

Supporting Information

Concept of Triphenylamine Side Chains with Four Electroactive Nitrogen Centers toward Record-High Stable Electrochromic Polyamides

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Table S1. Inherent Viscosity and Solubility^b of PAs.

| PA | $\eta_{inh}(\text{dL/g})^a$ | NMP | DMAc | <i>o</i> -Chlorophenol | THF |
|----|-----------------------------|-----|------|------------------------|-----|
| 5a | 0.40 | + | ++ | +— | +— |
| 5b | 0.32 | + | + | +— | — |
| 5c | 0.45 | + | + | +— | — |

^aMeasured in NMP on 0.5 g/dL at 30 °C. ^bQualitative solubility was determined using 0.01 g of polymer in 1 ml of solvent. ++ (soluble at room temperature); + (soluble on heating at 60°C); +— (partially soluble on heating at 60°C); — (insoluble in hot solvent).

Table S2. Thermal Properties of PAs.

| PA | T _g (°C) ^a | T _d (°C) ^b | | Char yield ^c (%) |
|----|----------------------------------|----------------------------------|-------------------|--------------------------------|
| | | In Air | In N ₂ | |
| 5a | 178 | 425 | 467 | 59 |
| 5b | 181 | 421 | 464 | 63 |
| 5c | 194 | 421 | 470 | 65 |

^aTemperature at which the middle of the heat capacity change occurred from the second DSC heating scan at a heating rate of 20°C/min. ^bTemperature at which 10% weight loss recorded by thermogravimetry at a heating rate of 20°C/min. ^cResidual weight% at 800°C in nitrogen.

Table S3. Optical and Electrochemical Data Collected for Coloration Efficiency.

| Cycles ^a | ΔOD^b | $\Delta T(\%)^c$ | $Q(\text{mC}/\text{cm}^2)^d$ | $\eta(\text{cm}^2/\text{C})^e$ | decay($\%)^f$ |
|---------------------|---------------|------------------|------------------------------|--------------------------------|----------------|
| 1 | 0.376 | 57.9 | 1.84 | 204 | 0.00 |
| 2500 | 0.370 | 57.4 | 1.82 | 203 | 0.49 |
| 5000 | 0.363 | 56.6 | 1.79 | 202 | 0.98 |
| 7500 | 0.357 | 56.0 | 1.78 | 199 | 2.45 |
| 10000 | 0.355 | 55.8 | 1.78 | 199 | 2.45 |
| 12500 | 0.339 | 54.3 | 1.74 | 194 | 4.90 |
| 15000 | 0.337 | 54.0 | 1.73 | 194 | 4.90 |
| 17500 | 0.329 | 53.1 | 1.71 | 192 | 5.88 |
| 20000 | 0.323 | 52.4 | 1.69 | 191 | 6.37 |
| 22500 | 0.321 | 52.2 | 1.69 | 190 | 6.86 |
| 24000 | 0.307 | 50.7 | 1.64 | 186 | 8.82 |

^aTimes of cyclic scan of **5a** by applying potential step: 0.0 V \leftrightarrow 0.5 V (V vs. Ag/AgCl). ^bOptical density change at 1404 nm. ^cOptical transmittance change at 1404 nm. ^dEjected charge determined from in situ experiments. ^eColoration efficiency is derived from the equation $\eta = \Delta OD/Q$. ^fDecay of coloration efficiency after cyclic scans.

Table S4. Optical and Electrochemical Data Collected for Coloration Efficiency.

| Cycles ^a | ΔOD^b | $\Delta T(\%)^c$ | $Q(\text{mC}/\text{cm}^2)^d$ | $\eta(\text{cm}^2/\text{C})^e$ | decay($\% \text{)^f$ |
|---------------------|---------------|------------------|------------------------------|--------------------------------|-----------------------|
| 1 | 0.331 | 53.4 | 2.97 | 111 | 0.00 |
| 2000 | 0.315 | 51.6 | 2.87 | 110 | 0.90 |
| 4000 | 0.310 | 51.0 | 2.86 | 108 | 2.70 |
| 6000 | 0.307 | 50.7 | 2.84 | 108 | 2.70 |
| 8000 | 0.300 | 49.9 | 2.80 | 107 | 3.60 |
| 10000 | 0.283 | 48.0 | 2.76 | 103 | 7.20 |
| 12000 | 0.281 | 47.7 | 2.75 | 102 | 8.11 |
| 14000 | 0.281 | 47.6 | 2.75 | 102 | 8.11 |
| 16000 | 0.278 | 47.3 | 2.74 | 101 | 9.01 |
| 18000 | 0.276 | 47.1 | 2.73 | 101 | 9.01 |
| 20000 | 0.267 | 46.0 | 2.68 | 100 | 9.91 |

^aTimes of cyclic scan of **5a** by applying potential step: 0.0 V \leftrightarrow 0.5 V (V vs. Ag/AgCl). ^bOptical density change at 440 nm. ^cOptical transmittance change at 440 nm. ^dEjected charge determined from in situ experiments. ^eColoration efficiency is derived from the equation: $\eta = \Delta OD/Q$. ^fDecay of coloration efficiency after cyclic scans.

Table S5. Optical and Electrochemical Data Collected for Coloration Efficiency.

| Cycles ^a | Δ OD ^b | Δ T(%) ^c | Q(mC/cm ²) ^d | η (cm ² /C) ^e | decay(%) ^f |
|---------------------|--------------------------|----------------------------|-------------------------------------|--|-----------------------|
| 1 | 1.05 | 91.1 | 7.22 | 145 | 0.00 |
| 500 | 1.03 | 90.7 | 7.20 | 144 | 0.69 |
| 1000 | 1.03 | 90.6 | 7.19 | 143 | 1.38 |
| 1500 | 1.02 | 90.4 | 7.17 | 142 | 2.07 |
| 2000 | 1.02 | 90.3 | 7.16 | 142 | 2.07 |
| 2500 | 1.00 | 90.0 | 7.14 | 140 | 3.45 |
| 3000 | 0.96 | 89.0 | 7.08 | 136 | 6.21 |
| 3500 | 0.95 | 88.7 | 7.06 | 134 | 7.59 |
| 4000 | 0.93 | 88.1 | 6.91 | 134 | 7.59 |
| 4500 | 0.92 | 88.1 | 6.91 | 134 | 7.59 |
| 5000 | 0.83 | 85.2 | 6.42 | 129 | 11.03 |

^aTimes of cyclic scan of **5a** by applying potential step: 0.0 V \leftrightarrow 0.7 V (V vs. Ag/AgCl). ^bOptical density change at 1404 nm. ^cOptical transmittance change at 1404 nm. ^dEjected charge, determined from in situ experiments. ^eColoration efficiency is derived from the equation: $\eta = \Delta$ OD/Q. ^fDecay of coloration efficiency after cyclic scans.

Table S6. NIR Absorption of Polymers at the First Stage of Oxidation.

| Polymer | Potential ^a (V) | λ_{max} ^b (nm) | Absorption Range ^b (nm) |
|---------|----------------------------|--|------------------------------------|
| 5a | 0.50 | 1404 | 800-1800 |
| P1 | 0.75 | 1062 | 800-1450 |
| P2 | 0.40 | 1252 | 800-1700 |

^aApplied potential for the first stage oxidation. ^bNIR absorption.

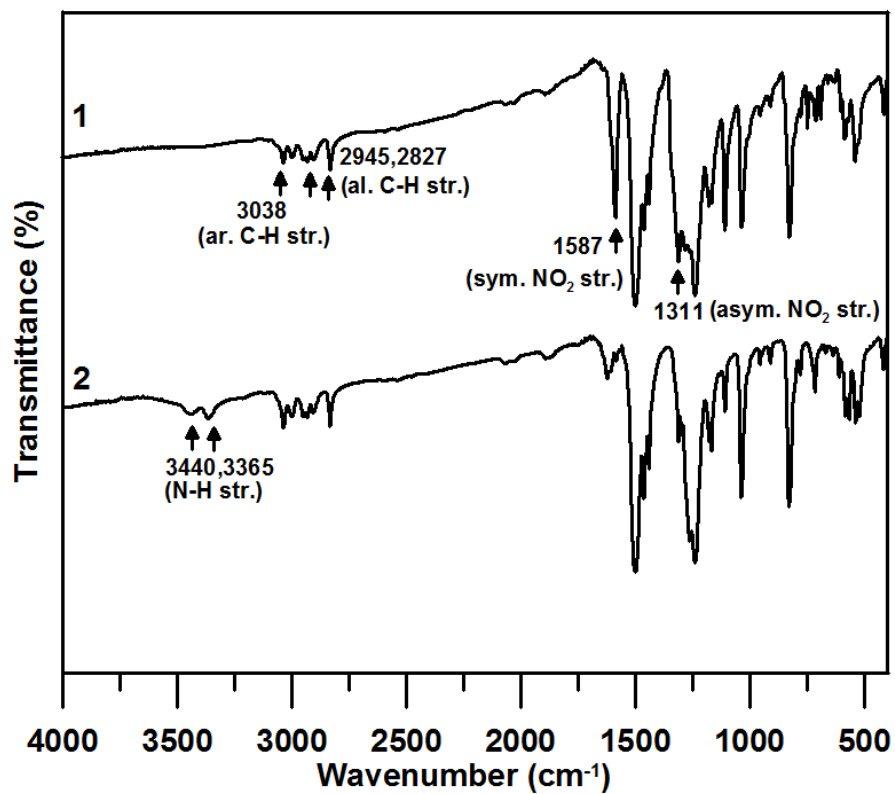


Fig. S1 FT-IR spectra of the compounds 1 and 2.

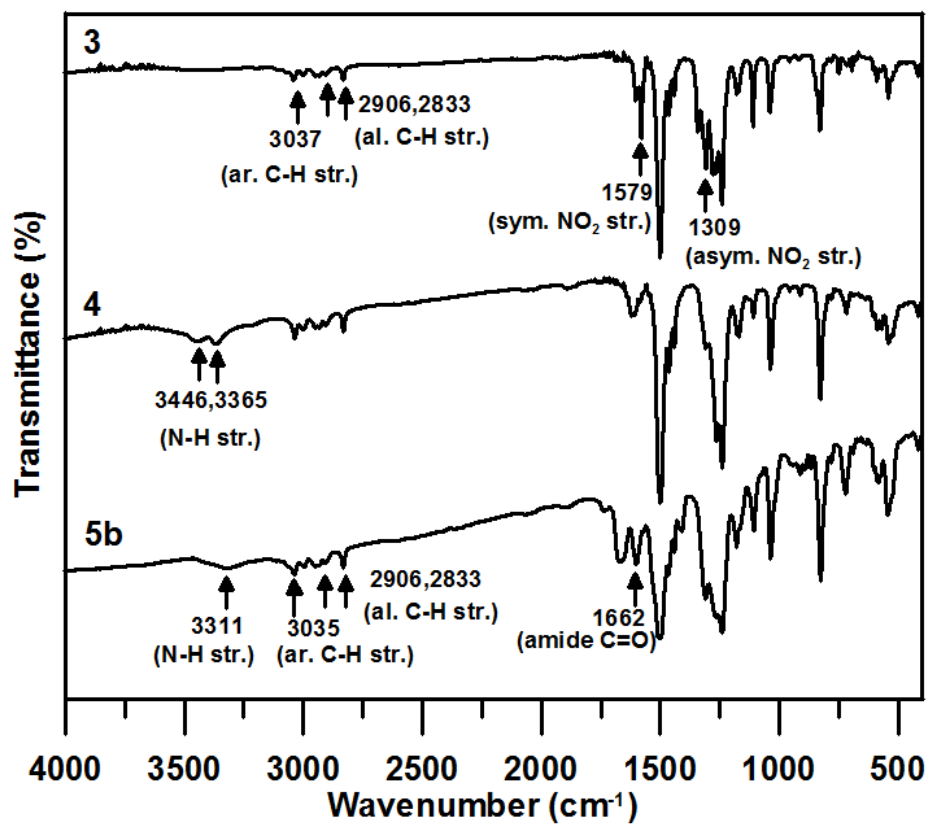


Fig. S2 FT-IR spectra of the compounds 3, 4, and PA 5b.

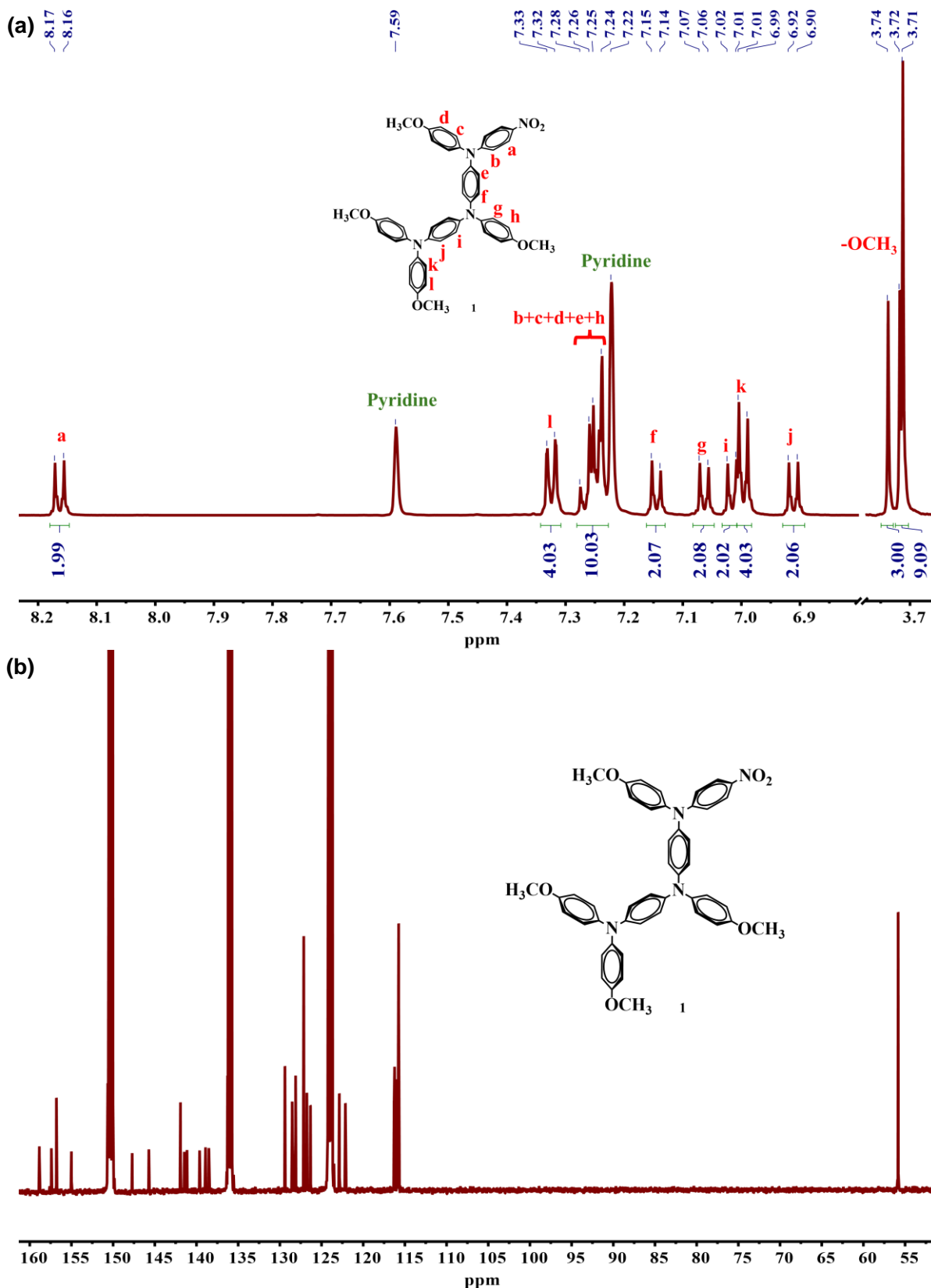


Fig. S3 (a) ^1H and (b) ^{13}C NMR spectra of compound **1**. (d-solvent: Pyridine- d_5)

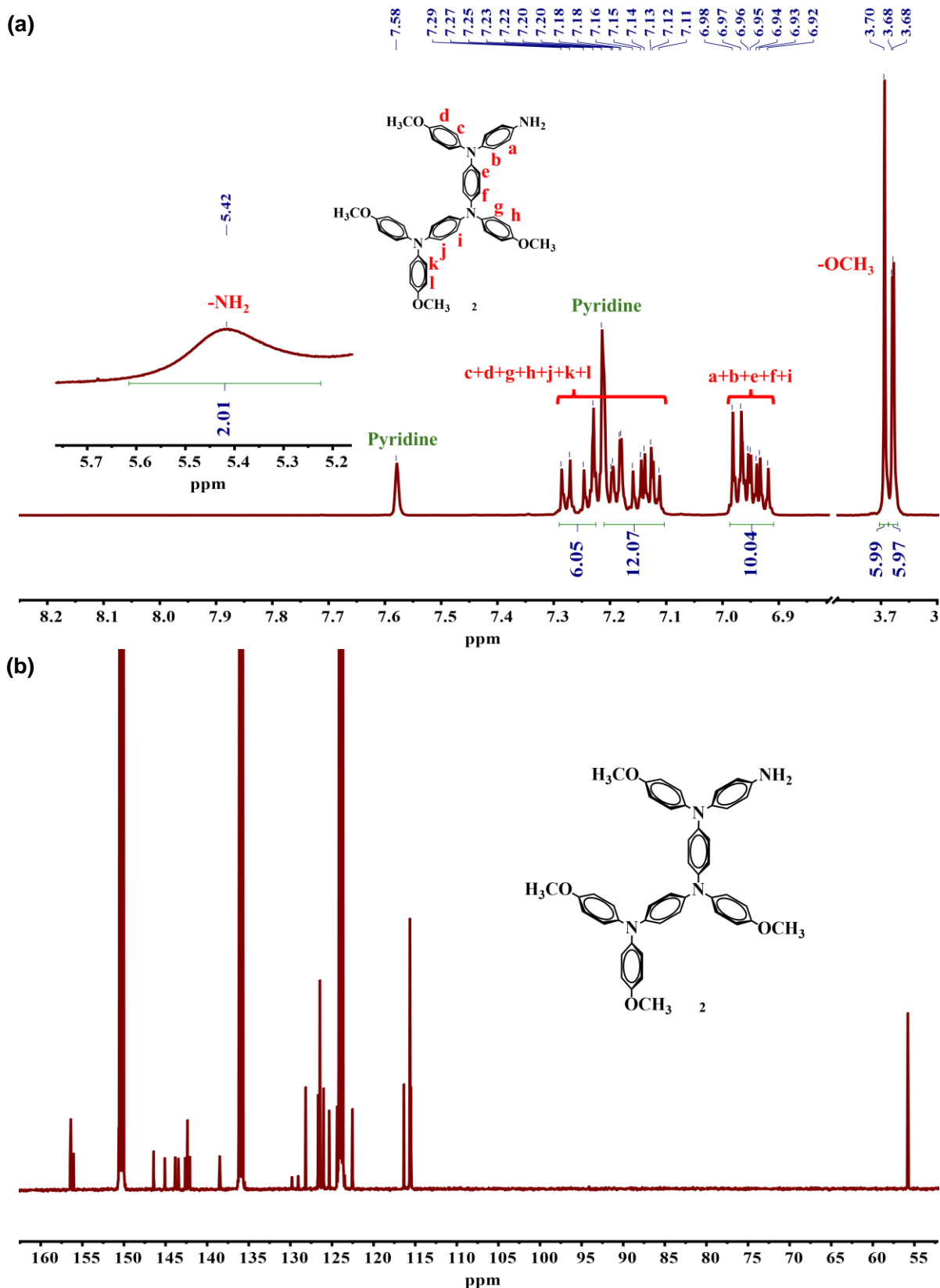


Fig. S4 (a) ^1H and (b) ^{13}C NMR spectra of compound **2**. (d-solvent: Pyridine- d_5)

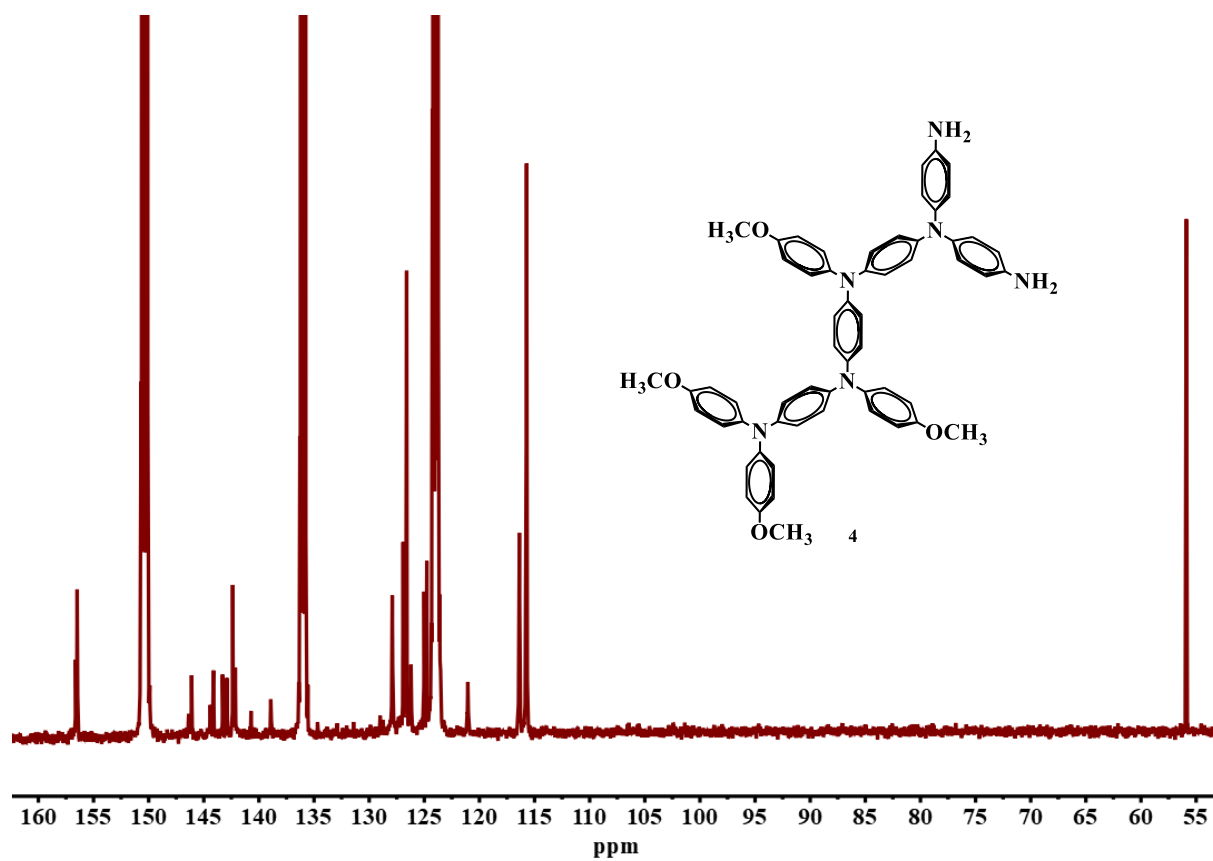


Fig. S5 ^{13}C NMR spectrum of compound 4. (d-solvent: Pyridine- d_5)

data02_20240416183538 #7-10 RT: 0.05-0.07 AV: 2 NL: 8.58E6
T: FTMS + p ESI Full ms [600.0000-1500.0000]

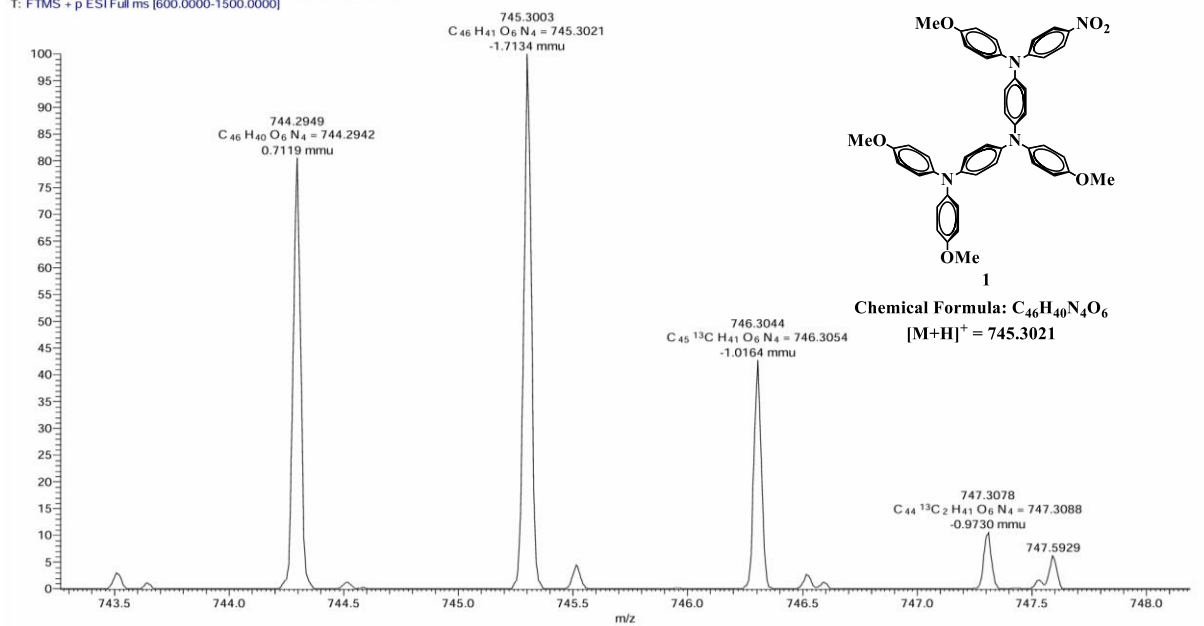


Fig. S6 ESIMS spectrum of compound **1**.

data03 #5-14 RT: 0.04-0.10 AV: 5 NL: 1.58E7
T: FTMS + p ESI Full ms [600.0000-1500.0000]

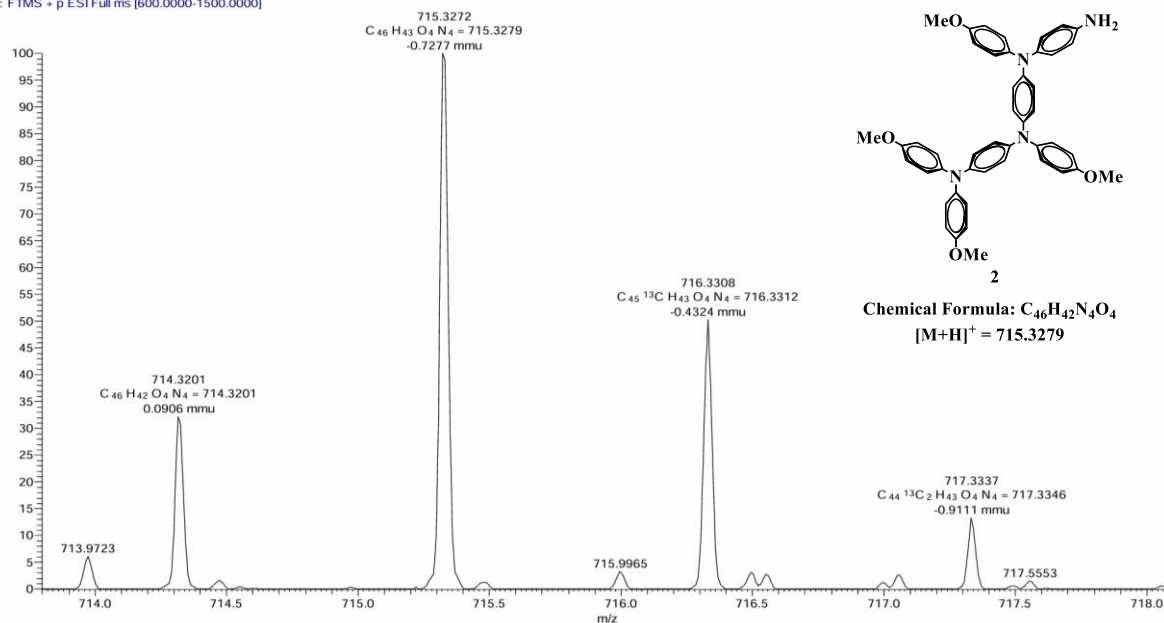


Fig. S7 ESIMS spectrum of compound 2.

data05_20240416185102 #4-13 RT: 0.04-0.10 AV: 5 NL: 8.10E5
T: FTMS + p ESI Full ms [600.0000-1500.0000]

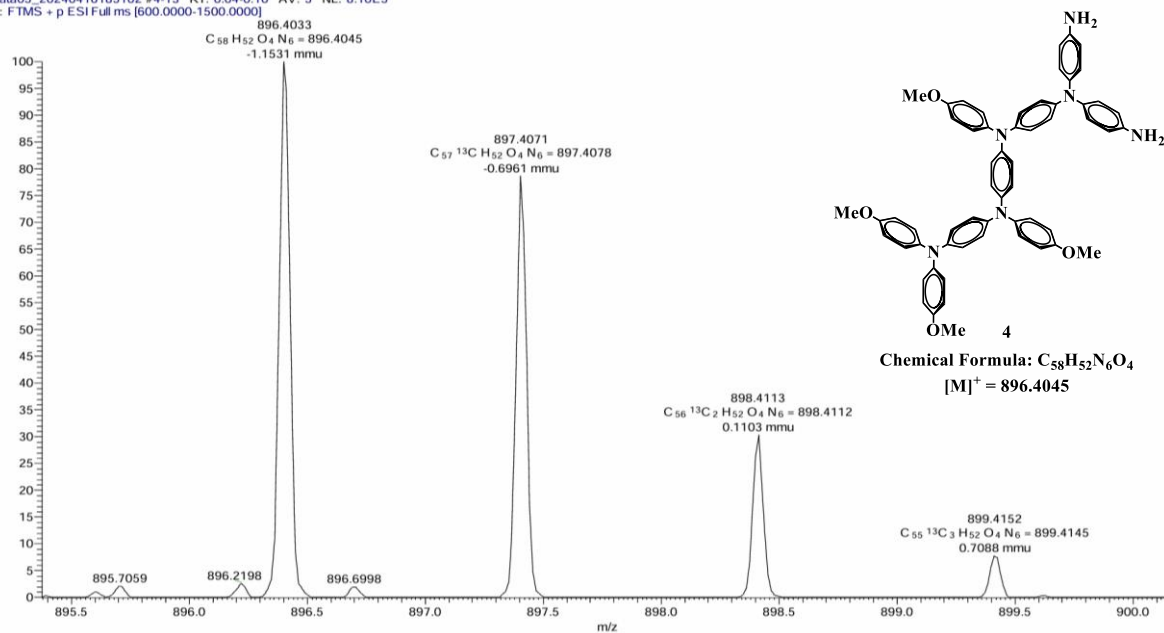


Fig. S8 ESIMS spectrum of compound 4.

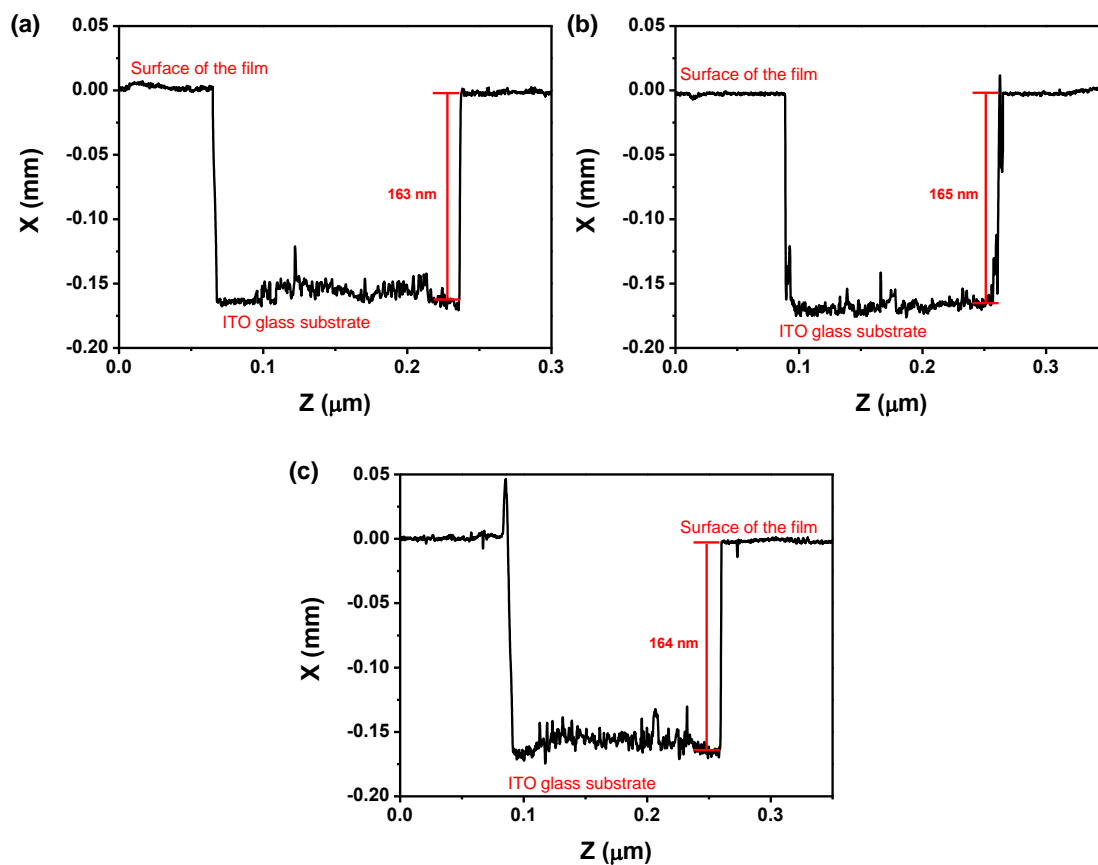


Fig. S9 Thickness and surface morphology of PAs (a) **5a**, (b) **5b**, and (c) **5c**.

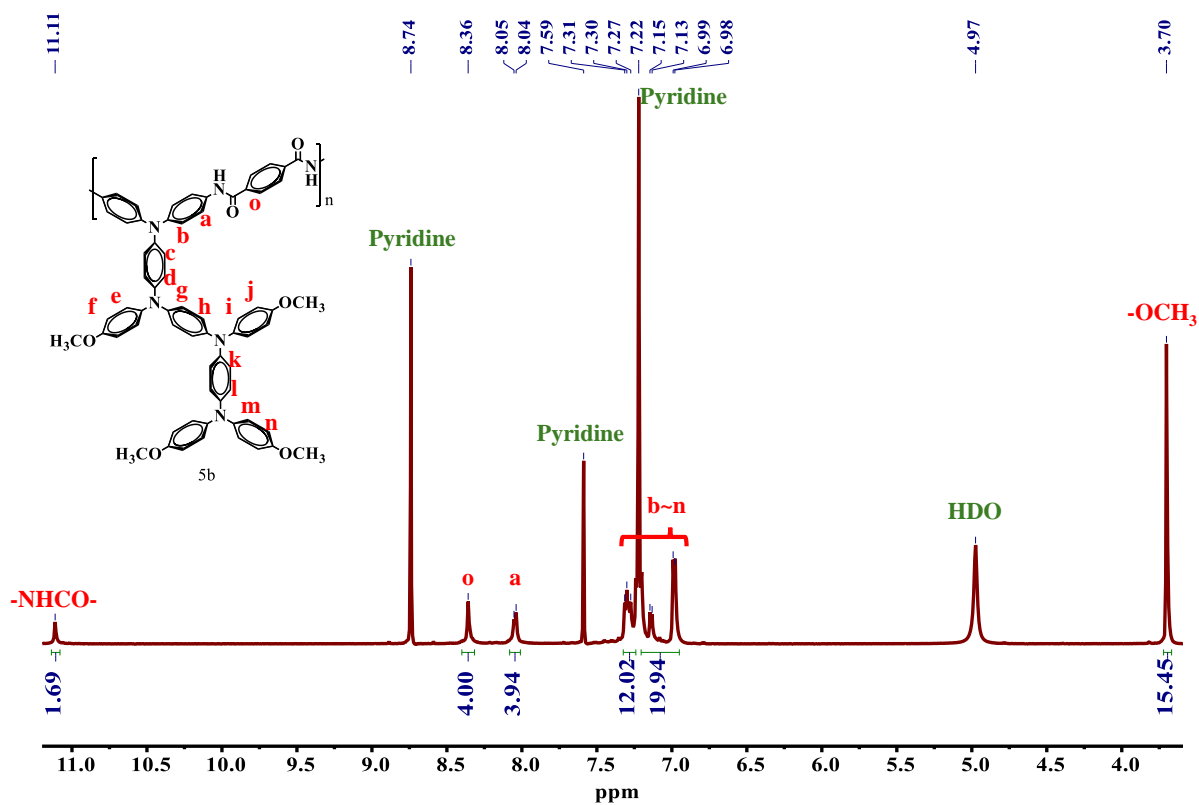


Fig. S10 ^1H NMR spectra of PA **5b**. (d-solvent: Pyridine- d_5)

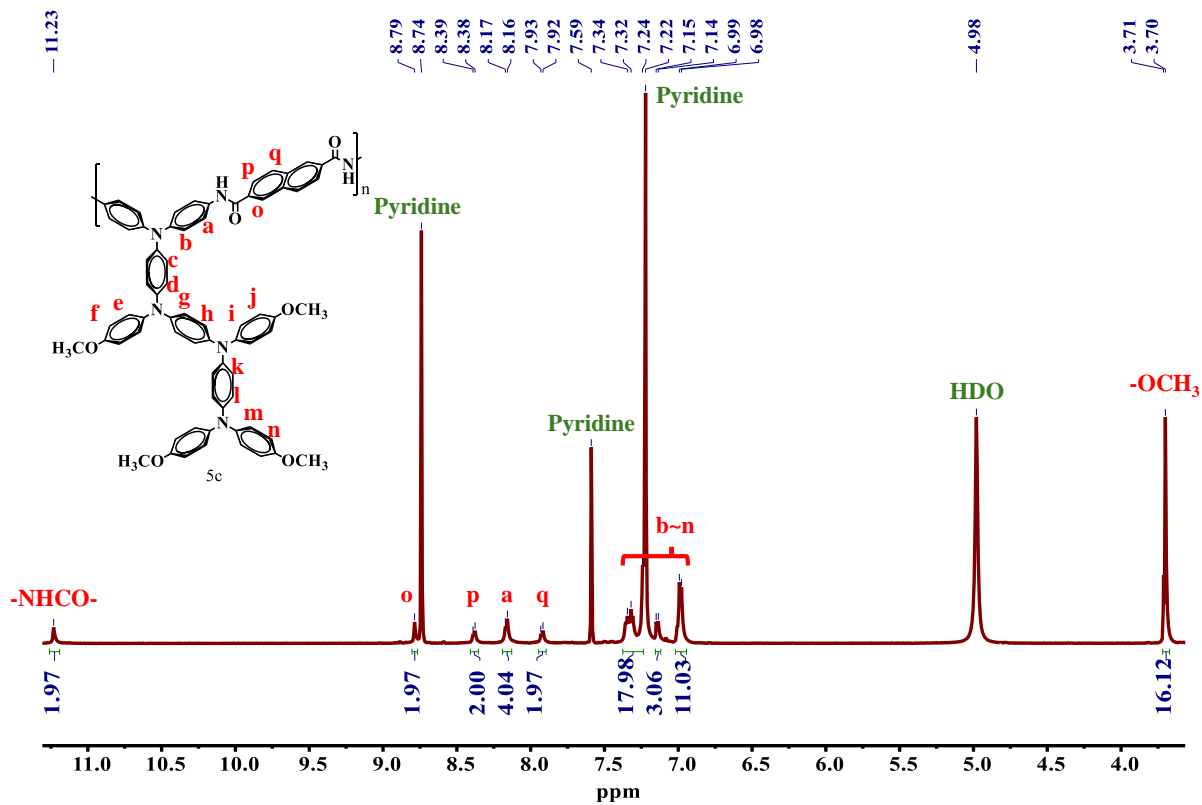


Fig. S11 ^1H NMR spectra of PA 5c. (d-solvent: Pyridine- d_5)

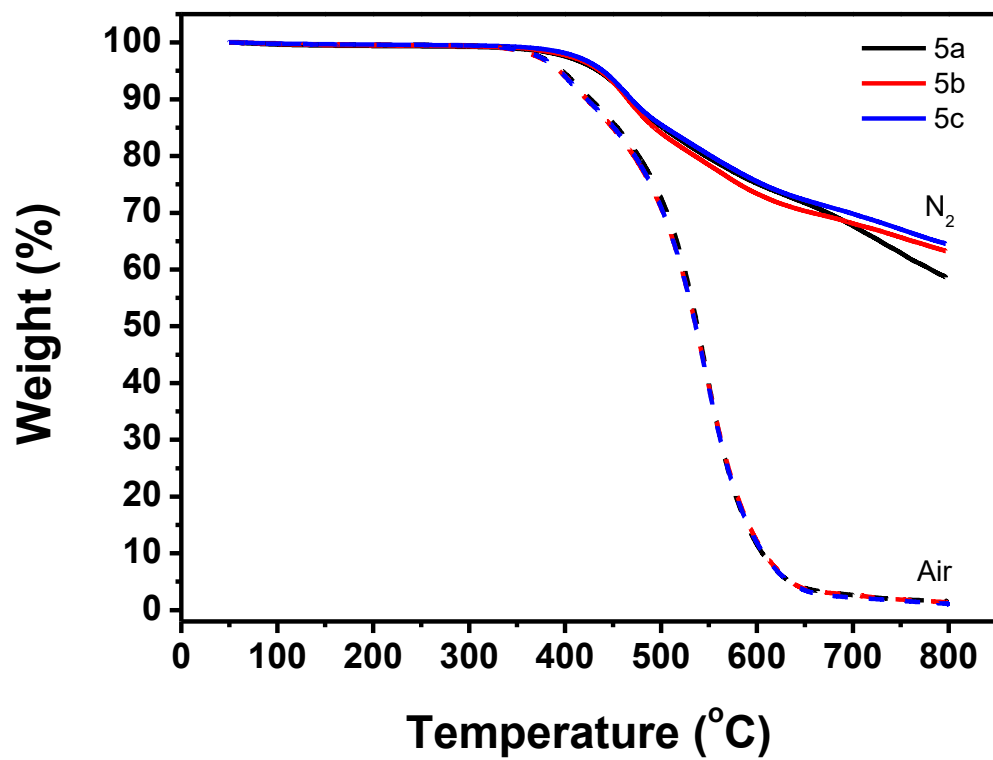


Fig. S12 TGA thermograms of PAs 5 at a heating rate of 20 °C min⁻¹ from 50 to 800 °C.

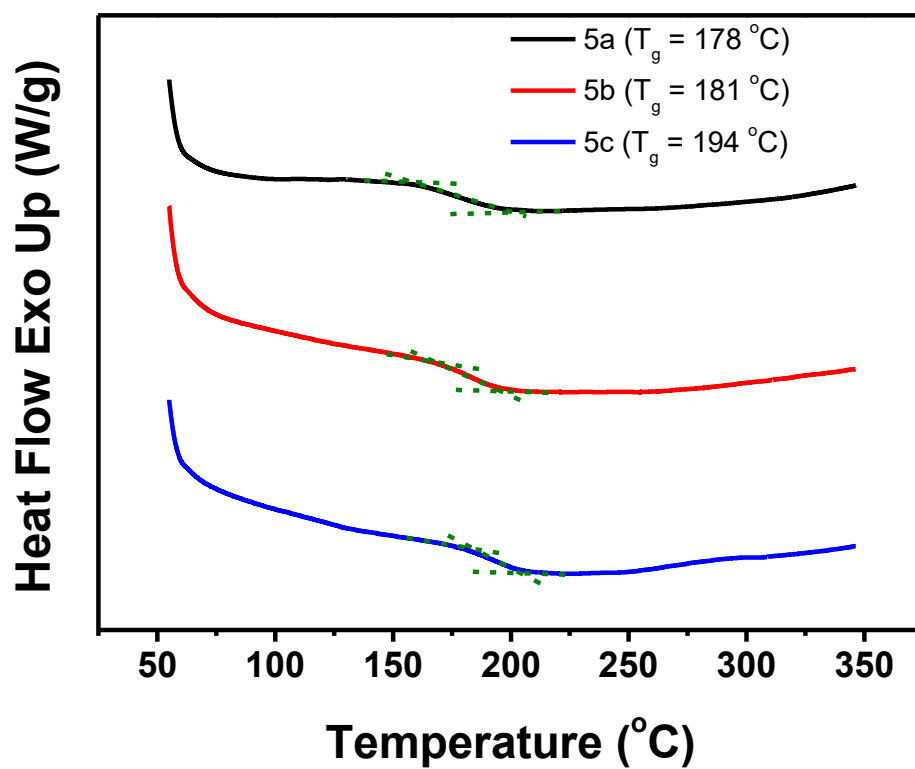


Fig. S13 DSC traces of PAs **5** at a heating rate of 20 °C min^{-1} from 50 to 350 °C.

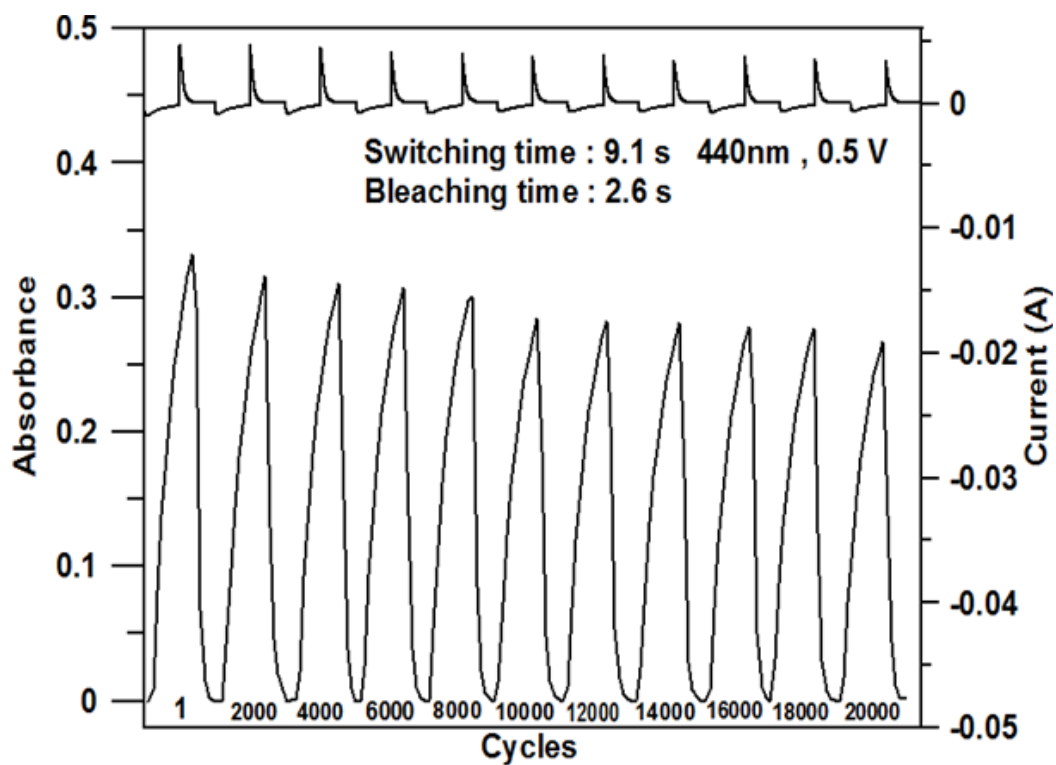


Fig. S14 Potential step absorptometry and current consumption of PA **5a** (in MeCN with 0.1 M TBAP as the supporting electrolyte) by applying a potential step 0.0 V \leftrightarrow 0.5 V, and cycle time 20 sec.

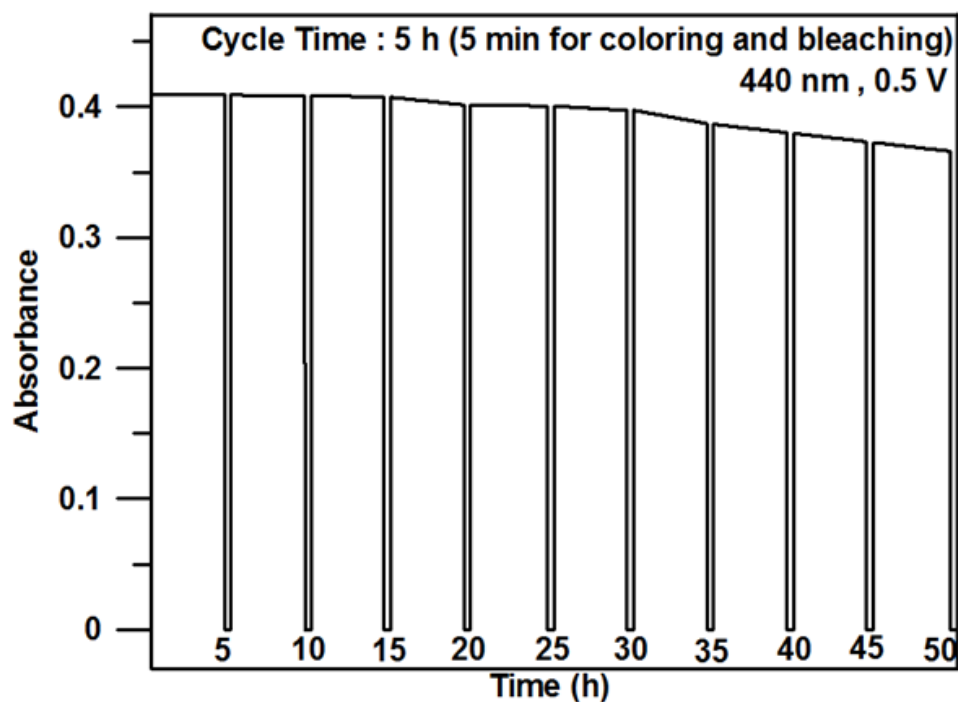


Fig. S15 Potential step absorptiometry during the continuous cycling test of PA **5a** (in MeCN with 0.1 M TBAP as the supporting electrolyte) by switching potentials step 0.00 V \leftrightarrow 0.50 V, with a cycle time of 5 h and 5 min for coloring and bleaching processes, respectively.

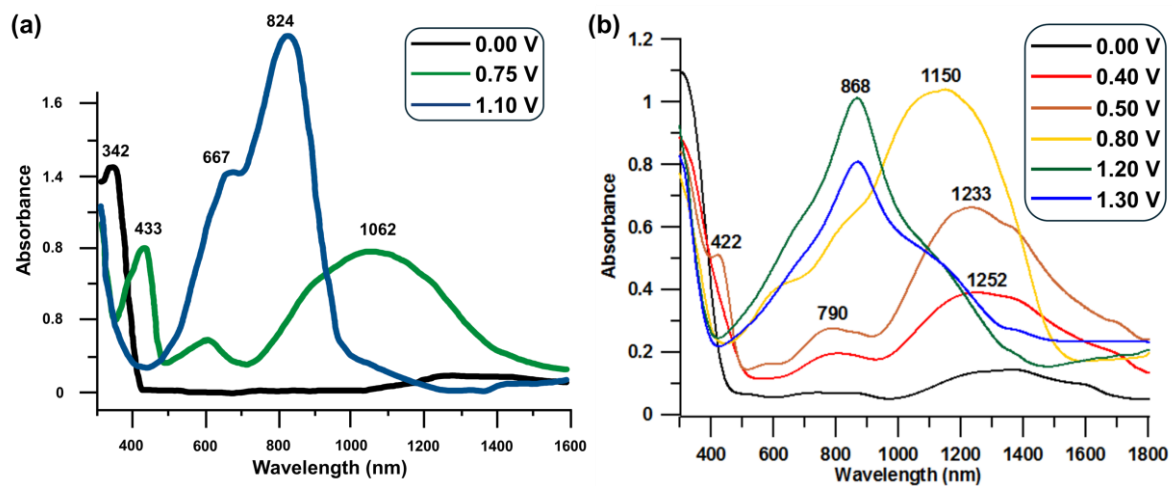


Fig. S16 Absorbance spectra of (a) P1 and (b) P2 thin-film electrode in 0.1 M TBAP/MeCN at different applied potentials.