Supporting Information

An Unexpected Discovery of One-Pot Synthesis for Carbazole-based Diamine and The Electrochromic Properties of Derived Polymers

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Fabrication of Electrochromic Devices (ECDs)

The polyamide film was drop-coated on ITO glass (25 mm \times 30 mm) and then overlapped by another clean ITO glass of the same size as the cathode, which was adhered by the full-auto dispenser with a 20 mm by 20 mm thermosetting area with a 1 cm width break. The gap between the two ITO glasses was confined to 120 µm and the device was baked at 125 °C for 6 hours. Then, the electrolyte solution was injected into the devices through a 1 cm width break in the vacuum encapsulation method. In the end, the break was sealed by UV-curing adhesive. The electrolyte solution was made of 165 mg (0.1 M) of TBABF₄, 40 mg (15 µM) of HV, and 5 mL of propylene carbonate (PC).

Measurements

Inherent viscosities of the polymers were measured by glass capillary viscometers in Tamson TV2000 viscometer bath with a concentration of 0.5 g/dL DMAc at 30 °C. Molecular weights are measured by gel permeation chromatographic (GPC) analysis on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Shodex GPC KD-803 and GPC KD-804 were connected in series with NMP and LiCl salt (20 mM) as the eluent at a flow rate of 0.35 mL/min at 40 °C and were calibrated with polystyrene standards. Fourier transform infrared (FT-IR) spectra were acquired with a PerkinElmer Spectrum. The ¹H NMR and ¹³C NMR spectra were run on a Bruker AVIII HD-600 (600 MHz), using dimethyl sulfoxide (DMSO-d₆) as solvent and tetramethylsilane (TMS; $\delta = 0$ ppm) as the internal standard. Transparency of the polymer films was measured by Jasco V-650 UV-vis spectrophotometer. High-resolution electrospray ionization mass spectrometry was carried out using Orbitrap QE Plus mass spectrometer (Thermo Scientific, San Jose, USA). Thermogravimetric analysis (TGA, TA instrument Q50) was used to analyze thermal stability and offered the decomposition temperature (T_d) at which a 5% or 10% weight loss and chard yield at a heating rate of 20 °C /min under nitrogen or air system (flowing rate: 20 cm³/min). Differential scanning calorimeter (DSC, TA Instruments Q-20) was used to analyze the melting point and the glass-transition

temperature (T_g) at a heating rate of 10 °C /min under a nitrogen atmosphere (flowing rate: 50 cm³/min). Electrochemical properties, including cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), were conducted through CH Instruments 6122E Electrochemical Analyzer under a three-electrode system consisting of a platinum counter electrode, a 0.6 cm by 3 cm polymer film coated on ITO glass as working electrode, and an Ag/AgCl reference electrode in 3 mL acetonitrile with 0.1 M TBABF₄ as supporting electrolyte, which the scanning rate of CV was 50 mV/s and the testing frequency of EIS was from 1MHz to 0.1Hz. The Agilent UV-vis spectrophotometer carried out the spectroelectrochemical experiments.



Scheme S1. The proposed reaction route of E-Cz.



Scheme S2. The proposed carbazole formation of E-Cz.



Fig. S1. TGA analyses of K-Cz with a heating rate of 10 °C/min under the nitrogen atmosphere.



Fig. S2. TGA analyses of the hybrid films with a heating rate of 10 °C/min under the air atmosphere.



Fig. S3. (a) ¹H-NMR and (b) ¹H-¹H COSY spectra of TPA-OBz in DMSO- d_6 .



Fig. S4. (a) ¹³C-NMR and (b) ¹H-¹³C COSY spectra of TPA-OBz in DMSO- d_6 .



Fig. S5. HRMS report of TPA-OBz.



Fig. S6. ¹³C-NMR spectrum of E-Cz in DMSO- d_6 .



Fig. S7. (a) $^{1}H^{-1}H$ COSY and $^{13}C^{-1}H$ HSQC spectra of E-Cz in DMSO- d_{6} .



Fig. S8. Overlay of ¹³C-NMR, DEPT 45, DEPT 90, and DEPT 135 of (a) **E-Cz** and (b) **K-Cz** from top to bottom in DMSO- d_6 .



Fig. S9. HRMS report of E-Cz.



Fig. S10. ¹³C-NMR spectrum of K-Cz in DMSO-d₆.



Fig. S11. (a) 1 H- 1 H COSY and 13 C- 1 H HSQC spectra of K-Cz in DMSO- d_{6} .



Fig. S12. HRMS report of K-Cz.



Fig. S13. (a) Cyclic voltammetric diagram of E-Cz and K-Cz. Spectroelectrochemical spectra of (b) E-Cz and (c) K-Cz at the different applied potentials. All the measurements are based on the OTTLE with 0.4 μ mole of the monomer in 800 μ L of 0.1 M TBABF₄/MeCN.



Fig. S14. TGA curves of **TPA-PA**, **E-Cz-PA**, and **co-OH-PA** in (a) N₂ and (b)Air. DSC curves of (a) **TPA-PA**, (b) **E-Cz-PA**, and (c) **co-OH-PA** under N₂ atmosphere with a heating rate of 10 °C/min.



Fig. S15. UV-vis spectra of prepared polyamide films (thickness: TPA-PA ($180 \pm 20 \text{ nm}$), E-Cz-PA ($200 \pm 30 \text{ nm}$), co-OH-PA ($210 \pm 20 \text{ nm}$), co-Zr10-PA ($220 \pm 20 \text{ nm}$), co-Zr20-PA ($240 \pm 30 \text{ nm}$) and co-Zr30-PA ($270 \pm 40 \text{ nm}$)) coated on ITO glasses (air as background for ITO-coated glass and ITO-coated glass as background for other polymer films).



Fig. S16. Partially enlarged CV diagrams (a) in oxidation potential and (b) in reduction potential on the ITO-coated glass substrate (coated area: $0.6 \text{ cm} \times 3 \text{ cm}$) in 0.1 M TBABF₄/MeCN at the scan rate of 50 mV/s.



Fig. S17. Switching response time at (a) 793 nm of **TPA-PA** (thickness: 180 ± 20 nm), (b) 768 nm of **co-OH-PA** (thickness: 210 ± 20 nm), (c) 768 nm of **co-Zr10-PA** (thickness: 220 ± 20 nm), (d) 768 nm of **co-Zr20-PA** (thickness: 240 ± 30 nm) and (e) 768 nm of **co-Zr30-PA** (thickness: 270 ± 40 nm) films on ITO glasses (coated area: $0.6 \text{ cm} \times 3 \text{ cm}$) in 0.1 M TBABF₄/MeCN with 1.0 V as colouring voltage and 0.0 V as bleaching voltage.



Fig. S18. Cyclic voltammograms of ECD-TPA-PA (thickness: 180 ± 20 nm), ECD-co-OH-PA (thickness: 200 ± 20 nm), and ECD-co-Zr20-PA (thickness: 240 ± 30 nm) at a scan rate of 50 mV/s with 0.1 M TBABF4 and 15 μ M HV in 48 μ L PC.

Polymers	$\eta_{\mathrm{inh}}(\mathrm{dL/g})^{a}$	$M_{\rm w}$ (kDa) b	$M_{\rm n}$ (kDa) ^b	PDI ^c
TPA-PA	0.91	171.3	105.7	1.62
E-Cz-PA	0.33	47.5	25.7	1.85
со-ОН-РА	0.31	15.7	10.5	1.50

Table S1. Inherent viscosities and molecular weights of TPA-PA, E-Cz-PA, and co-OH-PA.

^{*a*} Measured at a concentration of 0.5 g/dL in DMAc at 30 °C.

^bCalibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.35 mL/min at 40 °C.

^{*c*} Polydispersity index = M_w/M_n .

co-OH-PA

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Polymers	DMSO	NMP	DMAc	DMF	THF	CHCl ₃
TPA-PA	++	++	++	++	_	_
E-Cz-PA	++	++	++	++	_	_

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Table S2. Solubility behaviour of TPA-PA, E-Cz-PA, and co-OH-PA.^a

^{*a*} Measured at a concentration of 5 mg sample in 1 mL solvent.

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++: well dissolved at room temperature; -: totally not dissolved.

Polymer $T(^{\circ}C)^{a}$		$T_d {}^5 (^{\circ}C) {}^b$		T_{d}^{10} (°C) ^c		Char
	ig(C)	N ₂	Air	N_2	Air	Yield (%) ^d
ТРА-РА	184	375	345	390	390	25
E-Cz-PA	215	290	285	365	335	43
со-ОН-РА	140	330	320	385	378	33

Table S3. Thermal properties of TPA-PA, E-Cz-PA, and co-OH-PA.

 a T_g, glass transition temperature, was measured by DSC with a heating rate of 20 °C/min.

^b Temperature at weight loss of 5% polymer recorded by TGA at a heating rate of 20 °C /min and a gas flow rate of 20 cm³/min.

^{*c*} Temperature at weight loss of 10% polymer recorded by TGA at a heating rate of 20 °C /min and a gas flow rate of 20 cm³/min.

^d Residual weight percentage at 800 °C in nitrogen.

Polyamides	$\varDelta OD^{a}$	$Q. (mC/cm^2)^{b}$	$\eta (\mathrm{cm}^2/\mathrm{C})^c$
ТРА-РА	1.11	11.20	99.1
со-ОН-РА	1.13	13.78	82.0
co-Zr10-PA	1.19	9.88	120.4
co-Zr20-PA	1.10	8.38	131.3
co-Zr30-PA	1.01	6.83	147.8

Table S4. Parameters of coloration efficiency for all prepared polyamides.

^{an} Optical density is defined as $\triangle OD = \log [T_b/T_c]$, where the T_b and T_c are the transmittances of bleaching and colouring states.

^b The amount of ejected charge.

^{*c*} Coloration efficiency, which is defined as $\eta = \Delta OD/Q$.

Polyamides	$E_{\mathrm{ox}}(\mathrm{V})^{a}$	$E_{red}(\mathbf{V}) \ ^{b}$	$\Delta E(\mathbf{V})^{c}$
ECD-TPA-PA	1.30	1.01	0.29
ECD-co-OH-PA	1.33	0.98	0.35
ECD-co-Zr20-PA	1.21	1.02	0.19

Table S5. Redox peak potentials of ECD-TPA-PA and ECD-co-Zr20PA.

^{*a*} Oxidation potential at the peak.

^b Reduction potential at the peak.

 c Potential difference between oxidation and reduction peaks, $|\mathrm{E}_{\mathrm{ox}}-\mathrm{E}_{\mathrm{red}}|.$

Cycles	ΔT^{a}	$\delta \Delta T (\%)^{b}$
1	69.6	0.0
20	69.2	0.6
40	69.1	0.7
60	68.4	1.7
80	67.7	2.7
100	67.1	3.6

 Table S6. Optical data of ECD-co-Zr20-PA for 100 cycles.

^{*a*} Transmittance change at 760 nm.

^b Decay of transmittance change compared with the first cycle = $(\Delta T - \Delta T_0)/\Delta T_0 \ge 100\%$.