

Supporting Information

A facile approach to prepare porous polyamide films with enhanced electrochromic performance

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List of Contents for Supplementary Information:

| | |
|-----------------------------------|-------------|
| Experimental section | <u>SI-2</u> |
| Scheme S1 | <u>SI-2</u> |
| Characterization | <u>SI-3</u> |
| Figure S1 | <u>SI-5</u> |
| Figure S2 | <u>SI-5</u> |
| <u>5</u> | |
| Figure S3 | <u>SI-6</u> |
| <u>6</u> | |
| Figure S4 | <u>SI-7</u> |
| <u>7</u> | |
| Figure S5 | <u>SI-8</u> |
| <u>8</u> | |
| Figure S6 | <u>SI-8</u> |
| <u>8</u> | |

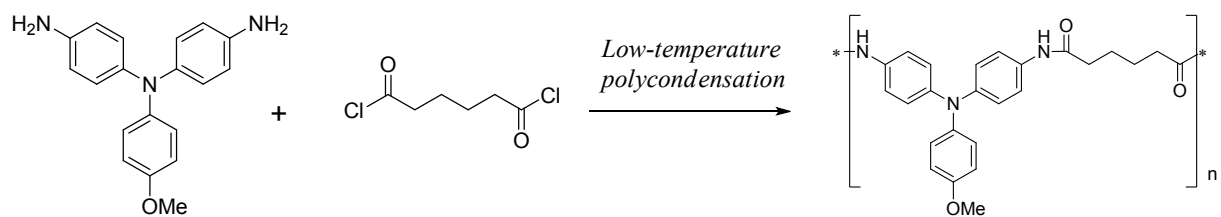
| | |
|-------------------------|--------------|
| Figure S7 | <u>SI-</u> |
| <u>9</u> | |
| Figure S8 | <u>SI-</u> |
| <u>9</u> | |
| Figure S9 | <u>SI-10</u> |
| Figure S10 | <u>SI-</u> |
| <u>11</u> | |
| Figure S11 | <u>SI-</u> |
| <u>12</u> | |
| Table S1 | <u>SI-13</u> |
| Table S2 | <u>SI-13</u> |
| Table S3 | <u>SI-13</u> |
| Table S4 | <u>SI-14</u> |
| Table S5 | <u>SI-14</u> |
| Table S6 | <u>SI-</u> |
| <u>14</u> | |
| Table S7 | <u>SI-</u> |
| <u>15</u> | |
| Table S8 | <u>SI-</u> |
| <u>15</u> | |
| Table S9 | <u>SI-</u> |
| <u>16</u> | |

Experimental section

Low-temperature Solution Polycondensation

A solution of 610.6 mg (2.0 mmol) of diamine monomer in 3.0 mL of DMAc was cooled with stirring at -40 °C on an ice/acetone/liquid nitrogen bath. After 0.8 mL propylene oxide was added to the mixture, 363.0 mg (2.0 mmol) of adipoyl dichloride was added into the mixture. The mixture was then stirred at -40 °C for 1 h then room temperature for 2 h. The resulting polyamide solution was poured into 400 mL of methanol. The precipitated polymer was collected by filtration, and dried at 100 °C in vacuum oven. The obtained polymer was firstly dissolved by DMAc then re-precipitated it into methanol. Then, the methanol was used as

solvent of Soxhelt extraction for 24 hours under reflux.



Scheme S1 Synthesis of PA

Characterization

Field emission scanning electron microscopy (FE-SEM, JEOL, JSM-6700F) was used to examine the surface morphology and microstructure of the porous polyamide films. The electron source for FE-SEM used in this paper is the type of cold cathode electron source. The sample was firstly cut into 0.5 cm × 0.5 cm then sputtered Platinum prior to FE-SEM tests. Atom force microscopy (AFM) measurement were obtained with a 3D Controller AFM (Digital Instruments, Santa Barbara, CA) operated in a tapping mode at room temperature was used to determine the surface roughness of the porous polyamide film. The AFM tip information is described below. Length: 125 μm; mean width: 30 μm; thickness: 4 μm; force constant: 42 N/m; resonance frequency: 330 kHz are as described below. Length: 125 μm; Mean width: 30 μm; Thickness: 4 μm; Force constant: 42 N/m; Resonance frequency: 330 kHz. Gel permeation chromatographic (GPC) analysis was carried out on a Waters chromatography unit interfaced with a Waters 2410 refractive index detector. Two Waters 5 μm Styragel HR-2 and HR-4 columns (7.8 mm I. D. × 300 mm) were connected in series with NMP as the eluent at a flow rate of 0.5 ml/min at 40 °C, and were calibrated with polystyrene standards. DSC analyses were performed on a PerkinElmer Pyris 1 DSC at a scan rate of 20 °C /min in flowing nitrogen and a gas-flow rate of 20 cm³/min. UV-vis spectra of the porous polyamide films were recorded by Hitachi U-4100 UV-vis-NIR spectrophotometer in the wavelength range of 400–800 nm. Thermogravimetric Analysis (TGA) was conducted with a TA instrument Q50. Experiments were carried out on approximately 3-5 mg film samples heated in flowing nitrogen or air (flow rate = 20 cm³/min) at a heating rate of 20 °C /min. Electrochemistry was performed with a CH Instruments 611B electrochemical analyzer. Voltammograms are presented with the positive potential pointing to the right and with increasing anodic currents pointing upwards. Cyclic voltammetry (CV) was conducted by the cast film on an ITO-coated glass side (25 mm x 6 mm) as working electrode and Pt wire as counter electrode in anhydrous PC using 0.1 M TBABF₄ as supporting electrolyte under nitrogen atmosphere for oxidation measurement. 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-vis cuvette using Hewlett-Packard 8453 UV-vis diode array spectrophotometer from 190 nm to 1100 nm wavelength region. The ITO-coated glass side was used as the working electrode, a platinum wire as the counter electrode, and an Ag/AgCl cell as the reference electrode. For electrochromic switching studies, the films were cast on ITO-coated glass sides, chronoamperometric and transmittance measurements were performed. While the films were switched, the

transmittance at the given wavelength was monitored as a function of time with UV-vis-NIR spectroscopy. CE (η) determines the amount of optical density change (δOD) at a specific absorption wavelength induced as a function of the ejected/injected charge (Q also termed as electroactivity) which is determined from the in situ experiments. CE is given by the equation: $\eta = \delta OD / Q = \log [T_b/T_c] / Q$, where η (cm^2 / C) is the coloration efficiency at a given wavelength, Q is the injected charge, and T_b and T_c are the bleached and colored transmittance values, respectively.

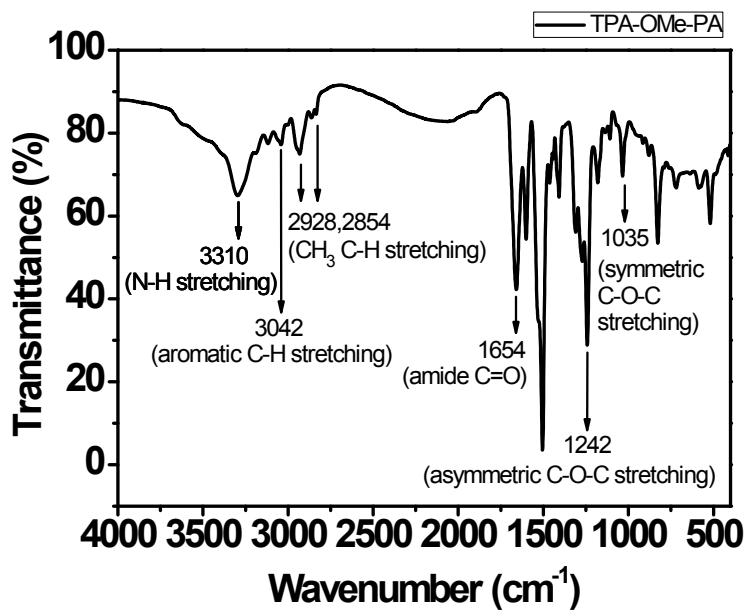


Figure S1. IR spectrum of the TPA-OMe polyamide.

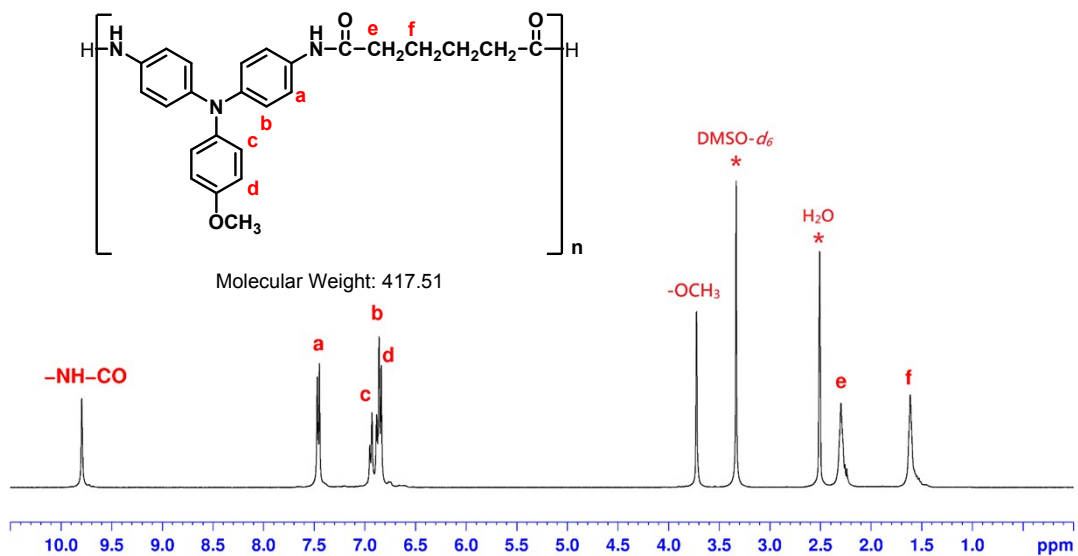


Figure S2. ¹H NMR spectrum of the TPA-OMe polyamide.

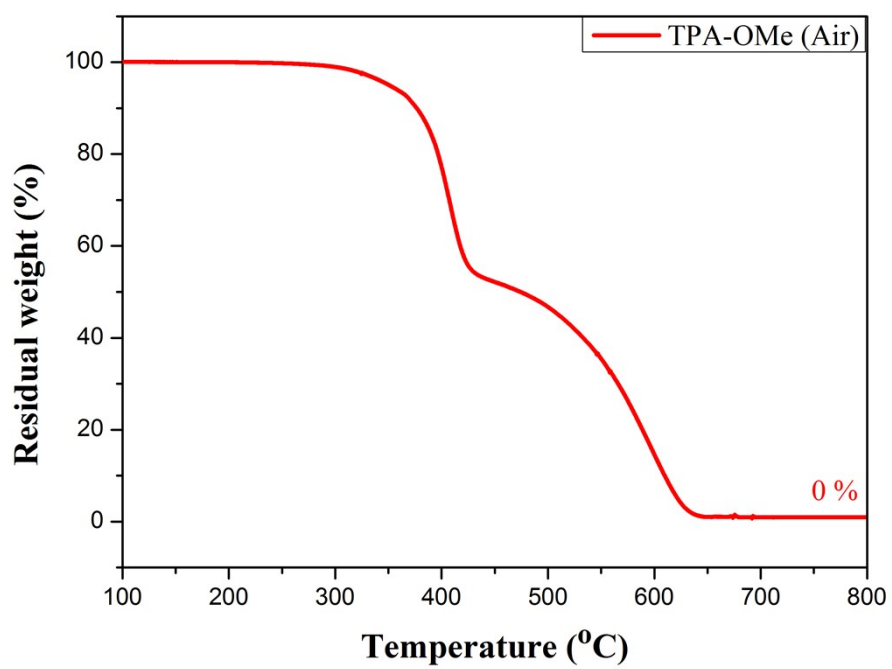
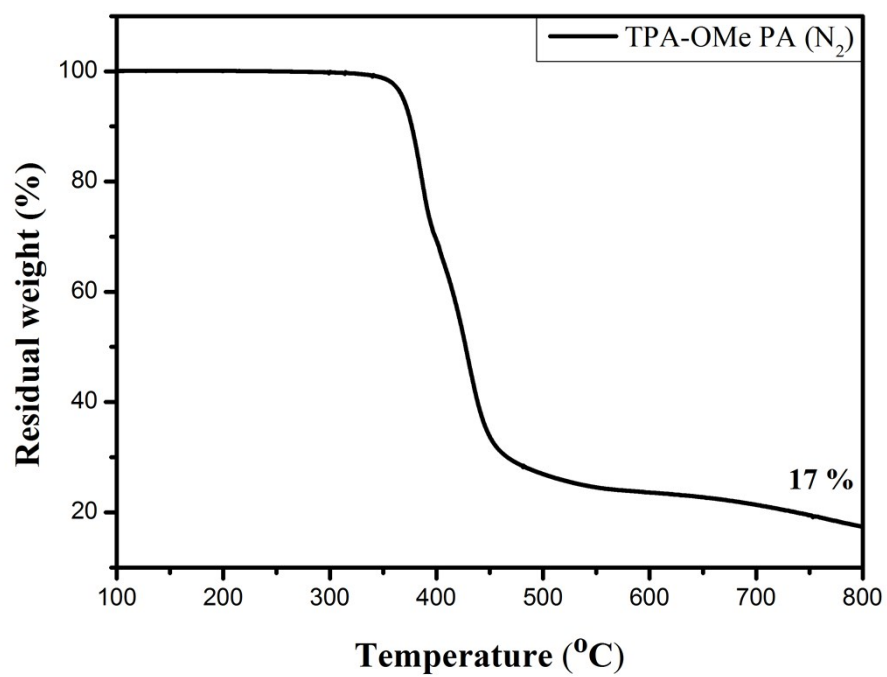


Fig. S3 TGA traces of the PA with a heating rate of 20 °C /min.

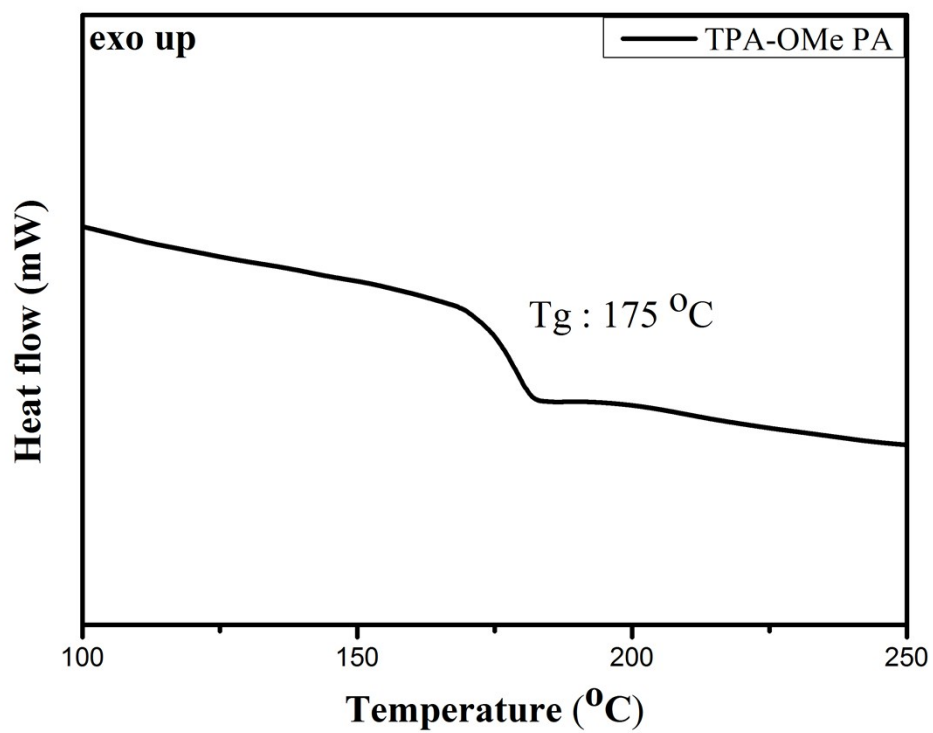


Fig. S4 DSC traces of PA with a heating rate of 20 °C/min nitrogen.

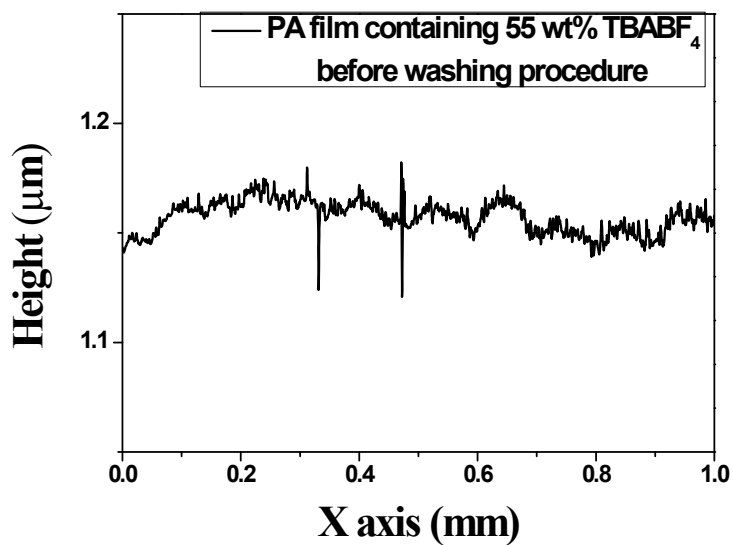


Fig. S5 Alpha-step profile of TPA-OMe PA film containing 55wt% TBABF₄ before washing procedure.

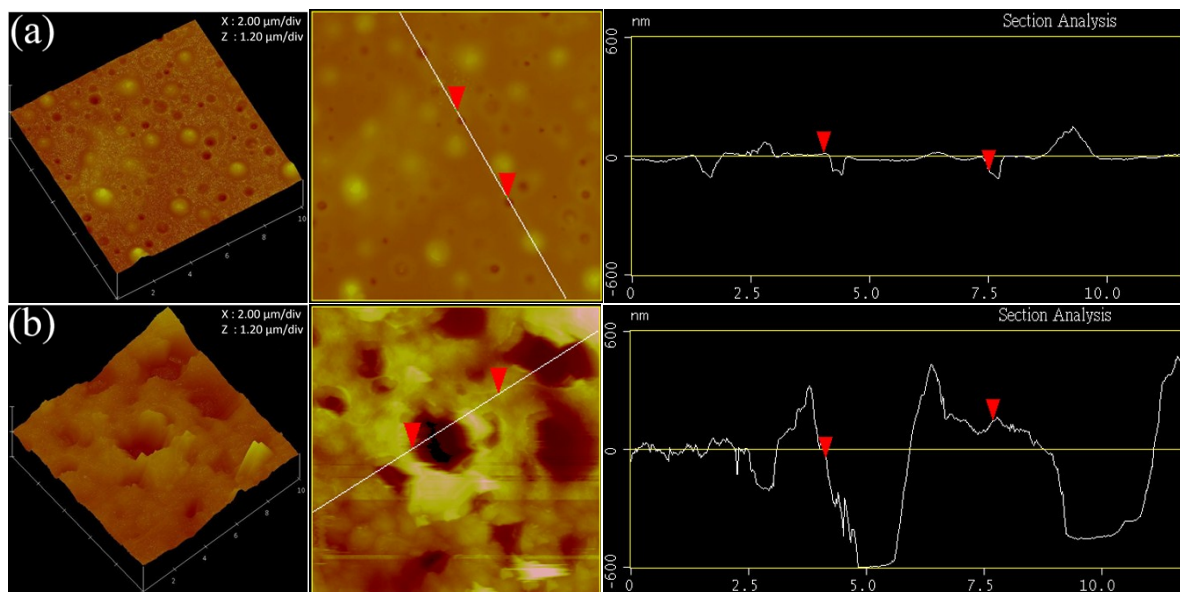


Fig. S6 AFM measurements of (a) the surface roughness analysis of porous PA film made by 44 wt% TBABF₄ and (b) the surface roughness analysis of porous PA film made by 67 wt% TBABF₄.

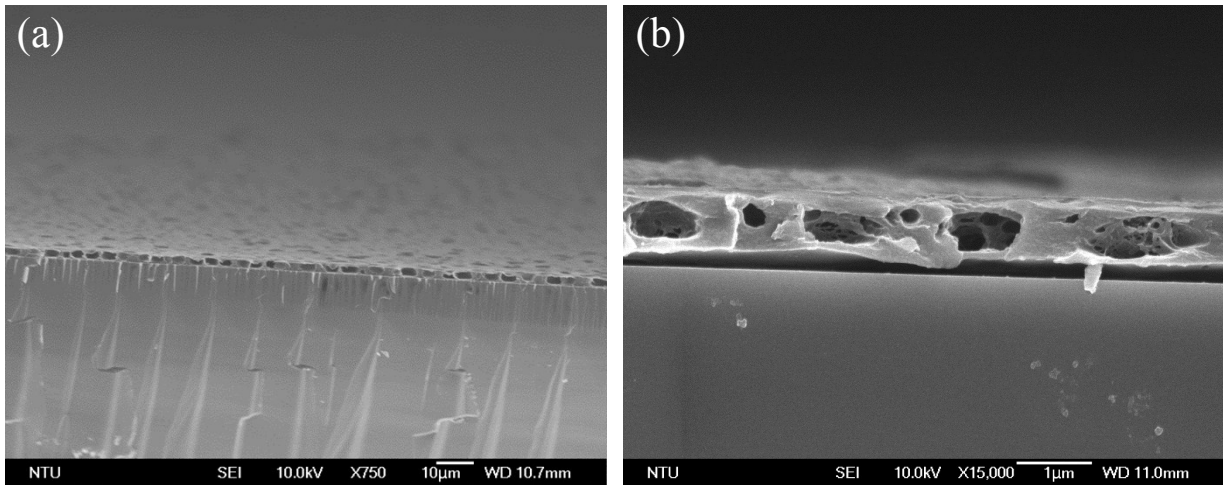


Fig. S7 (a) Cross-section SEM images of porous PA film made by 55 wt% TBABF₄. (b) The partial magnification from (a).

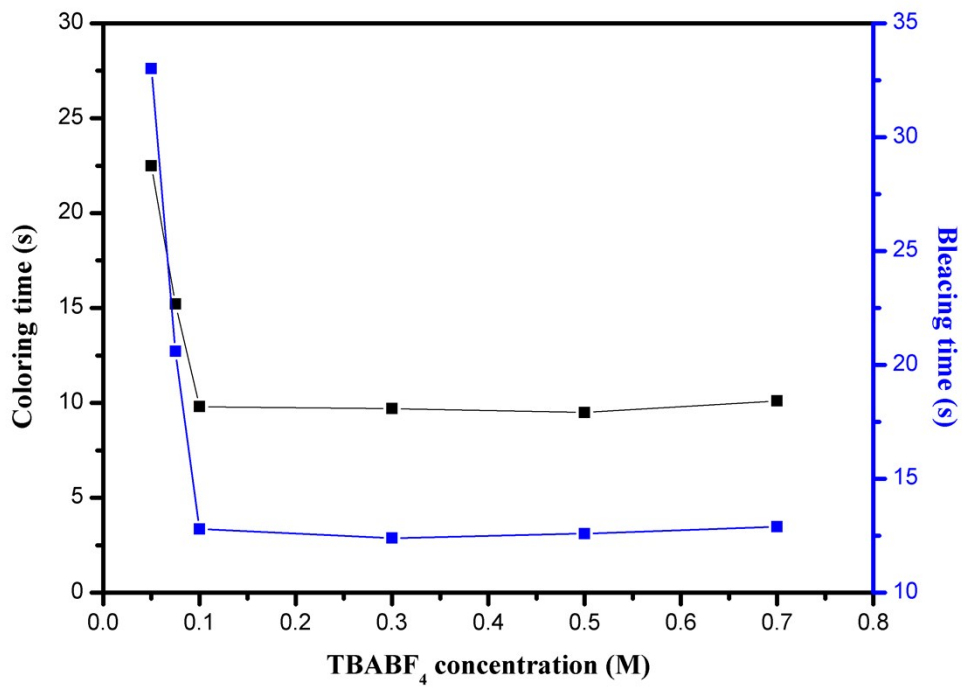


Fig. S8 Relationship between response time (s) and TBABF₄ concentration (M) in TPA-OMe PA ECDs.

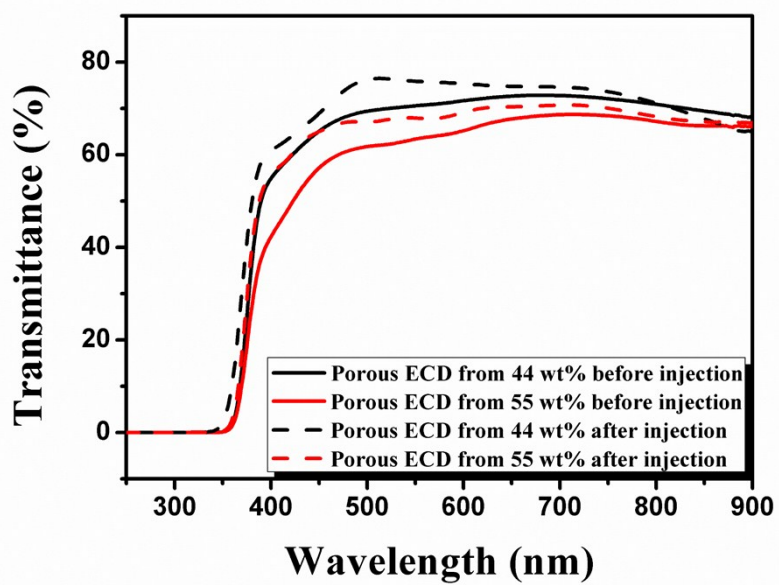


Fig. S9 UV-Vis transmittance spectra of the porous ECD before and after injecting gel electrolyte (air as background).

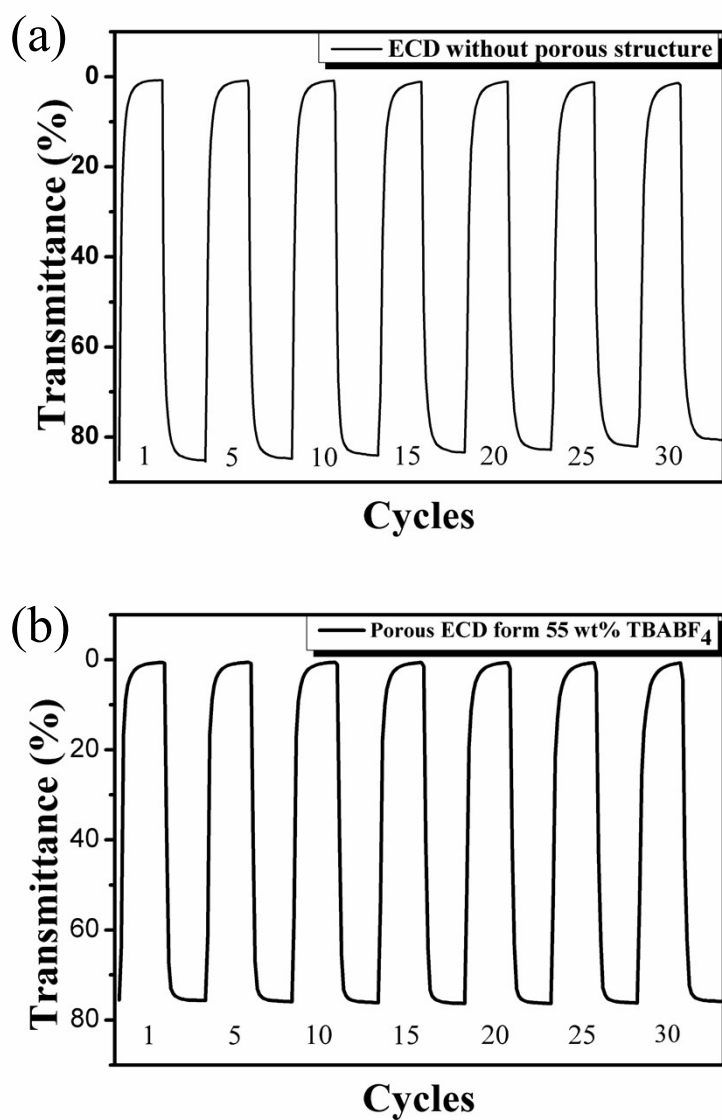


Fig. S10 Transmittance spectra (related to air) of ECDs switching at 770 nm (a) without porous structure at applied potential 2.10 V to -2.10 V (b) made from 55 wt% TBABF₄ porous PA film at applied potential of 1.95 V to -1.95 V (working area: 2cm x 2 cm) with a cycle time of 200 s for 30 cycles.

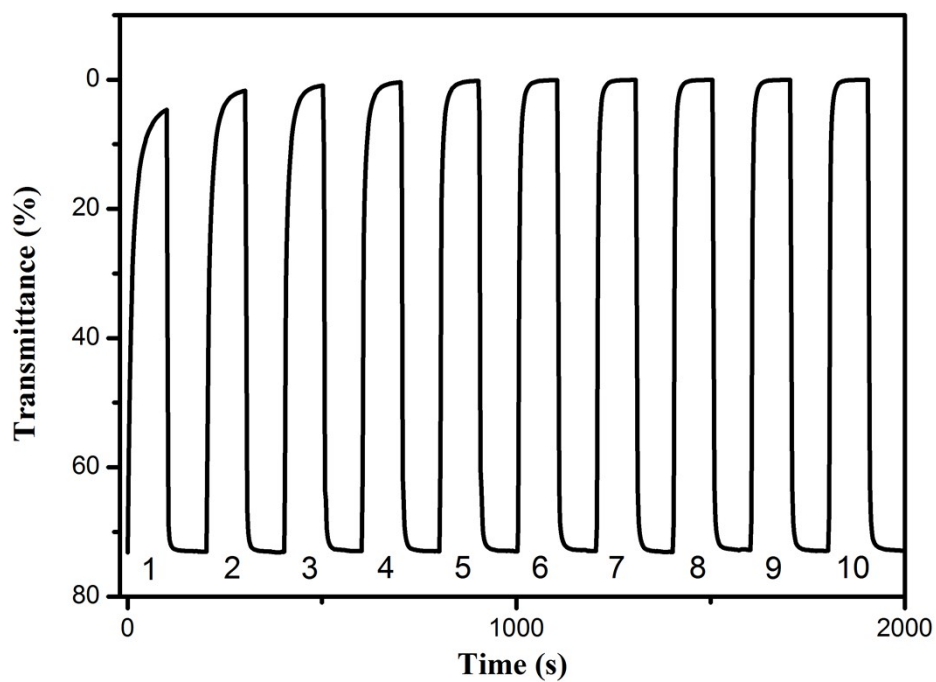


Fig. S11 Optical contrast at 770 nm of modified porous ECDs (55 wt% TBABF₄) at applied potential of 1.95 V to -1.95 V (working area: 2 cm x 2 cm) with a cycle time of 200 s.

Table S1 Inherent viscosity and molecular weights of the polyamide

| Code | η_{inh} (dL/g) ^a | M_w ^b | M_n ^b | PDI ^c |
|-------------------|---|--------------------|--------------------|------------------|
| TPA-OMe PA | 0.55 | 34000 | 17500 | 1.94 |

^a Measured at concentration of 0.5 g dL⁻¹ in DMAc at 30 °C.

^b Calibrated with polystyrene standards, using NMP as the eluent at a constant flow rate of 0.5 ml/min at 40 °C.

^c Polydispersity Index (M_w/M_n).

Table S2 Solubility behaviors of the polyamide

| Code | Solubility in various Solvent ^a | | | | | | |
|-------------------|--|------|-----|------|------------------|-----|-------------------|
| | NMP | DMAc | DMF | DMSO | <i>m</i> -cresol | THF | CHCl ₃ |
| TPA-OMe PA | ++ | ++ | ++ | ++ | ++ | +- | - |

^a Qualitative solubility was tested with 5 mg of a sample in 1 mL of solvent. ++, soluble at room temperature; +, soluble on heating; +-, partially soluble or swelling; -, insoluble even on heating.

Table S3 Thermal properties of the polyamides

| Polymer ^a | T_g (°C) ^b | T_d at 5 % weight loss (°C) ^c | | T_d at 10 % weight loss (°C) ^d | | char yield (wt%) ^e |
|----------------------|-------------------------|--|-----|---|-----|-------------------------------|
| | | N ₂ | Air | N ₂ | Air | |
| TPA-OMe PA | 175 | 370 | 350 | 380 | 370 | 17 |

^a The polymer film samples were heated at 200 °C for 1 h prior to all the thermal analyses.

^b Midpoint temperature of baseline shift on the second DSC heating trace (rate: 20 °C /min) of the sample after quenching from 300 °C to 50 °C (rate: 200 °C /min) in nitrogen.

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

^d Temperature at which 10% weight loss occurred.

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

Table S4 Properties of salt and the porous PA films

| | CaCl ₂ | LiCl | LiBF ₄ | TBAP | TBABF ₄ |
|---|-------------------|------|-------------------|---------|--------------------|
| Adhesion ^a | X | X | X | O | O |
| Saturated solubility (mg/ml) ^b | 2.0 | 8.5 | 25.0 | 150.0 | 190.0 |
| Interionic attraction - Melting point (°C) ^c | 772 | 605 | 296 | 211-215 | 155-161 |

^a The adhesion is determined by dipping the films in water for 30 min.

X: The films separated from the substrate; O: The films are still on substrate.

^b The maximum amount of a solute that can dissolve in DMAc at 25 °C and 1 atm

^c Ref : <http://www.chemicalbook.com>

Table S5 Optical properties of the porous PA films

| | Diameter of hole (nm) | Transmittance (%) at 550 nm |
|--|-----------------------|-----------------------------|
| Pure PA | - | 84.7 |
| Porous PA from TBAP ^a | 400 - 700 | 70.1 |
| Porous PA from TBABF ₄ ^a | 100 - 300 | 75.4 |

^a Salt content are both 50 wt%

Table S6 Optical properties of the porous PA films

| TBABF ₄ content (wt%) ^a | 0 | 44 | 55 | 62 | 67 |
|---|----------|------------|------------|------------|------------|
| Thickness (nm) | 900 ± 50 | 1100 ± 200 | 1600 ± 250 | 1800 ± 400 | 2100 ± 500 |
| Transmittance(%) at 550 nm | 84.7 | 80.4 | 71.9 | 58.8 | 53.1 |
| L* | 90.17 | 87.74 | 75.81 | 65.25 | 58.06 |

^a Porous PA films made from different weight ratio of TBABF₄

Table S7 Optical and EC data collected from coloration efficiency measurements of ECD without porous structure.

| Cycling times ^a | ΔT^b | δOD^c | Q (mC/cm ²) ^d | η (cm ² /C) ^e | η decay (%) ^f | ΔT decay (%) ^g |
|----------------------------|--------------|---------------|--------------------------------------|--|-------------------------------|-----------------------------------|
| 1 | 91.6 | 2.07 | 15.33 | 133.3 | 0 | 0 |
| 5 | 90.9 | 2.01 | 15.22 | 132.0 | 0.97 | 0.98 |
| 10 | 90.0 | 1.98 | 15.10 | 131.1 | 1.67 | 1.74 |
| 15 | 89.3 | 1.93 | 15.01 | 128.6 | 3.52 | 2.51 |
| 20 | 88.6 | 1.91 | 14.89 | 128.2 | 3.82 | 3.27 |
| 25 | 87.7 | 1.85 | 14.80 | 125.2 | 6.07 | 4.25 |
| 30 | 85.7 | 1.82 | 14.69 | 123.8 | 7.12 | 6.44 |

^a Switching between 2.10 V and -2.10 V

^b Transmittance change at 770 nm.

^c Optical density (δOD)= $\log[T_{\text{bleached}}/T_{\text{colored}}]$, where T_{colored} and T_{bleached} are the maximum transmittance in the oxidized and neutral states, respectively.

^d Ejected charge, determined from the in situ experiments.

^e Coloration efficiency is derived from the equation $\eta = \delta OD / Q$.

^f Decay of coloration efficiency after cyclic scans = $(\eta_0 - \eta) / \eta_0 \times 100 \%$.

^g Decay of transmittance after cyclic scans = $(\Delta T_0 - \Delta T) / \Delta T_0 \times 100 \%$.

Table S8 Optical and EC data collected from coloration efficiency measurements of porous ECD made from 55 wt% TBABF₄ porous PA film.

| Cycling times ^a | ΔT^b | δOD^c | Q (mC/cm ²) ^d | η (cm ² /C) ^e | η decay (%) ^f | ΔT decay (%) ^g |
|----------------------------|--------------|---------------|--------------------------------------|--|-------------------------------|-----------------------------------|
| 1 | 75.46 | 1.99 | 15.38 | 129.3 | 0 | 0 |
| 5 | 75.03 | 1.96 | 15.35 | 127.6 | 1.31 | 0.57 |
| 10 | 74.66 | 1.95 | 15.30 | 127.4 | 1.46 | 1.06 |
| 15 | 74.01 | 1.92 | 15.22 | 126.1 | 2.47 | 1.92 |
| 20 | 73.34 | 1.89 | 15.12 | 125.0 | 3.30 | 2.80 |
| 25 | 72.45 | 1.84 | 14.99 | 122.7 | 5.11 | 3.98 |
| 30 | 71.18 | 1.80 | 14.88 | 120.9 | 6.49 | 5.67 |

^a Switching between 1.95 V and -1.95 V

^b Transmittance change at 770 nm.

^c Optical density (δOD)= $\log[T_{\text{bleached}}/T_{\text{colored}}]$, where T_{colored} and T_{bleached} are the maximum transmittance in the oxidized and neutral states, respectively.

^d Ejected charge, determined from the in situ experiments.

^e Coloration efficiency is derived from the equation $\eta = \delta OD / Q$.

^f Decay of coloration efficiency after cyclic scans = $(\eta_0 - \eta) / \eta_0 \times 100 \%$.

^g Decay of transmittance after cyclic scans = $(\Delta T_0 - \Delta T) / \Delta T_0 \times 100 \%$.

Table S9 Composition of porous ECD

| TPA-PA (mg) | TBABF ₄ (mg) in PA film | TBABF ₄ weight (%) ^a | TBABF ₄ (mmole) ^b | TPA-PA repeating unit (mmole) ^c | TBABF ₄ concentration (M) in ECD ^d |
|----------------|---------------------------------------|---|--|--|--|
| | 0.8 | 44 | 2.4 x 10 ⁻³ | | 0.1 M |
| | 1.0 | 50 | 3.0 x 10 ⁻³ | | 0.1 M |
| 1 | 1.2 | 55 | 3.4 x 10 ⁻³ | 2.4 x 10 ⁻³ | 0.1 M |
| | 1.6 | 62 | 4.8 x 10 ⁻³ | | X |
| | 2.0 | 67 | 6.0 x 10 ⁻³ | | X |

^a TBABF₄ : TPA-PA weight ratio

^b TBABF₄ Mw : 329.27 g.

^c PA repeating unit Mw : 415.48 g.

^d Calculate from [TBABF₄ (mmole)/0.048 mL PC (ECD volume)], by injecting supporting electrolyte to ECD to supply additional TBABF₄ reaching 0.1 M.