

## Supporting Information

### Electrochemical synthesis of electrochromic polycarbazole films from *N*-phenyl-3,6-bis(*N*-carbazolyl)carbazoles

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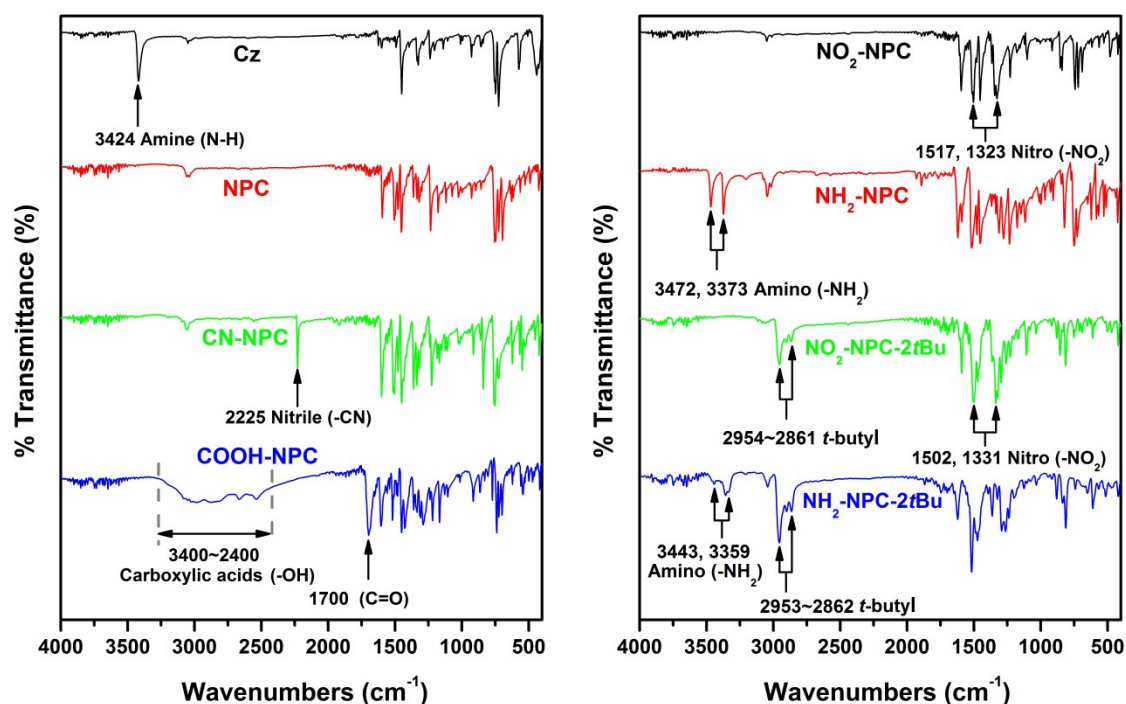
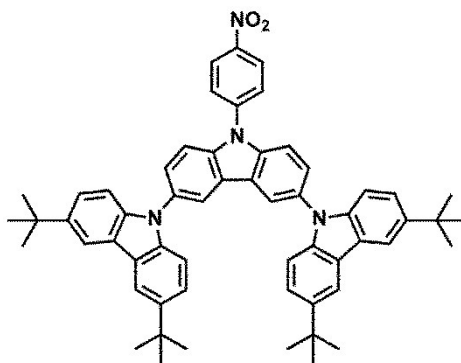


Fig. S1 IR spectra of *N*-phenylcarbazoles.

#### Synthesis of model compounds

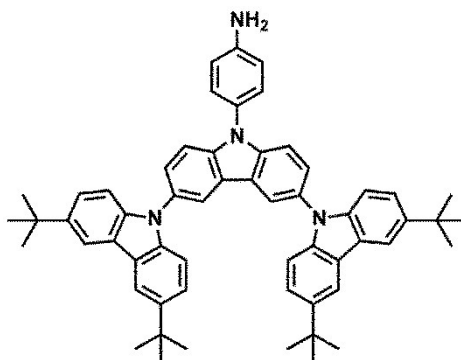
##### *3,6-Di(3,6-di-tert-butylcarbazole-9-yl)-N-(4-nitrophenyl)carbazole (NO<sub>2</sub>-3Cz-tBu)*

A mixture of 3,6-dibromo-*N*-(4-nitrophenyl)carbazole (5 mmol, 2.23 g), 3,6-di-*tert*-butylcarbazole (11 mmol, 3.07 g), copper powder (12 mmol, 0.76 g), potassium carbonate (13 mmol, 1.8 g) and TEGDME (8 mL) was stirred under nitrogen atmosphere at 180 °C for 12 h. The reaction mixture was poured into excess of methanol to precipitate the product. The yellow precipitate was collected by filtration and washed thoroughly by methanol. The crude product was filtered and re-precipitation from DMF/methanol to afford 2.53 g of **NO<sub>2</sub>-3Cz-tBu** as yellow powder. FT-IR (KBr): 2955 cm<sup>-1</sup> (*t*-butyl C-H stretch), 1500, 1337 cm<sup>-1</sup> (-NO<sub>2</sub> stretch).



### 3,6-Di(3,6-di-tert-butylcarbazole-9-yl)-N-(4-nitrophenyl)carbazole ( $\text{NH}_2\text{-3Cz-tBu}$ )

In the 250-mL three-neck round-bottomed flask equipped with a stirring bar, 2 g (2.37 mmol) of  $\text{NO}_2\text{-3Cz-tBu}$ , and 0.02 g of 10 % Pd/C were dissolved/suspended in 150 mL ethanol. The suspension solution was heated to reflux under nitrogen atmosphere, and 0.3 mL of hydrazine monohydrate was added slowly to the mixture, then the solution was stirred at 80 °C. After a further 20 h of reflux, the solution was filtered to remove Pd/C, and the filtrate was cooled under a nitrogen flow to precipitate the product. The precipitated product was collected by filtration and dried in vacuo at 80 °C to give 1.56 g of  $\text{NH}_2\text{-3Cz-tBu}$  in 81 % yield. FT-IR (KBr): 2955  $\text{cm}^{-1}$  (*t*-butyl C–H stretch), 3472, 3373  $\text{cm}^{-1}$  ( $-\text{NH}_2$  stretch).

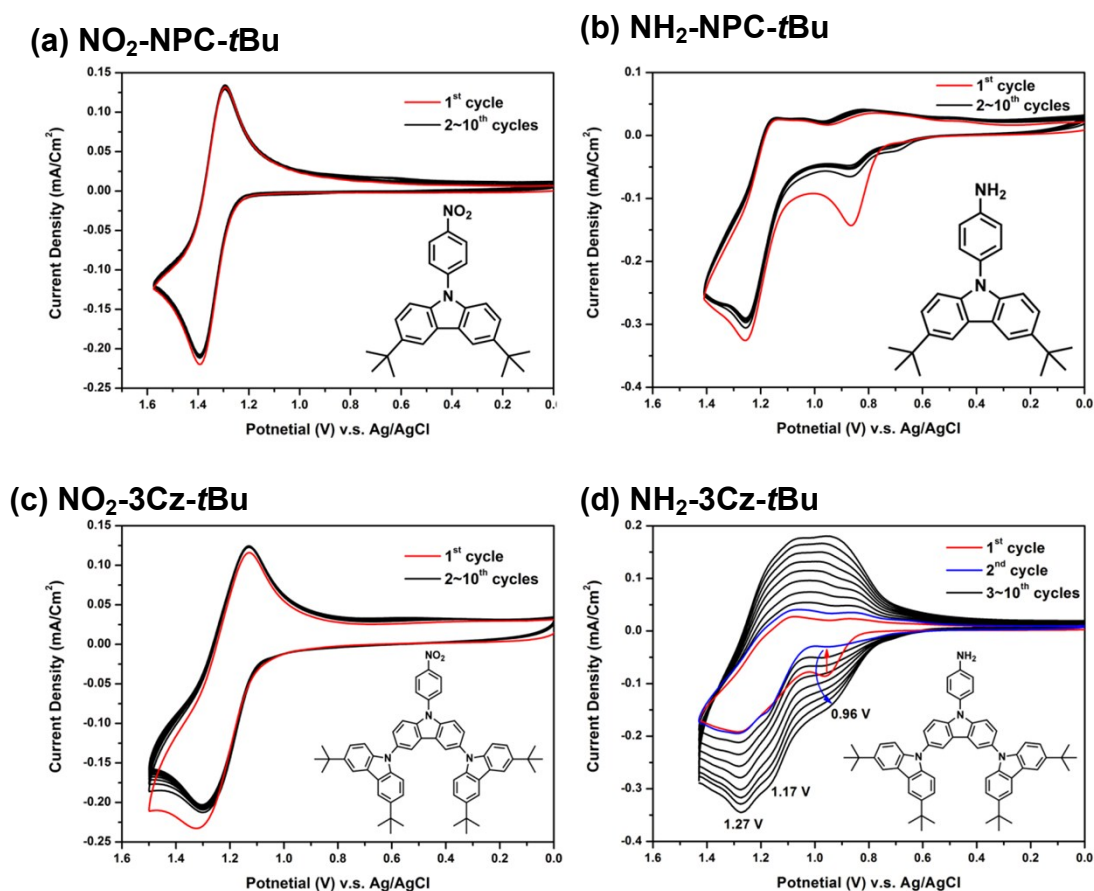


### Electrochemical properties of *tert*-Butyl-substituted NPCs and NPC dendrons

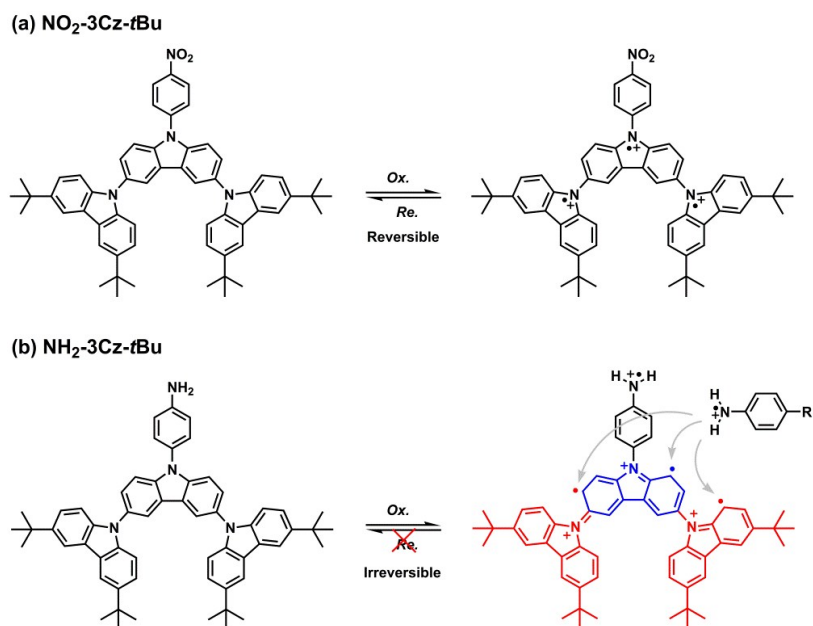
The CV behaviors of the NPCs and NPC dendrons with *tert*-butyl groups substituted on their reactive carbazole sites are shown in Fig. S2. As shown in Figs. S2(a) and S2(c),  $\text{NO}_2\text{-NPC-tBu}$  and  $\text{NO}_2\text{-3Cz-tBu}$  show reversible redox couples at  $E_{\text{pa}} = 1.3\text{--}1.4$  V. Repeated scans between 0 and 1.5 V produced almost the same patterns as that observed in the first scan and no new peaks were detected under these experimental conditions. The electrochemical stability of these two compounds can be attributed to the blocking of the active sites of carbazole by the bulky *tert*-butyl groups. Therefore, no electrochemical oxidative coupling reaction occurs and no polymer films were built on the electrode surface. As shown in Fig. S2(b),  $\text{NH}_2\text{-NPC-tBu}$  displays two oxidation peaks at around 0.80 and 1.22 V in the first CV scan due to the respective oxidations of amino and carbazole groups. As the CV scan continued, the first

oxidation wave decreased in current intensity, implying the oxidized form of this compound is not very stable. The *N*-phenyl group is nearly perpendicular to the carbazole plane and the resonance effect is minimal.<sup>18b</sup> Although the amino group of NH<sub>2</sub>-NPC-*t*Bu is at the *para* position of the carbazole nitrogen, its oxidized amino group cannot receive too much electron cloud for stabilization from the carbazole nitrogen. Because the active sites of terminal carbazoles are blocked with *tert*-butyl group, the effective coupling reactions do not take place and no polymer film is developed on the electrode surface.

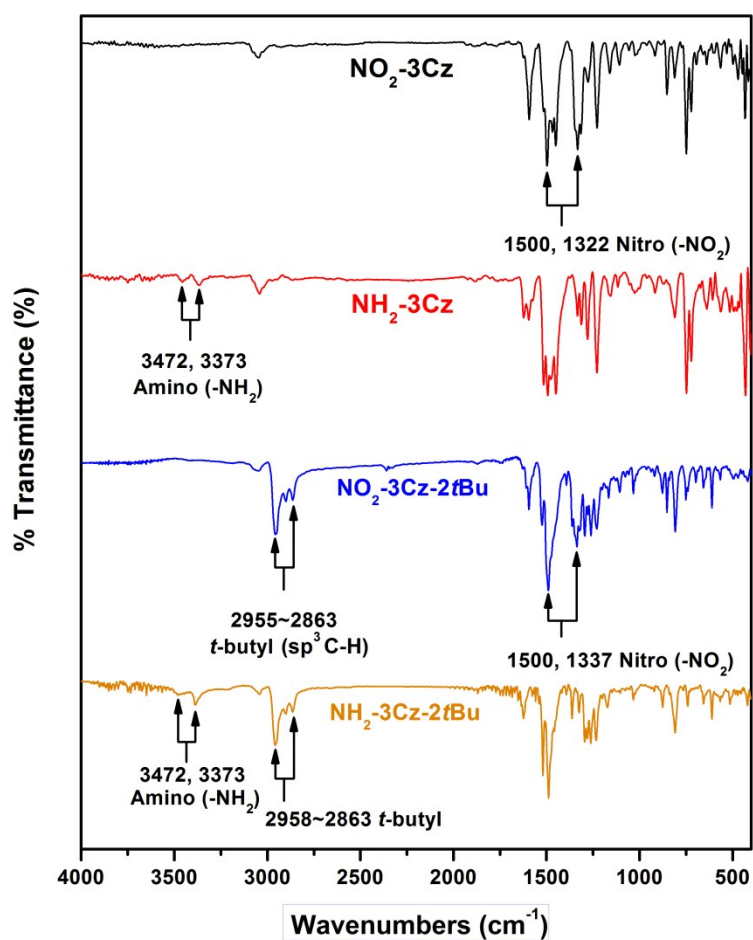
It is worthy to note that, the CV behavior of NH<sub>2</sub>-3Cz-*t*Bu as shown in Fig. S2(d) is a little similar to those of NH<sub>2</sub>-NPC and NH<sub>2</sub>-3Cz. In the first scan, NH<sub>2</sub>-3Cz-*t*Bu displayed three oxidation peaks at 0.96, 1.17 and 1.27 V, which may come from amino group, central carbazole unit, and external carbazole units, respectively. When the potential was continuously cycled, a new oxidation wave appeared at 1.17 V and we observed a progressive growth in all peak currents and the polymer film was built on the electrode surface. We propose that oxidative coupling processes might occur between the oxidized amino group and the carbazole radical cation at 1,8- or 2,7-positions of carbazole, as shown in Scheme S1.



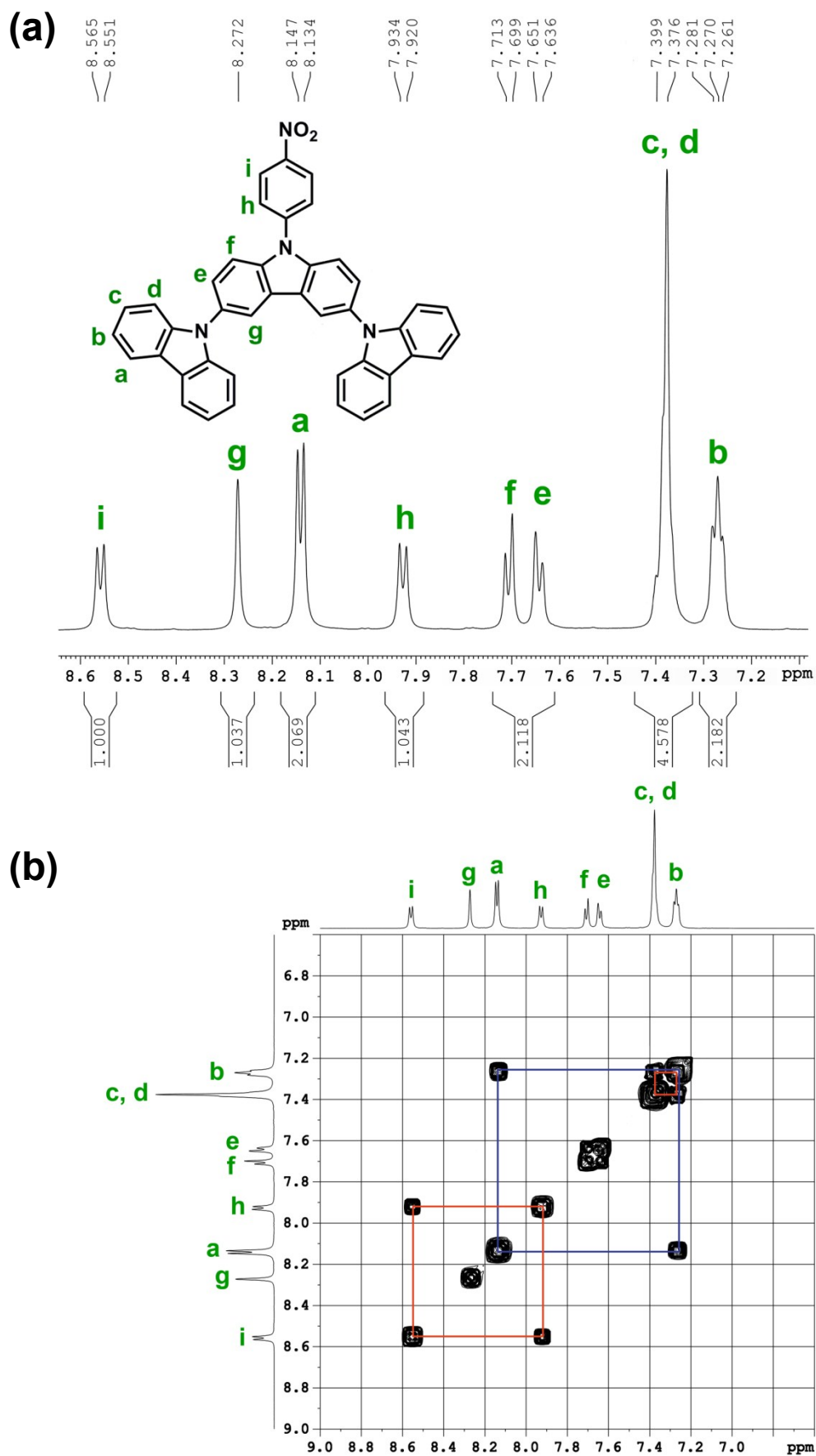
**Fig. S2** Repetitive cyclic voltammograms of  $5 \times 10^{-4}$  M monomer in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/MeCN (CH<sub>2</sub>Cl<sub>2</sub> for NO<sub>2</sub>-3Cz-2*t*Bu) solution at a scan rate of 50 mV s<sup>-1</sup>.



**Scheme S1** The anodic oxidation pathways of the  $\text{NO}_2\text{-3Cz-tBu}$  and  $\text{NH}_2\text{-3Cz-tBu}$ .



**Fig. S3** IR spectra of 3,6-bis(*N*-carbazolyl)-*N*-phenylcarbazoles.



**Fig. S4** (a)  $^1\text{H}$  NMR and (b) H-H COSY spectra of  $\text{NO}_2\text{-3Cz}$  in  $\text{CDCl}_3$ .

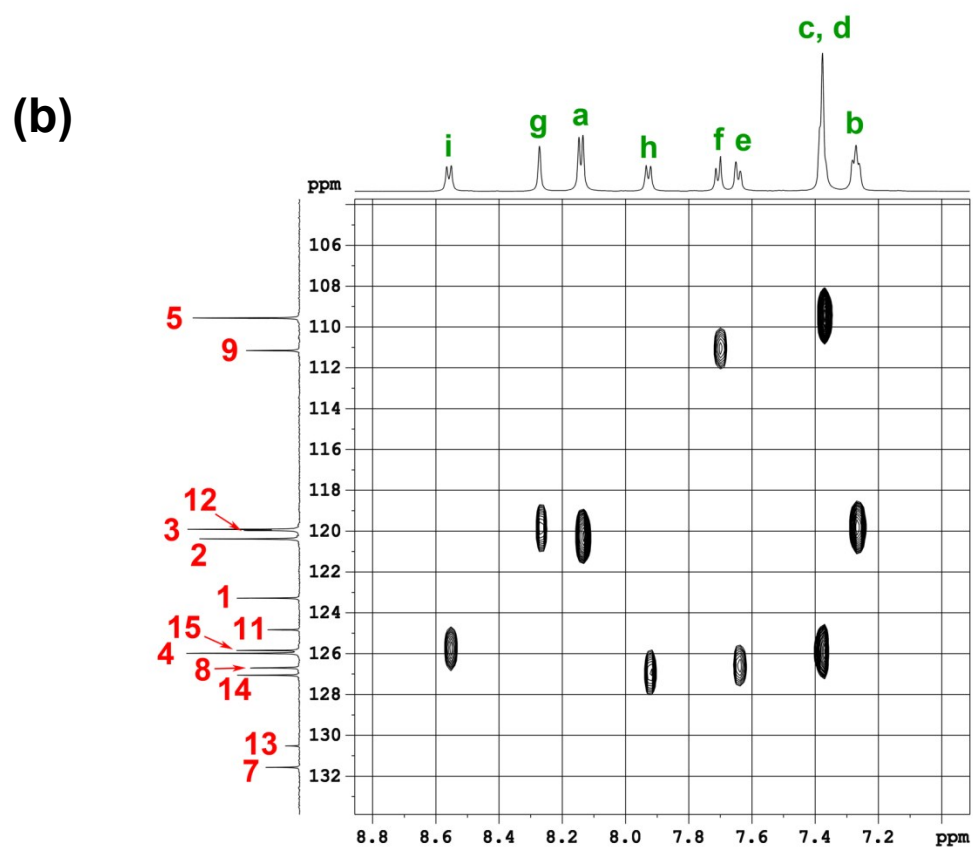
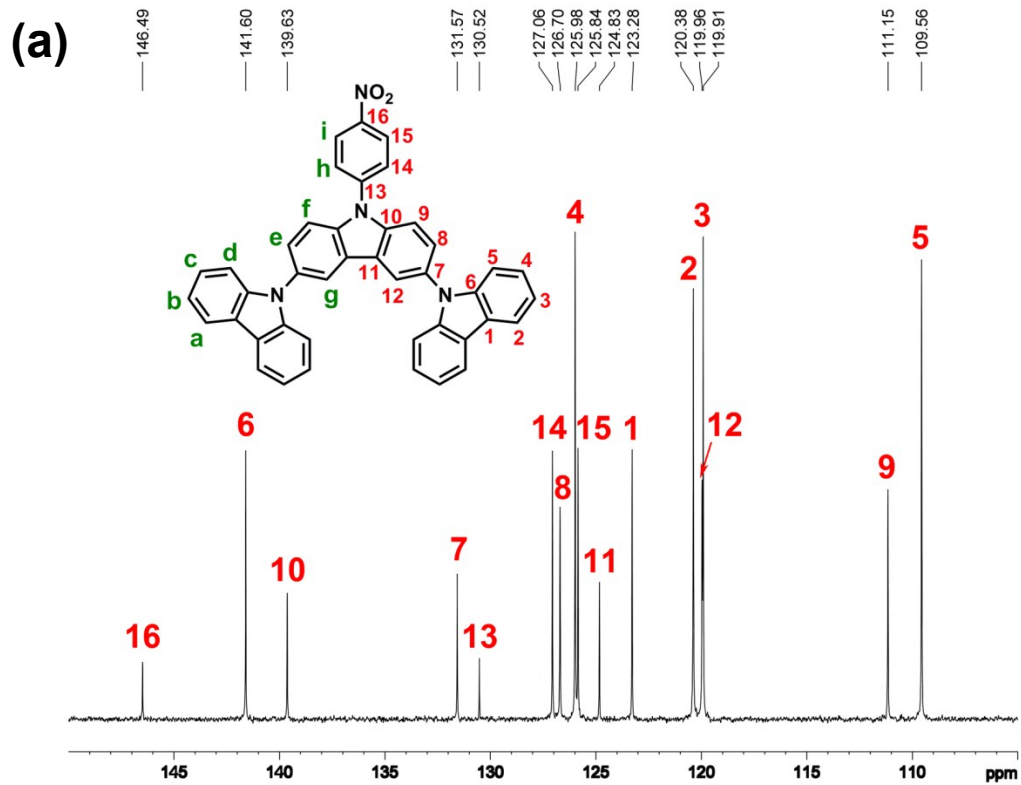


Fig. S5 (a) <sup>13</sup>C NMR and (b) C-H HMQC spectra of **NO<sub>2</sub>-3Cz** in CDCl<sub>3</sub>.

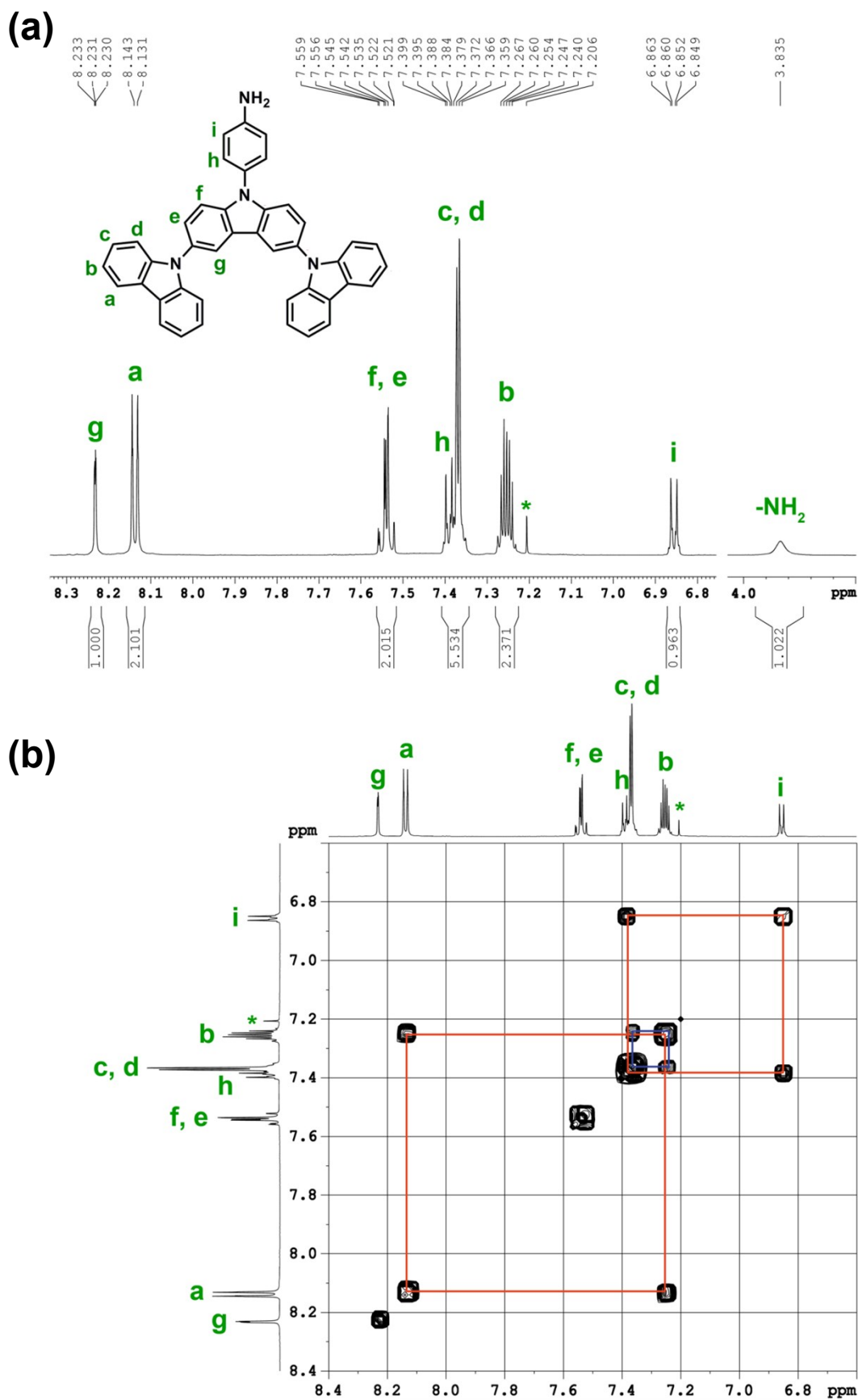


Fig. S6 (a)  $^1\text{H}$  NMR and (b) H-H COSY spectra of  $\text{NH}_2\text{-3Cz}$  in  $\text{CDCl}_3$  (\* solvent peak).

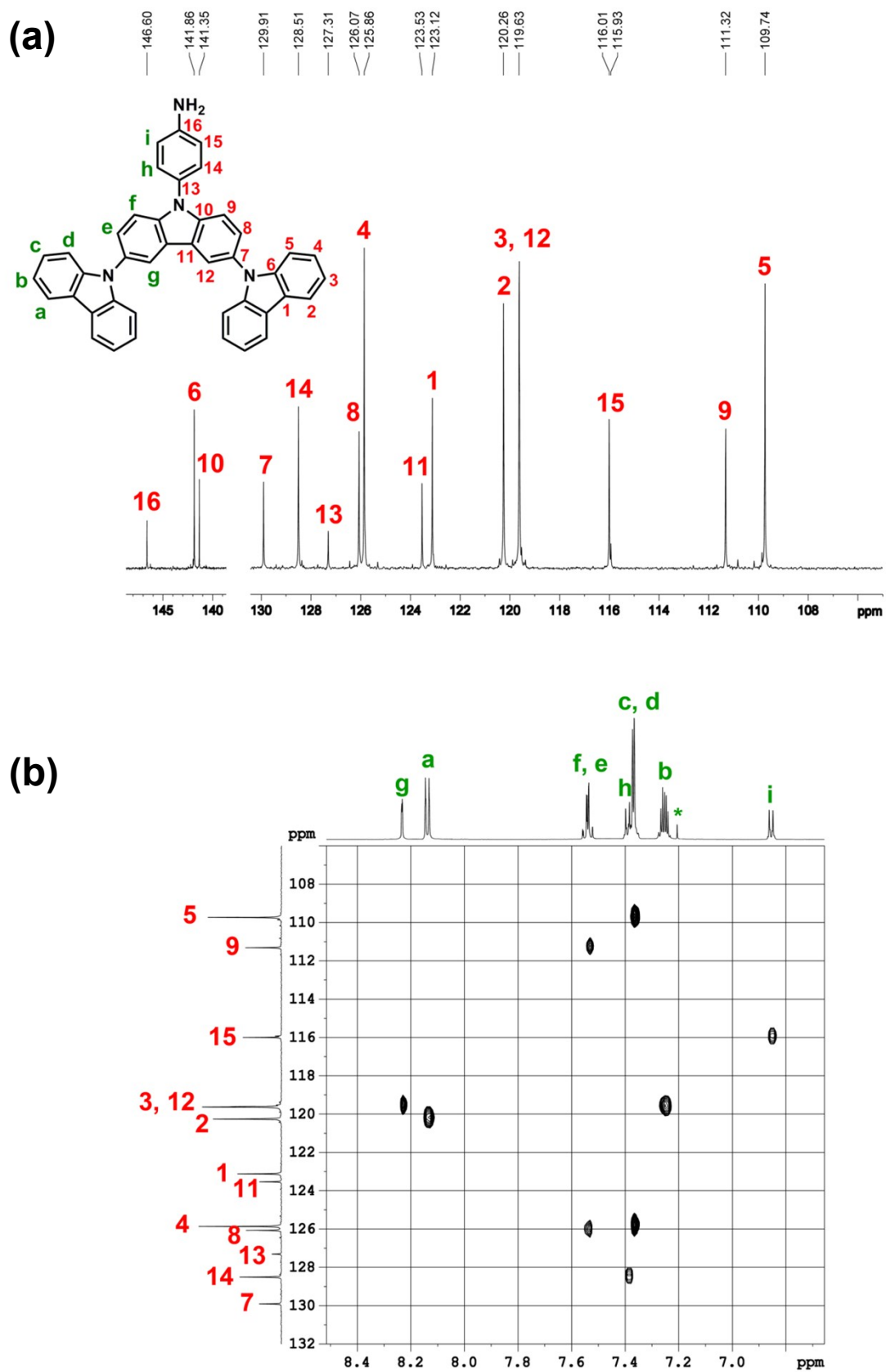
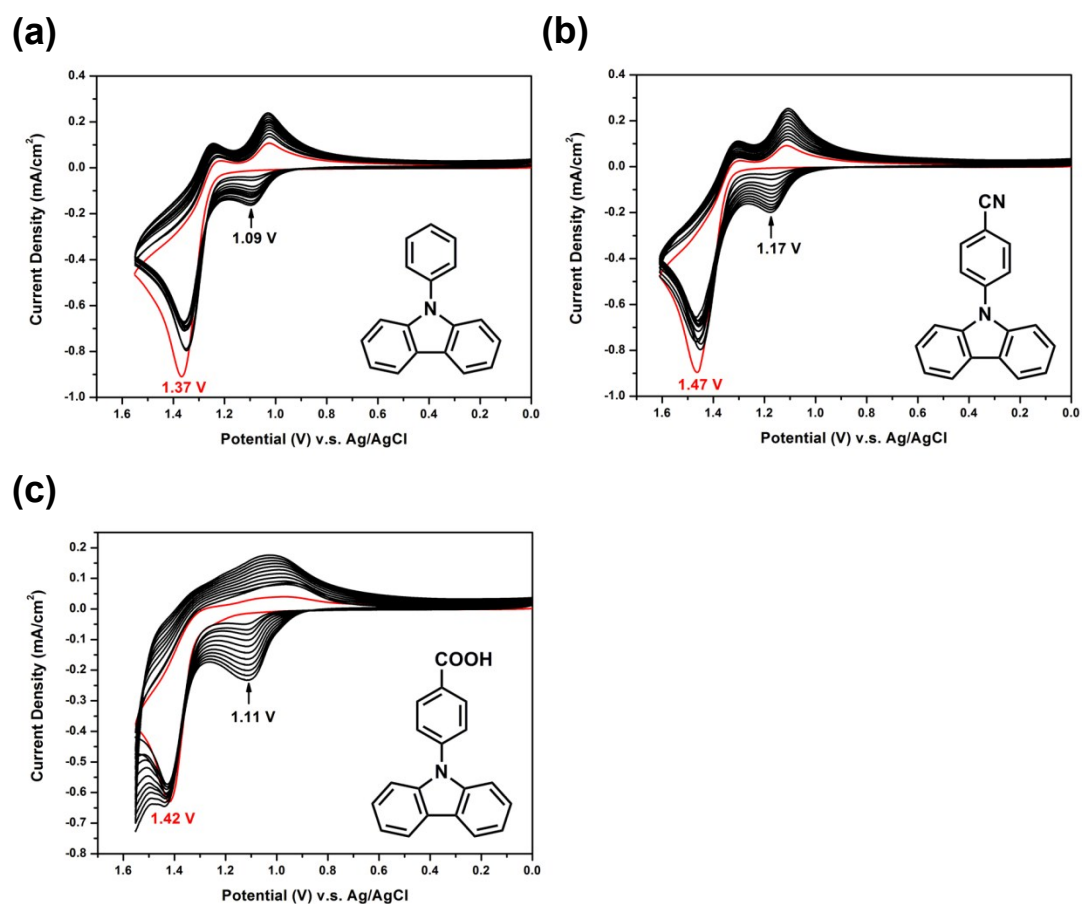
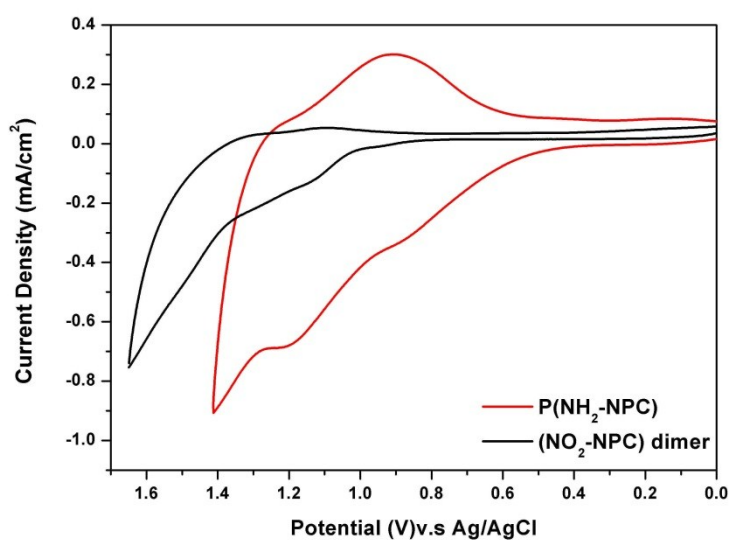


Fig. S7 (a)  $^{13}\text{C}$  NMR and (b) C-H HMQC spectra of  $\text{NH}_2\text{-3Cz}$  in  $\text{CDCl}_3$  (\* solvent peak).

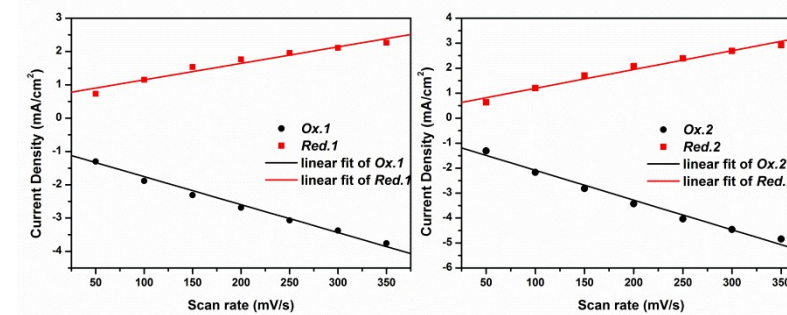
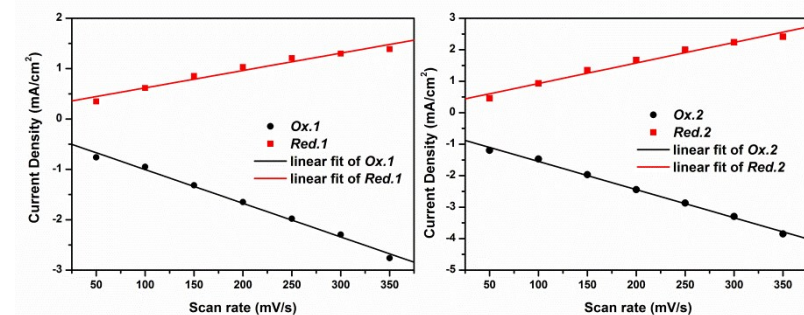
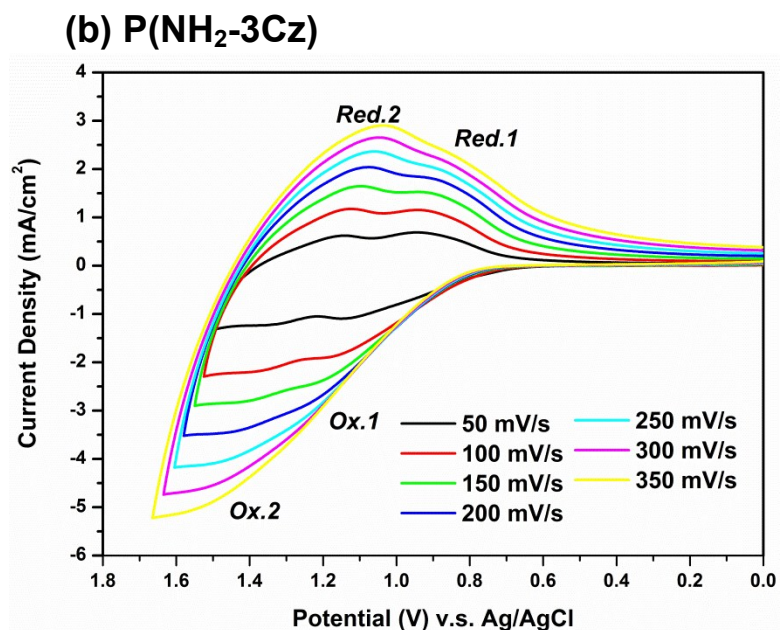
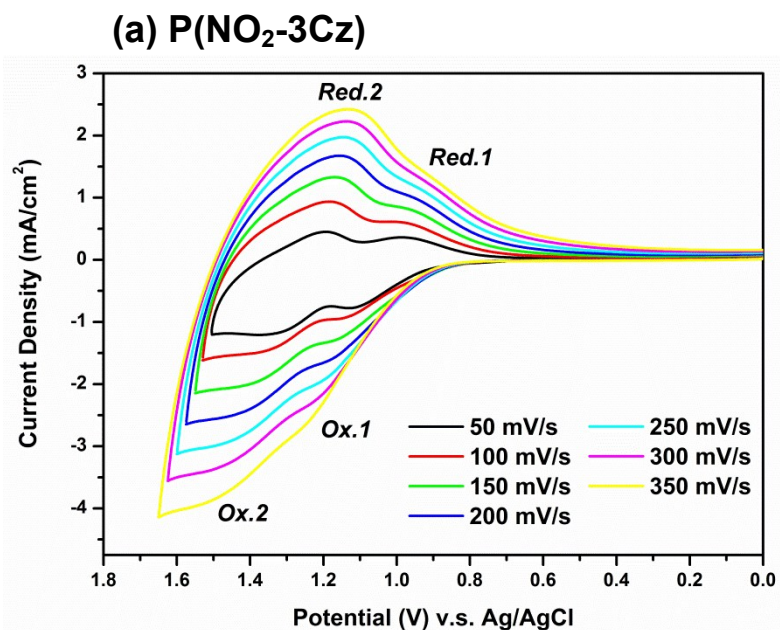




**Fig. S8** Repetitive cyclic voltammograms of  $5 \times 10^{-4}$  M (a) NPC, (b) CN-NPC, and (c) COOH-NPC in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/MeCN solution at a scan rate of 50 mV s<sup>-1</sup>.

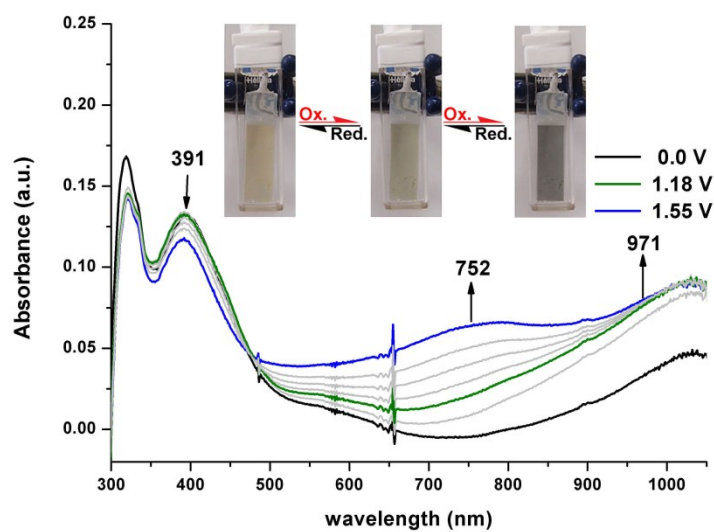


**Fig. S9** Cyclic voltammograms of P(NH<sub>2</sub>-NPC) film and (NO<sub>2</sub>-NPC) dimer on the ITO-coated glass slide in monomer-free 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/MeCN solution at a scan rate of 50 mV s<sup>-1</sup>.

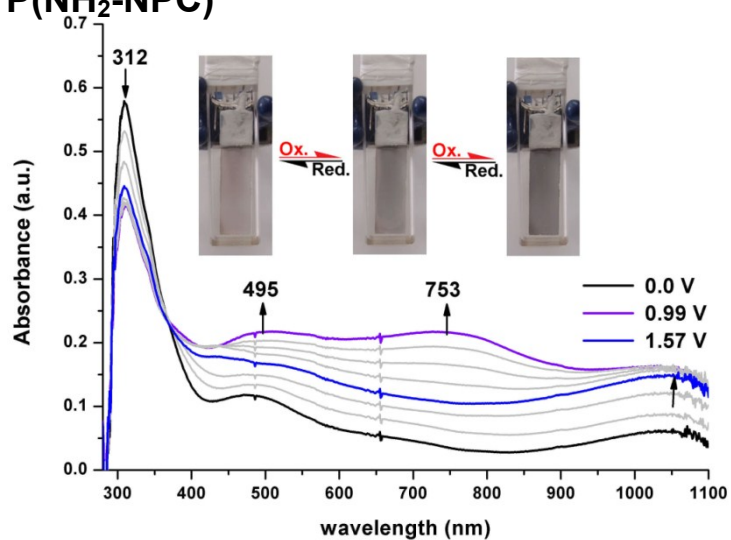


**Fig. S10** Scan rate dependence of P(NO<sub>2</sub>-3Cz) and P(NH<sub>2</sub>-3Cz) films on ITO-coated glass slide in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/MeCN at different scan rates between 50 and 350 mV.

**(a) (NO<sub>2</sub>-NPC) dimer**



**(b) P(NH<sub>2</sub>-NPC)**



**Fig. S11** Spectroelectrograms and color changes of (a) (NO<sub>2</sub>-NPC) dimer and (b) P(NH<sub>2</sub>-NPC) thin films on ITO-coated glass in 0.1 M Bu<sub>4</sub>NClO<sub>4</sub>/MeCN at various applied voltages.