermoset epoxies **I** and **II** were prepared by the diamines **1**, **2a** and **2b** with **DGEBA** *via* thermosetting process as shown in **Scheme S1**, respectively. There were two steps in the curing reaction. The pre-epoxy polymers were synthesized in first step at different temperature with each of the diamines, respectively. After spin-coating onto indium tin oxide (ITO) glass substrate and curing under the program *in vacuo*, the thermoset epoxies were identified by the DSC (**Fig. S1**). The DSC curve did not show any exothermic peak around the curing temperature comparing with the uncured epoxy-diamine mixture. Typical TGA, TMA and DMA curves of thermoset epoxy resins and hybrid materials were shown in **Fig. S2**, **Fig. S3** and **Fig. S4**, respectively.



Scheme S1. Scheme of electrochromic thermoset epoxy resins.

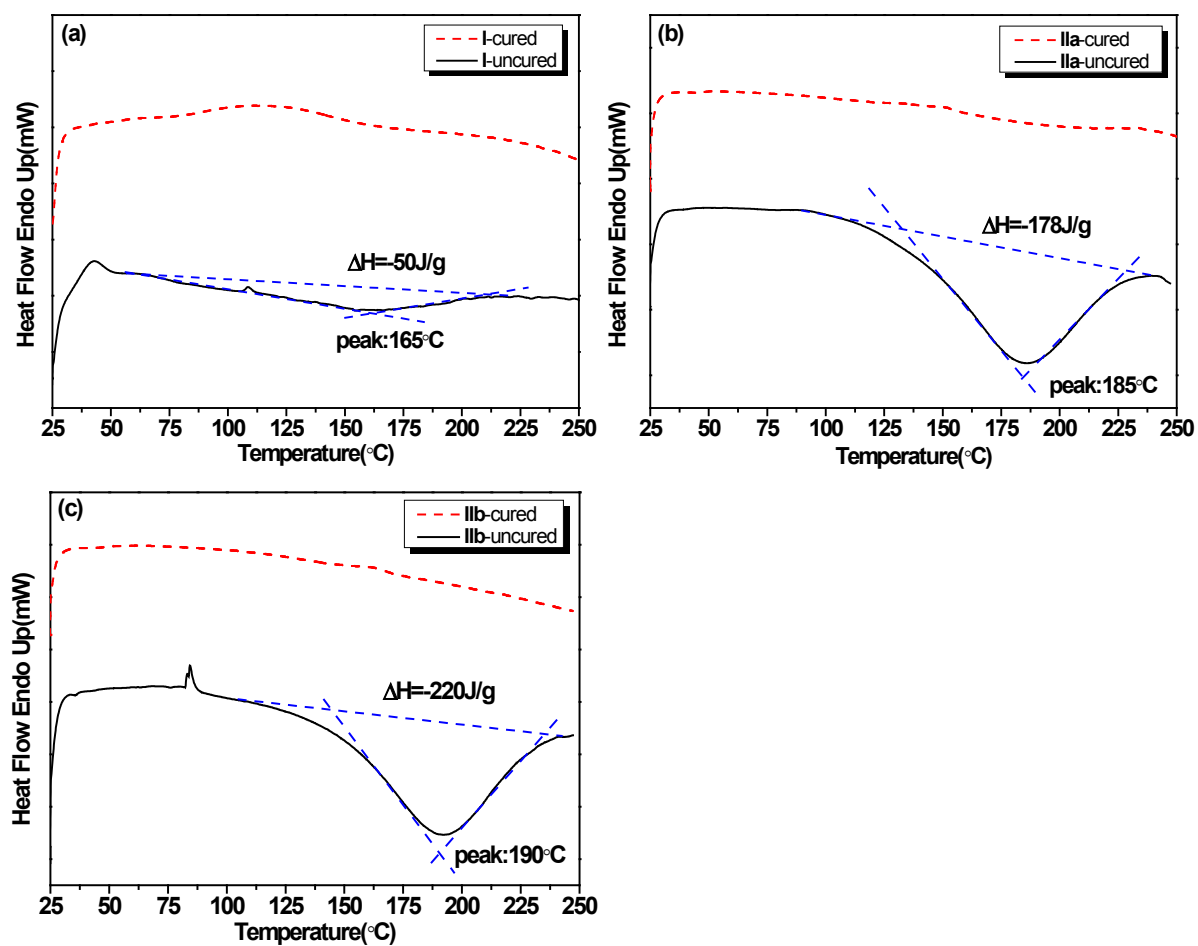


Figure S1. DSC curves of cured and uncured epoxy resins.

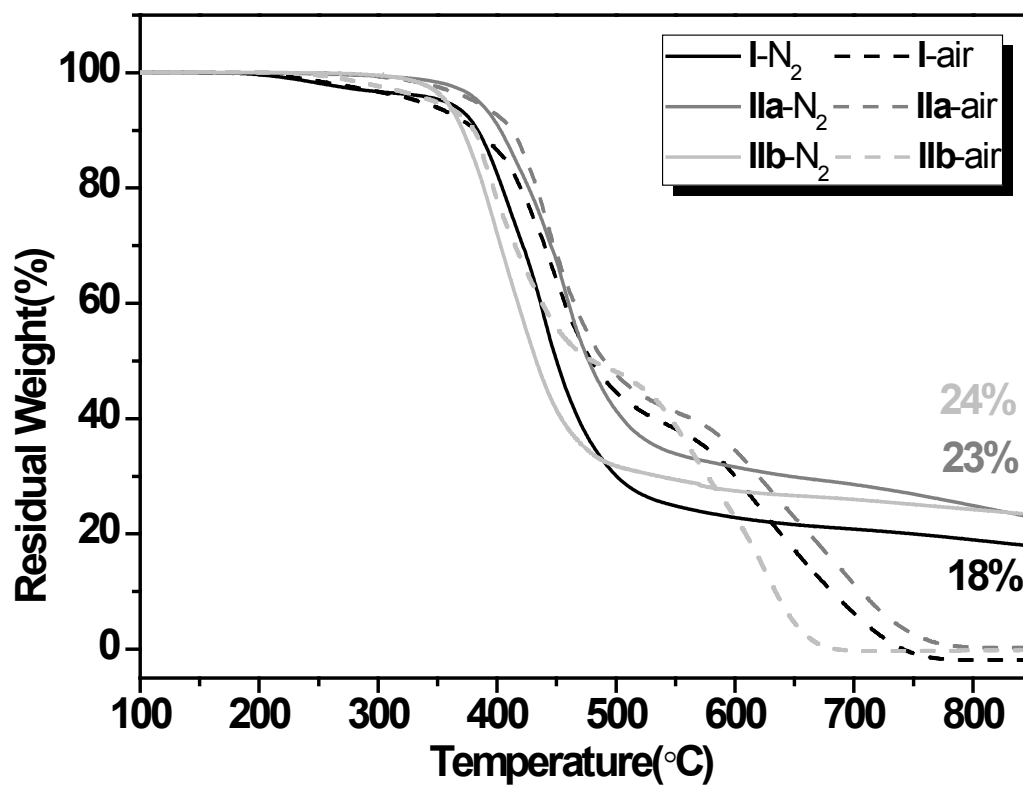


Figure S2. TGA thermograms of thermoset epoxy materials.

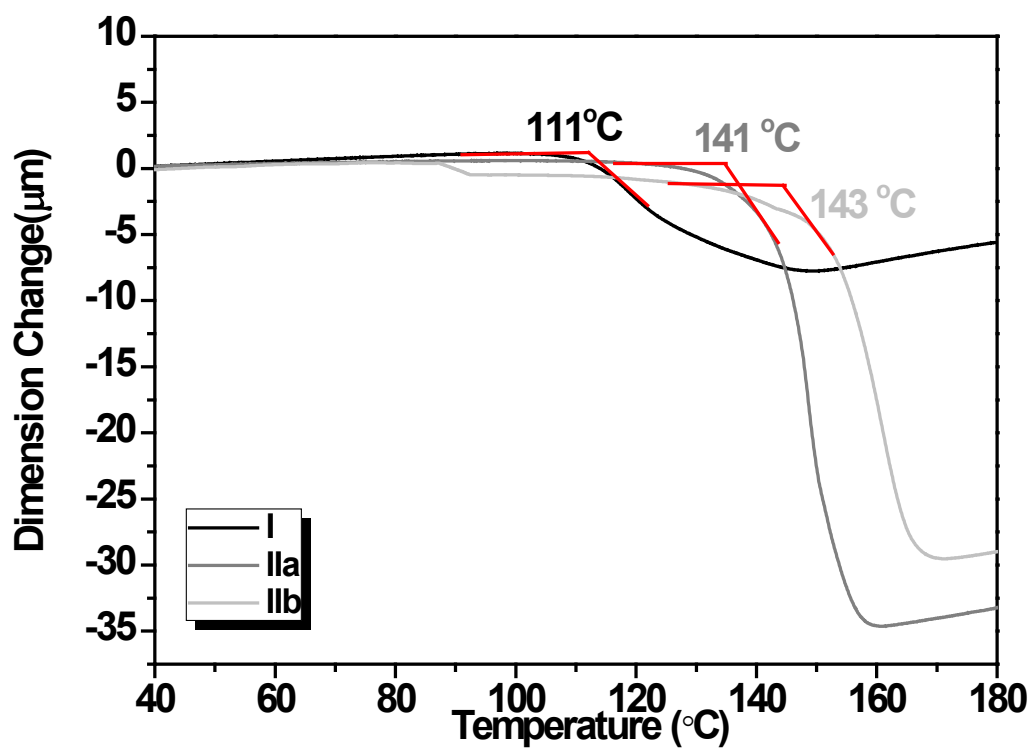


Figure S3. TMA curves of thermoset epoxy materials.

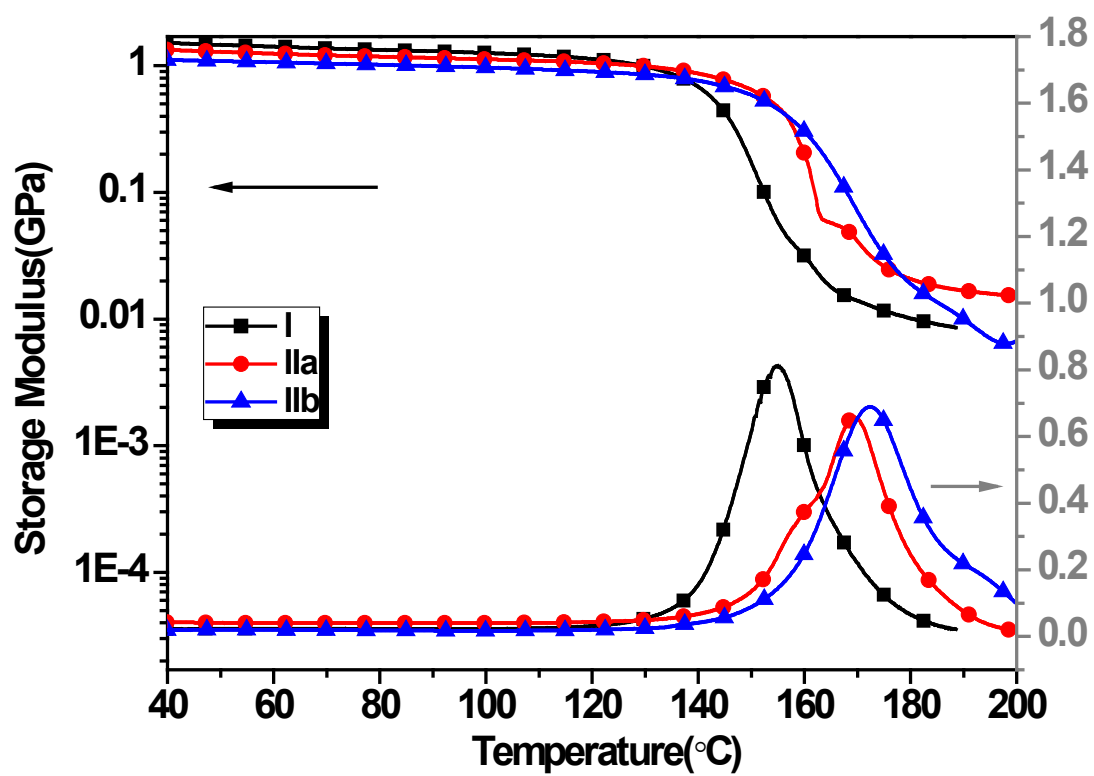


Figure S4. DMA curves of thermoset epoxy materials.

Notes and References:

- S1. (a) C. W. Chang, G. S. Liou, S. H. Hsiao *J. Mater. Chem.*, 2007, **17**, 1007; (b) H. J. Yen, G. S. Liou, *Chem. Mater.*, 2009, **21**, 4062; (c) H. J. Yen, K. Y. Lin, G. S. Liou, *J. Mater. Chem.*, 2011, **21**, 6230.