Supplementary Information

Electrochemical fabrication of electroactive polymer films from diamide- or diimide-cored *N*-phenylcarbazole dendrons for electrochromic applications

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Synthesis and characterization of *N*-phenylcarbazole dendrons

6CzSO$_2$-DA

In a 50 mL round-bottom flask equipped with a stirring bar, a mixture of 2.65 g (4.5 mmol) of NH$_2$-3Cz, 0.67 g (2.2 mmol) of bis(4-carboxyphenyl) sulfone, 0.60 mL of triphenyl phosphite (TPP), 0.20 mL of pyridine, and 1.5 mL of NMP was heated with stirring at 120 °C for 3 h. The solution was poured slowly with stirring into 150 mL of methanol to precipitate white product. The precipitated product was collected by filtration, washed repeatedly with methanol and hot water, and dried to give 3.02 g (95 % yield) of the desired monomer 6CzSO$_2$-DA as pale yellow powder. IR (KBr): 1679 cm^{-1} (amide C=O stretching), 3370 cm^{-1} (amide N−H stretching). ^{1}H NMR (600 MHz, CDCl$_3$, δ, ppm): 7.23 (m, 8H, H$_b$), 7.33 (16H, H$_c$ + H$_d$), 7.55 (8H, H$_h$ + H$_i$), 7.66 (d, *J* = 8.4 Hz, 4H, H$_e$), 7.95 (d, *J* = 8.4 Hz, 2H, H$_f$) 7.99 (8H, H$_j$ + H$_k$), 8.11 (d, *J* = 7.8 Hz, 8H, H$_a$), 8.24 (s, 4H, H$_g$), 8.51 (s, 2H, amide N−H).

6Cz6F-DA was prepared from condensation of 2,2-bis(4-carboxyphenyl)-hexafluoropropane with NH$_2$-3Cz in a similar procedure.
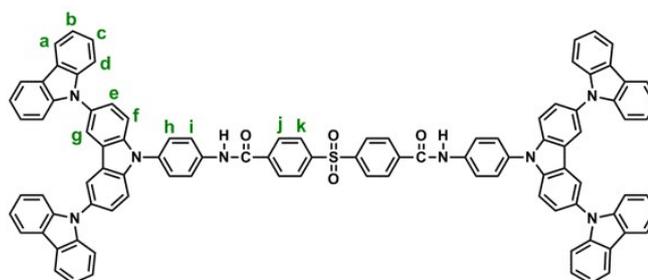
6Cz6F-DI

A mixture of 2.65 g (4.5 mmol) of NH$_2$-3Cz and 0.98 g (2.2 mmol) 6FDA was dissolved

in 15 mL of anhydrous DMAc in a 50 mL round-bottom flask. The reaction mixture was stirred at room temperature for 1 h, and then into which 4 mL of acetic anhydride and 2 mL of pyridine were added. After further 1 h stirring at room temperature, the solution was poured into 150 mL of methanol. The precipitate pale yellow product was collected by filtration and dried to give 3.10 g (89 % yield) of the desired monomer 6Cz6F-DI as pale yellow powder. IR (KBr): 1784 and 1725 cm^{-1} (imide ring C=O stretching). ^{1}H NMR (600 MHz, CDCl$_3$, δ, ppm): 7.26 (m, 8H, H$_b$), 7.38 (d, 16H, H$_c$ + H$_d$), 7.62 (dd, J = 8.4, 1.8 Hz, 4H, H$_e$), 7.72 (d, J = 8.4 Hz, 4H, H$_f$), 7.79 (d, J = 8.4 Hz, 4H, H$_h$), 7.88 (d, J = 8.4 Hz, 4H, H$_i$), 7.97 (d, J = 7.8 Hz, 2H. H$_l$), 8.05 (s, 2H, H$_j$), 8.13 (d, 2H, H$_k$), 8.14 (d, J = 7.8 Hz, 8H, H$_a$), 8.28 (d, J = 1.8 Hz, 4H, H$_g$).

6CzSO$_2$-DI was prepared from condensation of 3,3′,4,4′-diphenylsulfone-tetracarboxylic dianhydride with NH$_2$-3Cz in a similar procedure.
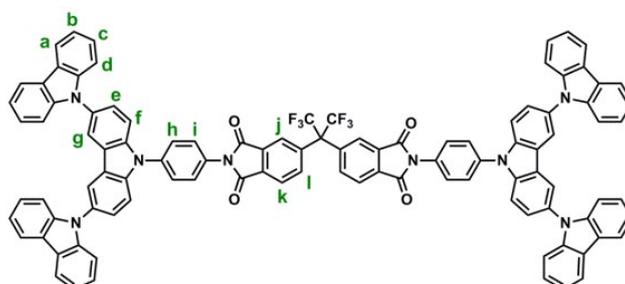
6CzSO$_2$-DA-tBu (M1)

A mixture of 0.81 g (1 mmol) of NH$_2$-3Cz-tBu, 0.15 g (0.48 mmol) bis(4-carboxyphenyl) sulfone, 0.3 mL of triphenyl phosphite (TPP), 0.1 mL of pyridine, and 0.1 mL of NMP was heated with stirring at 120 ^{o}C for 3 h. The solution was poured slowly with stirring into 150 mL of methanol to precipitate white product. The precipitated product was collected by filtration, washed thoroughly with methanol and hot water, and dried to give 0.79 g (87% yield) of 6CzSO$_2$-DA-tBu as white powder. IR (KBr): 1674 cm^{-1} (amide C=O stretching), 3370 cm^{-1} (amide N–H stretching), 2963–2861 cm^{-1} (t-butyl C–H stretching). ^{1}H NMR (600 MHz, CDCl$_3$, δ, ppm): 1.44 (s, 72H, t-butyl), 7.32 (d, J = 8.4 Hz, 8H, H$_d$), 7.43 (d, J = 8.4 Hz, 8H, H$_c$), 7.59 (8H, H$_h$ + H$_i$), 7.72 (d, J = 8.4 Hz, 4H, H$_e$), 8.00 (m, 4H, H$_f$), 8.02 (m, 8H, H$_j$ + H$_k$), 8.16 (s, 8H, H$_a$), 8.25 (s, 4H, H$_g$), 8.63 (s, 2H, amide N–H).
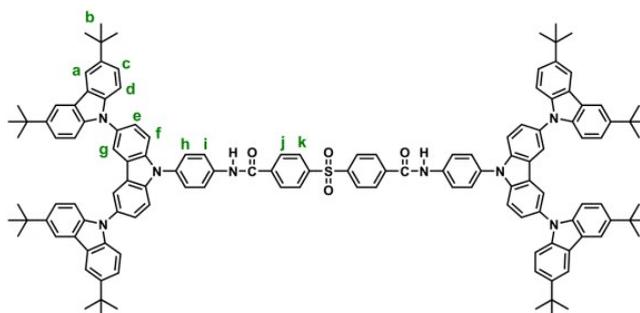
6Cz6F-DI-tBu (M2)

A mixture of 0.81 g (1 mmol) NH_2-3Cz-*t*Bu and 0.21 g (0.48 mmol) 6FDA was dissolved in 0.3 mL of anhydrous DMAc in a 50 mL round-bottom flask. The mixture was stirred until completely dissolved, and then added 0.4 mL of acetic anhydride and 0.2 mL of pyridine. After stirring at room temperature for 1 h, the solution was poured slowly with stirring into 150 mL of methanol, and then the precipitate pale yellow product was collected by filtration and dried to give 0.90 g (90 %) of 6Cz6F-DI-*t*Bu as pale yellow powder. IR (KBr): 1784 and 1725 cm^{-1} (imide ring C=O stretching), 2961–2863 cm^{-1} (*t*-butyl C-H stretch). ^{1}H NMR (600 MHz, CDCl$_3$, δ, ppm): 1.46 (s, 72H, *t*-butyl), 7.35 (d, *J* = 8.4 Hz, 8H, H$_d$), 7.45 (dd, *J* = 8.4 Hz, 1.8 Hz, 8H, H$_c$), 7.64 (dd, *J* = 8.4 Hz, 1.8 Hz, 4H, H$_e$), 7.73 (d, *J* = 8.4 Hz, 4H, H$_f$), 7.82 (d, *J* = 8.4 Hz, 4H, H$_i$), 7.92 (d, *J* = 8.4 Hz, 4H, H$_h$), 7.98 (d, *J* = 7.8 Hz, 2H, H$_l$), 8.06 (s, 2H, H$_j$), 8.15 (d, 2H, H$_k$), 8.16 (d, *J* = 1.8 Hz, 8H, H$_a$), 8.26 (d, *J* = 1.8 Hz, 4H, H$_g$).
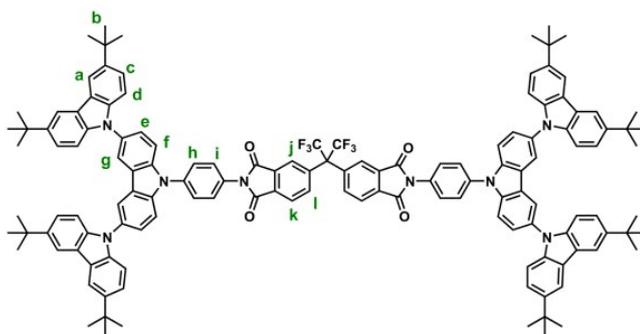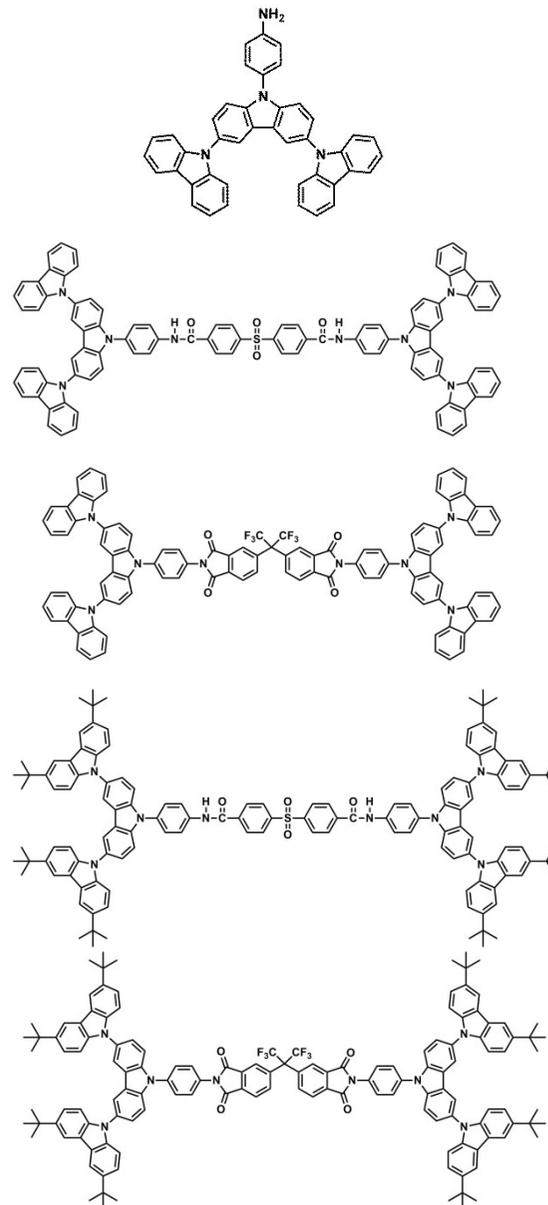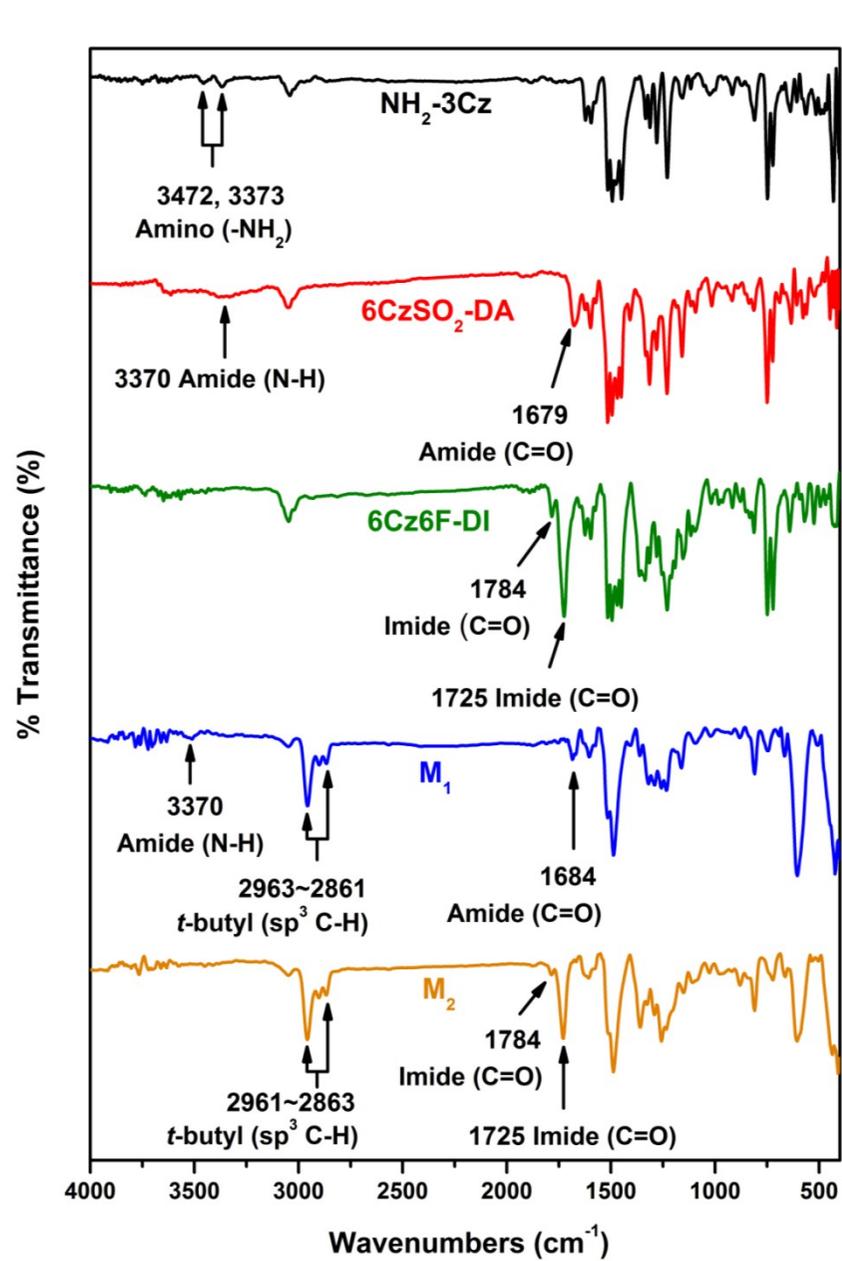
Fig. S1. IR spectra of some of the synthesized compounds.

(a) 8.508 8.240 8.119 8.106 7.987 7.964 7.950 7.674 7.660 7.566 7.551 7.533 7.343 7.337 7.245 7.238 7.231 7.227 7.218

c, d

a j, k h, i b

g

f e

—O=C—H—N—

8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 ppm

1.000 2.237 5.179 3.868 2.276 2.230 4.568 9.935 6.256

(b)

c, d

g a j, k h, i b

—O=C—H—N— f e

ppm

b — 7.2

c, d — 7.4

h, i — 7.6
e

7.8

j, k f — 8.0
a
g — 8.2

8.4

—O=C—H—N— — 8.5

8.6

8.8

8.8 8.6 8.4 8.2 8.0 7.8 7.6 7.4 7.2 ppm
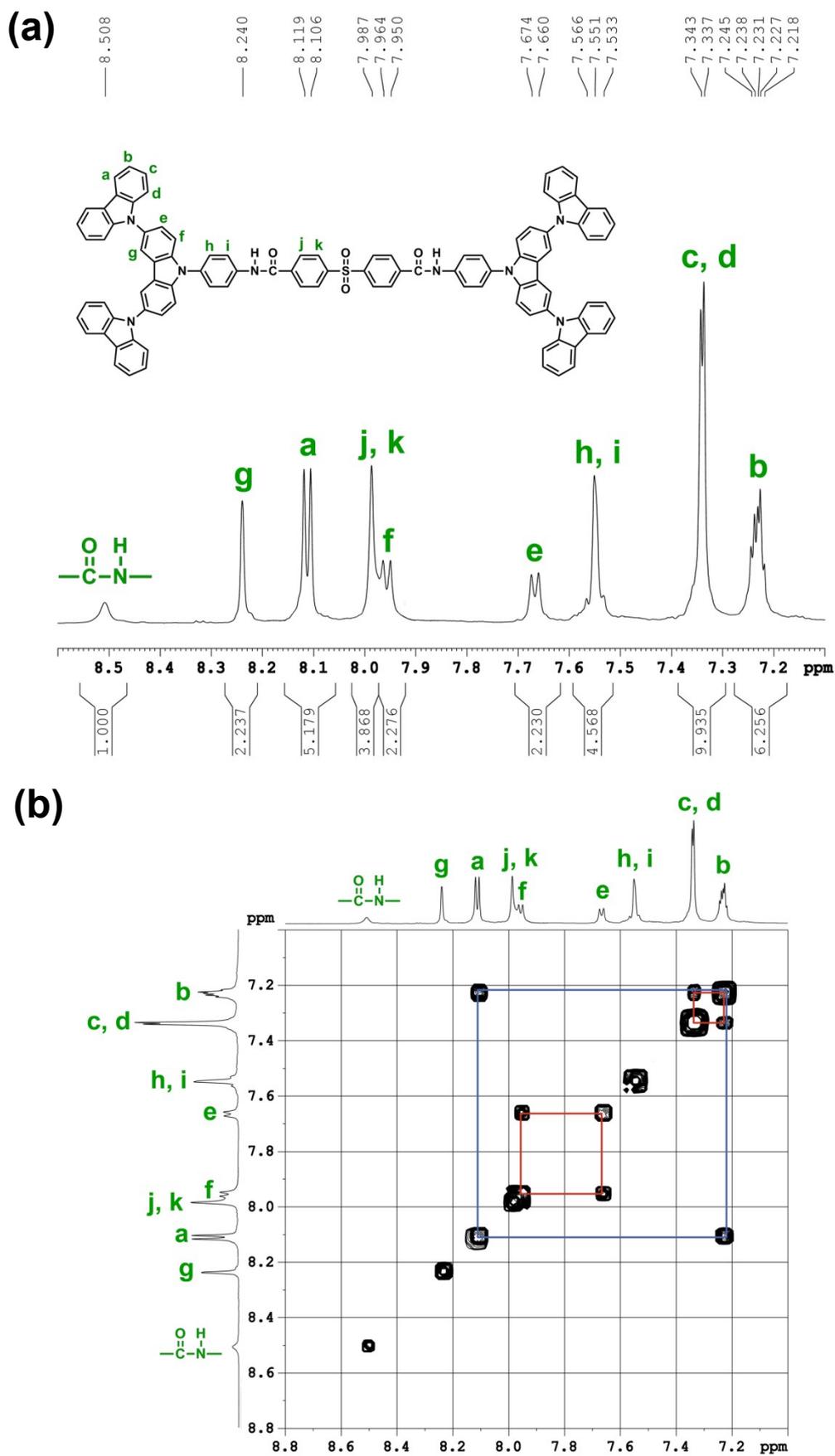
Fig. S2. (a) ^{1}H NMR and (b) H-H COSY spectra of 6CzSO$_2$-DA in CDCl$_3$.
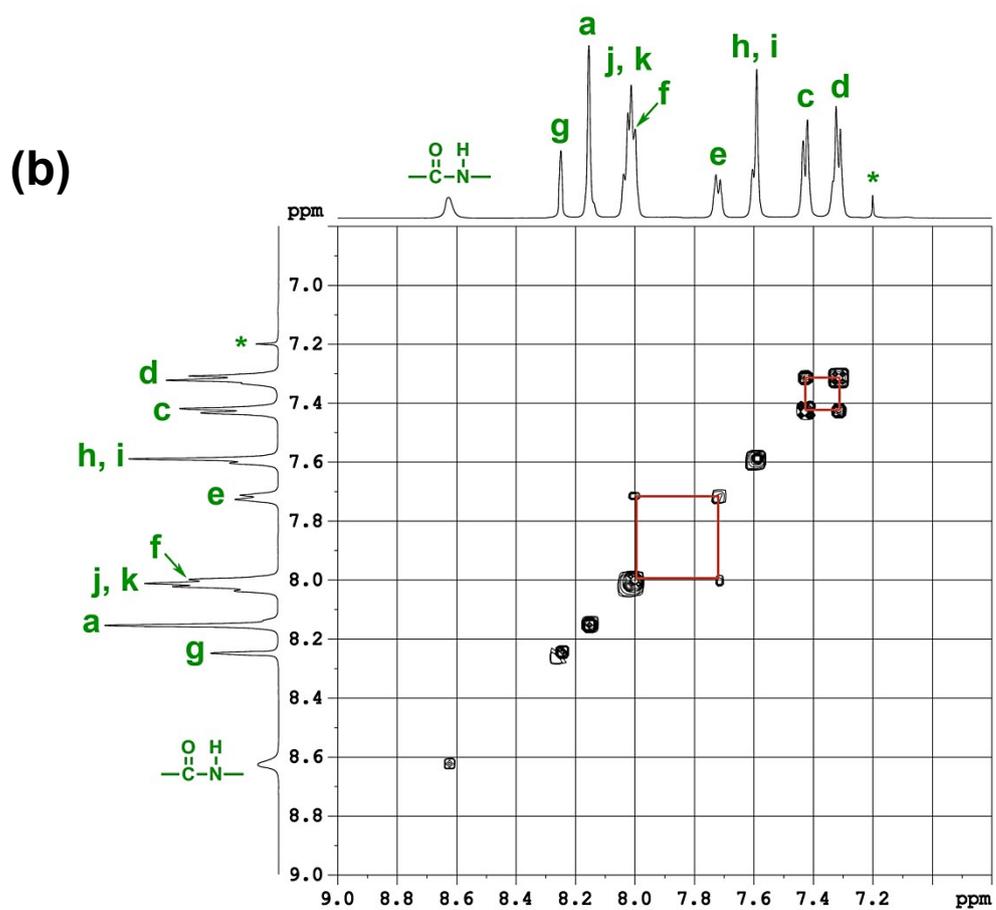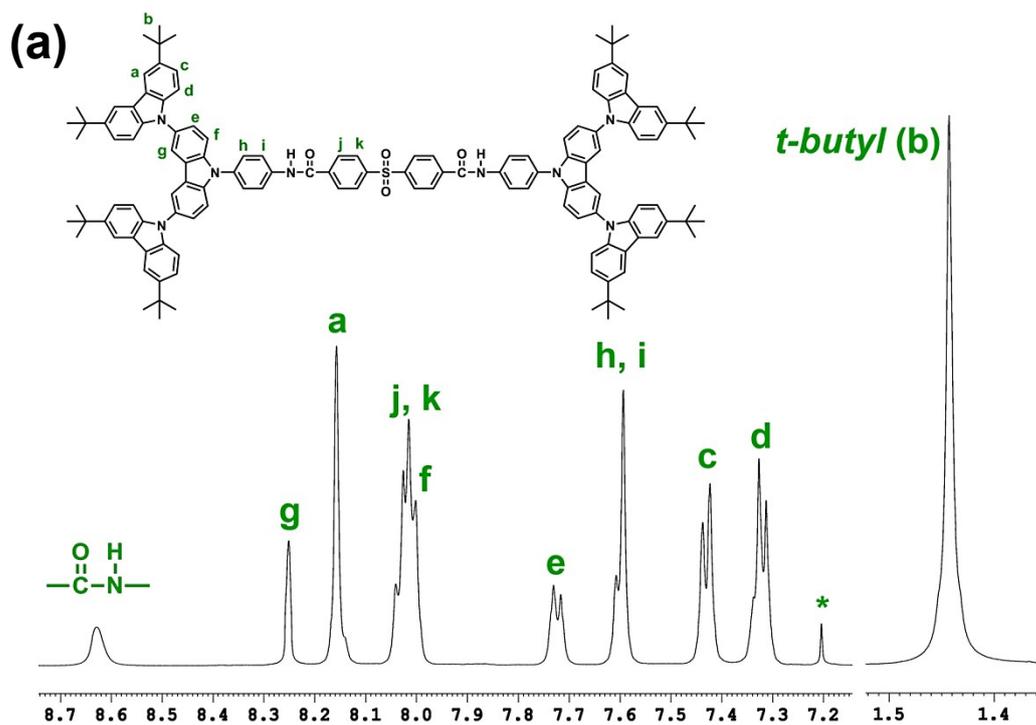
Fig. S3. (a) ^{1}H NMR and (b) H-H COSY spectra of **M₁** in CDCl₃.
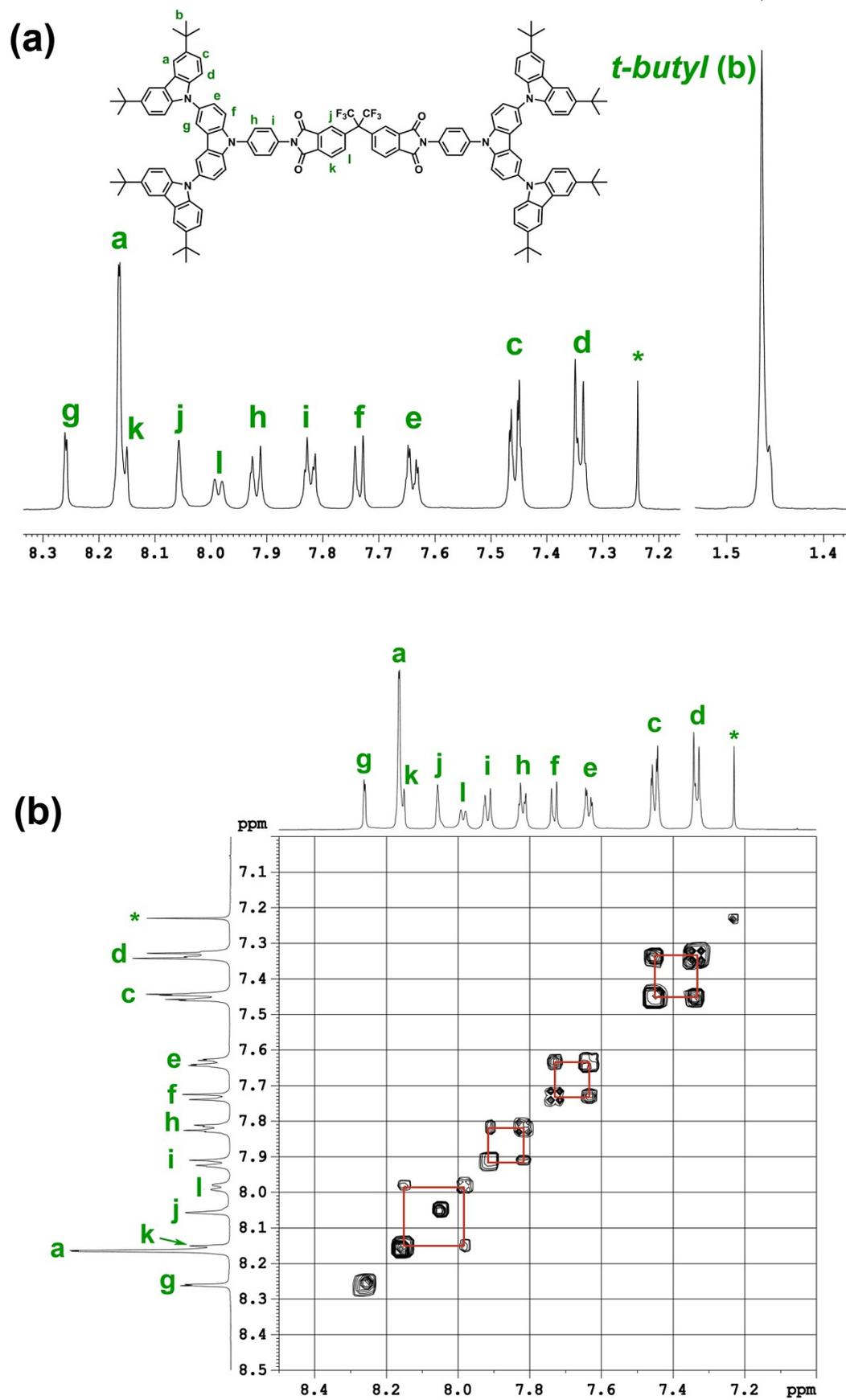
Fig. S4. (a) ^{1}H NMR and (b) H-H COSY spectra of **M$_2$** in CDCl$_3$.
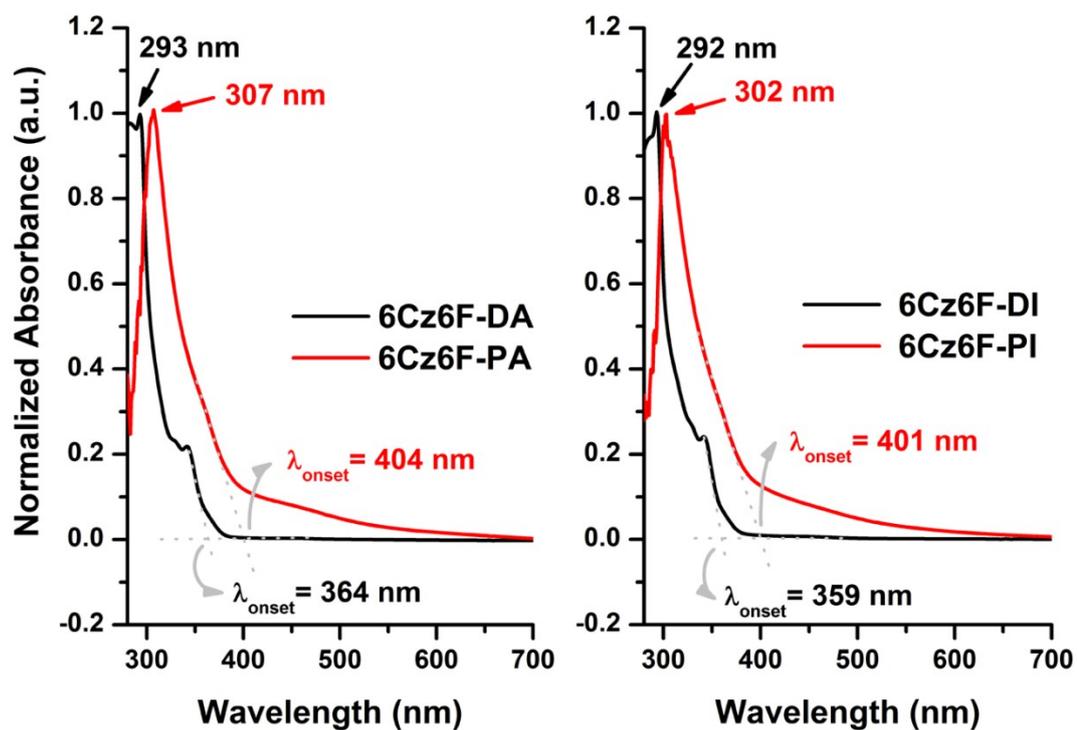
Fig. S5. UV-vis absorption spectra of 6Cz6F-DA and 6Cz6F-DI in CH_2Cl_2 and the deposited polymer films of 6Cz6F-PA and 6Cz6F-PI on ITO-glass.
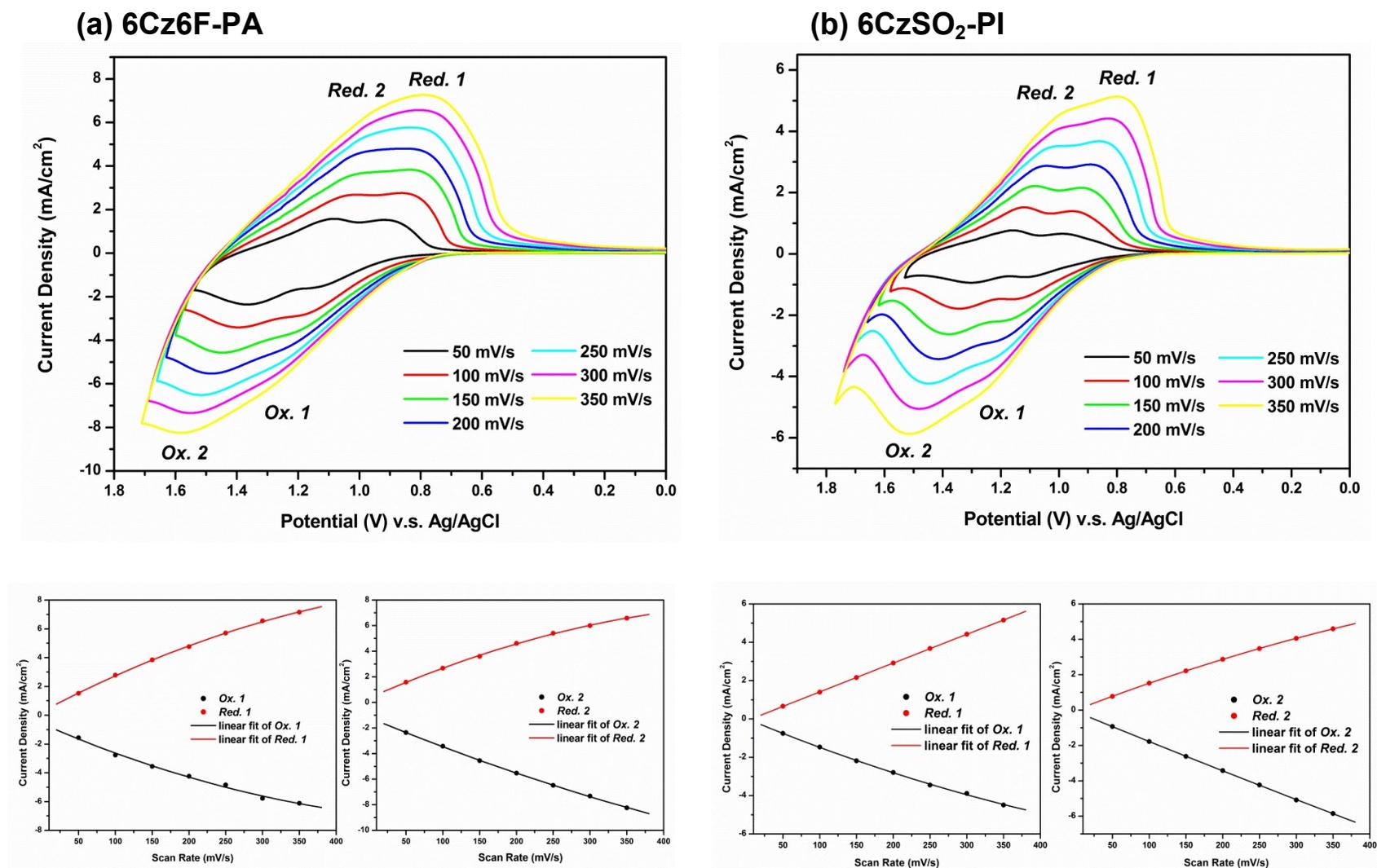
Fig. S6. Scan rate dependence of 6Cz6F-PA and 6CzSO$_2$-PI films on ITO-coated glass slide in 0.1 M Bu$_4$NClO$_4$/MeCN at different scan rates between 50 and 350 mV s^{-1}.
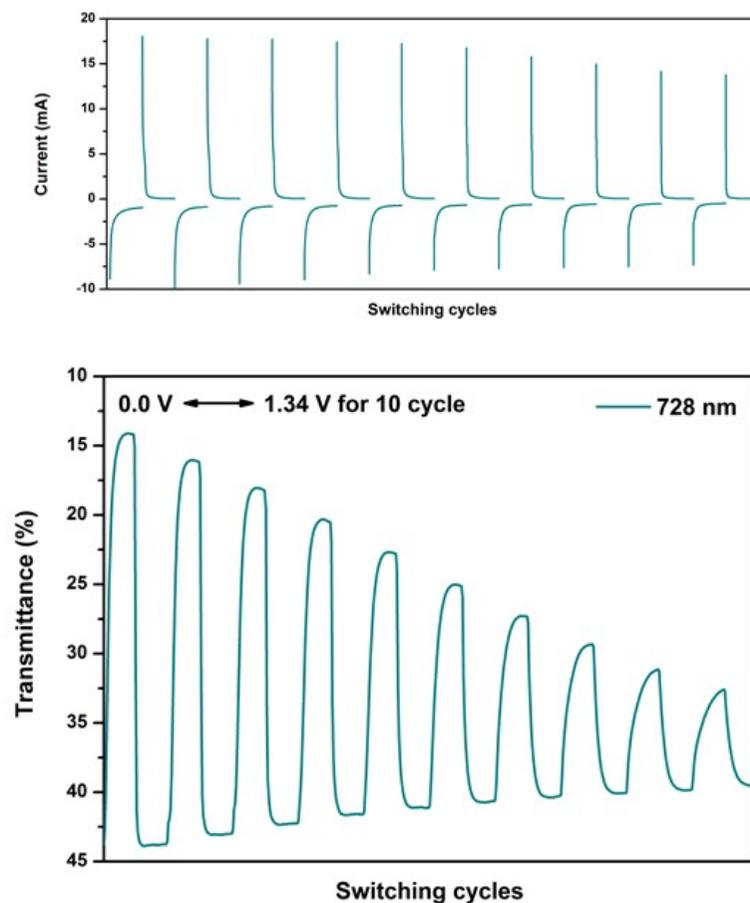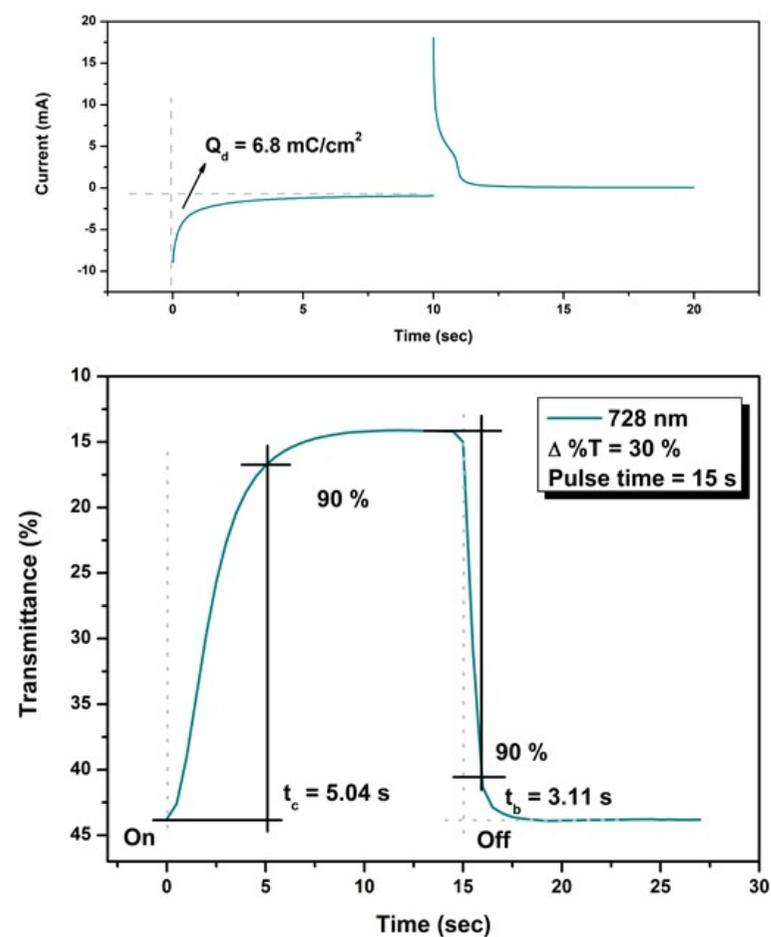
Fig. S7. Potential step absorptiometry of the cast films of $6CzSO_2$-PA on the ITO-glass slide (coated area ~ 1 cm²) (in MeCN with 0.1 M Bu_4NClO_4 as the supporting electrolyte) by applying a potential step: (a) optical switching at potential 0.00 V ⇔ 1.34 V (10 cycles) with a pulse width of 15 s, monitored at λ_{max} = 728 nm; (b) the 1st cycle transmittance change for the $6CzSO_2$-PA thin film.
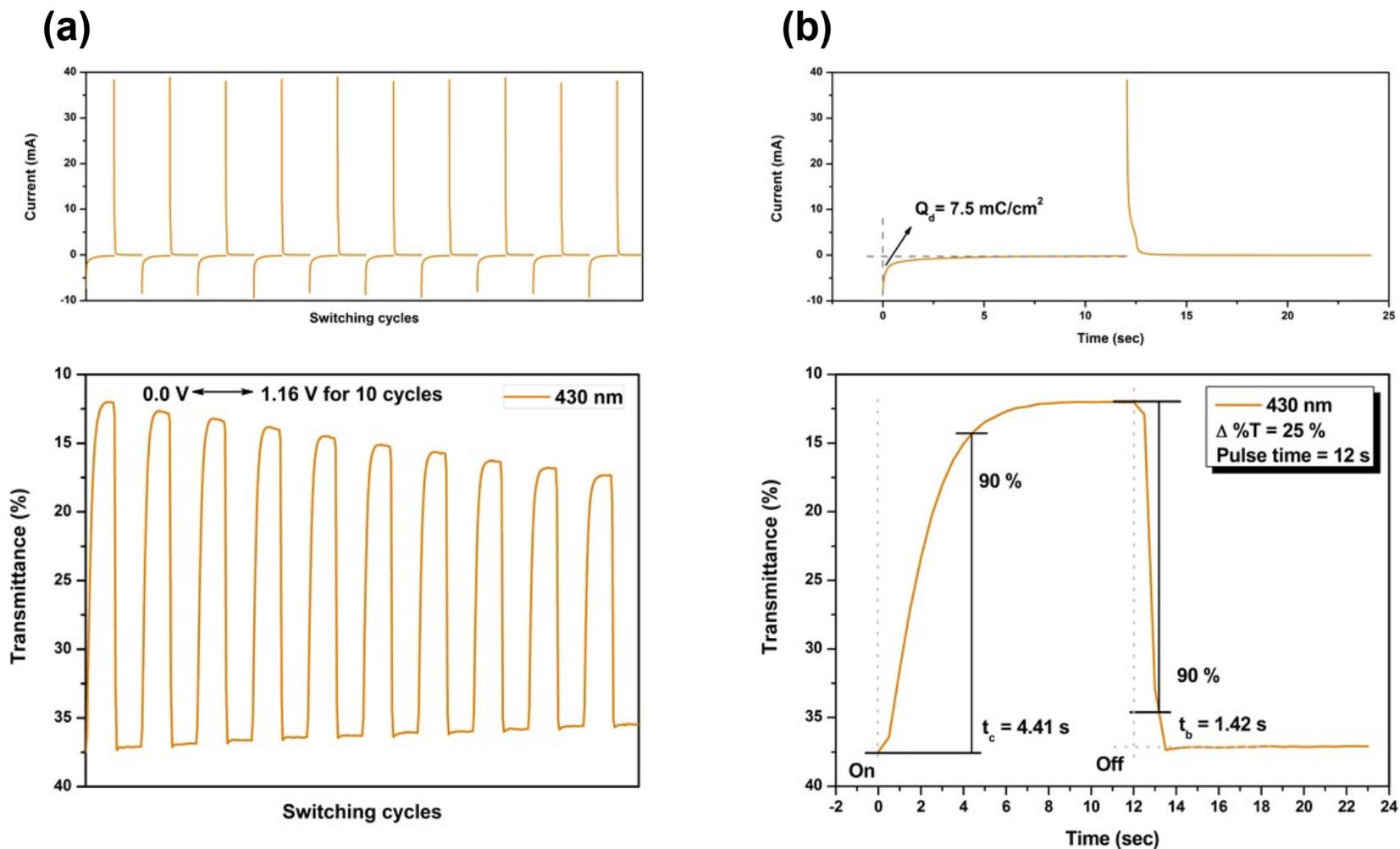
Fig. S8. Potential step absorptiometry of the cast films of 6CzSO$_2$-PI on the ITO-glass slide (coated area ~ 1 cm^2) (in MeCN with 0.1 M Bu$_4$NClO$_4$ as the supporting electrolyte) by applying a potential step: (a) optical switching at potential 0.00 V ⇔ 1.16 V (10 cycles) and a pulse width of 12 s, monitored at λ$_{max}$ = 430 nm; (b) the 1st cycle transmittance change for the 6CzSO$_2$-PI thin film.
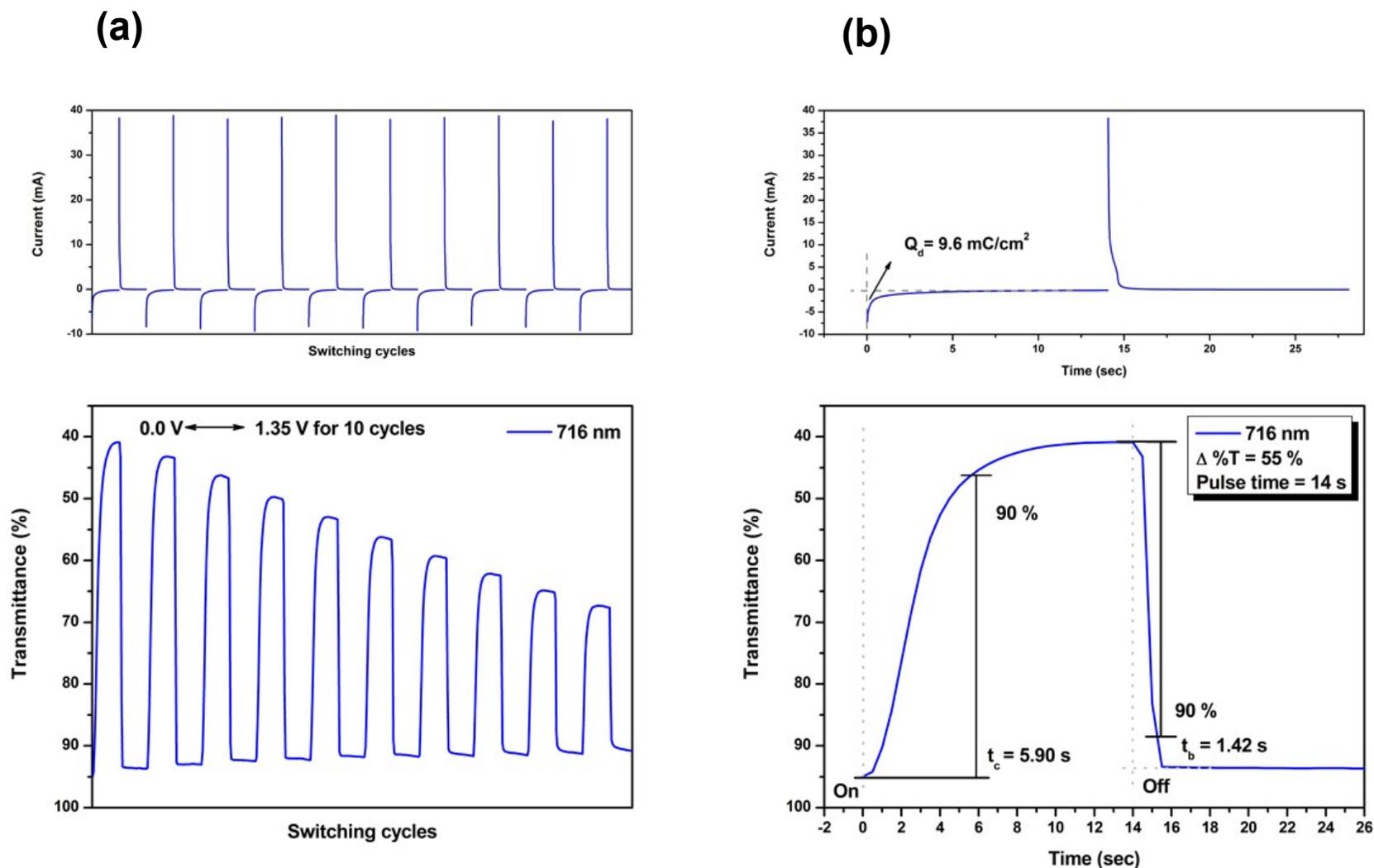
Fig. S9. Potential step absorptiometry of the cast films of 6CzSO$_2$-PI on the ITO-glass slide (coated area ~ 1 cm^2) (in MeCN with 0.1 M Bu$_4$NClO$_4$ as the supporting electrolyte) by applying a potential step: (a) optical switching at potential 0.00 V ⇔ 1.35 V (10 cycles) with a pulse width of 14 s, monitored at λ_{max} = 716 nm; (b) the 1st cycle transmittance change for the 6CzSO$_2$-PI thin film.

Table S1. Electrochromic properties of the polymer films

Polymer	$\lambda_{max}{}^{a}$ (nm)	$\Delta\%T$	Response time[b]		ΔOD^{c}	$Q_{d}{}^{d}$ (mC/cm^2)	CE[e] (cm^2/C)
			t_{c} (s)	t_{b} (s)			
6CzSO$_2$-PA	433	31	3.87	0.97	0.355	9.3	38
	728	30	5.04	3.11	0.323	6.8	48
6CzSO$_2$-PI	430	25	4.41	1.42	0.321	7.5	43
	716	55	5.90	1.42	0.430	9.6	45

[a] Wavelength of absorption maximum.

[b] Time for 90% of the full-transmittance change.

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

[d] Q_{d} is ejected charge, determined from the in situ experiments.

[e] Coloration efficiency (CE) = $\Delta OD/Q_{d}$.