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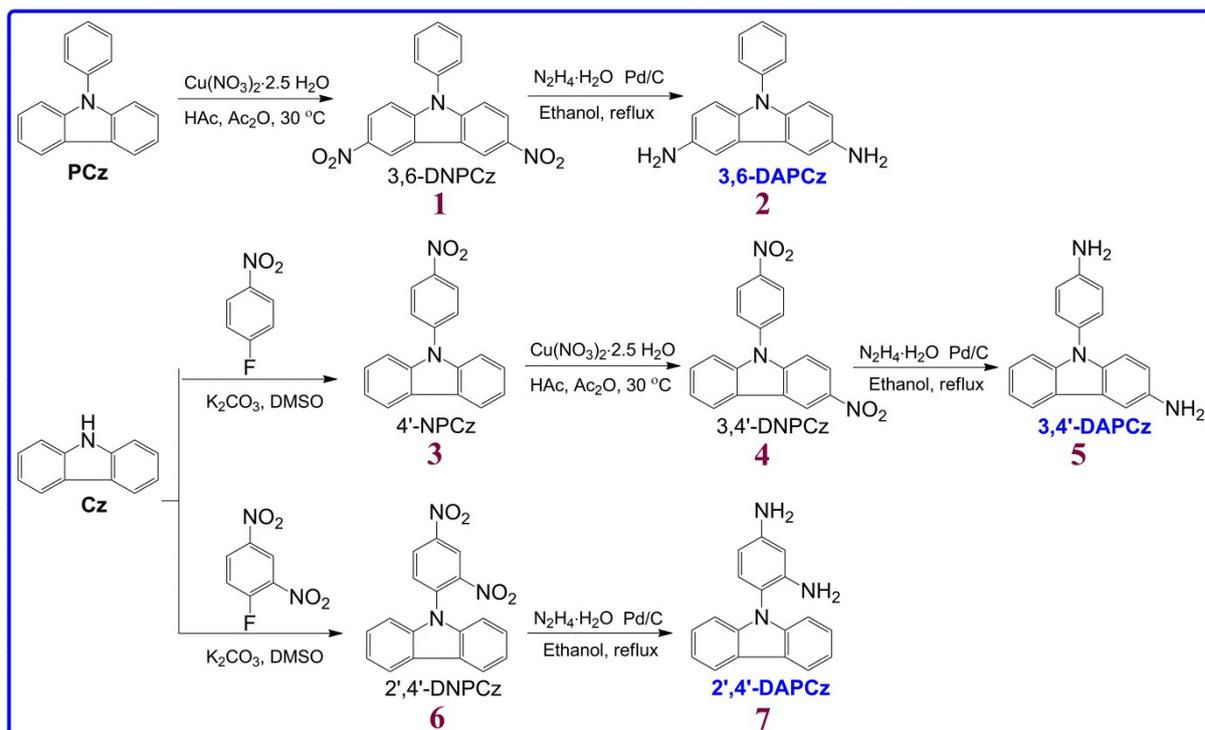
**Asymmetric Isomerization: An Efficient Strategy to Tune the Electrical Resistive  
Memory Behaviors of Functional Polyimides Containing N-phenylcarbazole  
Moieties**

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## Synthesis of the isomeric diamine monomers:



**Scheme S1.** Synthesis of the diamines: 3,6-DAPCz, 3,4'-DAPCz and 2',4'-DAPCz

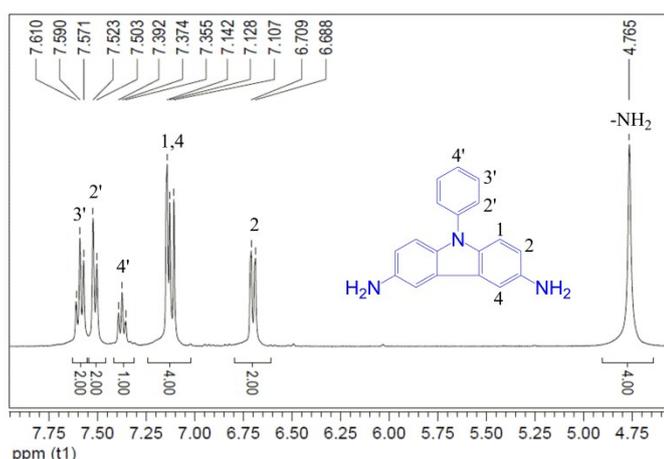
**Scheme S1** shows the synthetic routes for the three phenylcarbazole-containing diamine monomers with isomeric structures, i.e., the N-phenyl-3,6-diaminocarbazole (3,6-DAPCz, **2**), the N-(4'-aminophenyl)-3-aminocarbazole (3,4'-DAPCz, **5**), and the N-(2',4'-diaminophenyl)-carbazole (2',4'-DAPCz, **7**). Details on their preparation and characterization are given below.

### Synthesis of N-phenyl-3,6-diaminocarbazole (3,6-DAPCz, **2**)

N-phenyl-3,6-dinitrocarbazole (3,6-DNPCz, **1**).<sup>1</sup> In a mixture of 5 ml of acetic acid and 10 ml of acetic anhydride, 3 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  (12.9 mmol) was dissolved at room temperature and 1 g (4.17 mmol) of N-phenylcarbazole (PCz) was added to the solution portion-wise. The reaction temperature was controlled at 30 °C by using a water bath. The mixture was stirred at this temperature for 60 min and then poured into 150 ml of distilled water. The precipitate was collected

by filtration, and washed with water. The product was purified by recrystallization from 1,2-dichlorobenzene to afford pure di-nitro compound 1.1 g with a yield of 80 %. FT-IR (KBr): 1518, 1336  $\text{cm}^{-1}$  ( $-\text{NO}_2$ ).  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ , 400MHz),  $\delta$ (ppm): 9.33(d, 1H,  $J=2.3$  Hz), 8.56(m, 3H), 8.36(dd,  $J=9.1$  Hz,  $J=2.3$  Hz), 8.03(d, 2H,  $J=9.0$  Hz), 7.47-7.66(m, 4H).

N-phenyl-3,6-diaminocarbazole (3,6-DAPCz, **2**).<sup>1</sup> In a 100 ml round-bottom flask equipped with magnetic stirring, 1 g of N-phenyl-3,6-dinitrocarbazole and 0.3 g 10 % Pd/C were suspended in 30 ml of ethanol and 20 ml of hydrazine monohydrate was added to the mixture dropwisely. The solution was heated to reflux for 48 h. The solution was filtered hot to remove Pd/C. The solvent was evaporated under reduced pressure to afford a grey white powder 0.58 g with a yield of 71 %. DSC ( $\text{N}_2$ , 5  $^\circ\text{C min}^{-1}$ ): m.p.155  $^\circ\text{C}$ . FT-IR (KBr): 3392, 3291  $\text{cm}^{-1}$  ( $-\text{NH}_2$ ).  $^1\text{H}$  NMR ( $\text{DMSO-d}_6$ , 400MHz),  $\delta$ (ppm): 7.59 (t, 2H,  $J=7.7$  Hz), 7.50(d, 2H,  $J=7.7$  Hz), 7.37 (t, 1H,  $J=7.3$  Hz), 7.11-7.14 (m, 4H), 6.69 (d, 2H,  $J=8.6$  Hz), 4.77 (s, 4H). MS (m/z):  $[\text{M}]^+$  calc. for  $\text{C}_{18}\text{H}_{15}\text{N}_3$ , 274.1. Found, 274.1. Elemental analysis: calc. for  $\text{C}_{18}\text{H}_{15}\text{N}_3$  (%), C, 79.10; H, 5.53; N, 15.37. Found: C, 79.09; H, 5.48; N, 15.43.



**Figure S1.**  $^1\text{H}$ -NMR spectrum of the N-(3,6-diaminophenyl)-carbazole (3,6-DAPCz, **2**) measured in  $\text{DMSO-d}_6$ .

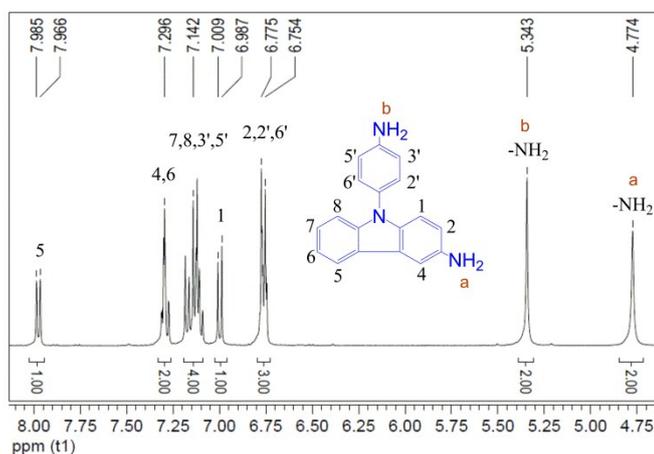
### Synthesis of N-(4'-aminophenyl)-3-aminocarbazole (3,4'-DAPCz, 5)

N-(4'-nitrophenyl)-carbazole (4'-NPCz, 3). In a 250 ml round-bottom flask equipped with magnetic stirring, 8.35 g (0.05 mol) of carbazole (Cz) and 4.136 g (0.03 mol) potassium carbonate were dissolved in 100 ml of dimethyl sulfoxide (DMSO) and 5.3 ml (0.05 mol) of 4-fluoro-nitrobenzene was added to the mixture under nitrogen protection. The solution was heated at 150 °C for 12 h. After cooling, the mixture was poured to 500 ml of methanol under stirring and the precipitate was filtered to obtain the pure product as yellow flaky crystals 12.45 g with a yield of 86.4 %. FT-IR (KBr): 1506, 1324  $\text{cm}^{-1}$  ( $-\text{NO}_2$ ).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400MHz),  $\delta$ (ppm): 8.50(d, 2H, J=9.0 Hz), 8.28(d, 2H, J=7.7 Hz), 7.98(d, 2H, J=9.0 Hz), 7.56(d, 2H, J=8.2 Hz), 7.49(d, 2H, J=7.7 Hz), 7.36(d, 2H, J=7.4 Hz)

N-(4'-nitrophenyl)-3-nitrocarbazole (3,4'-DNPCz, 4).<sup>1</sup> In a mixture of 3 ml of acetic acid and 6ml of acetic anhydride, 1.116 g (4 mmol) of  $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$  was dissolved at room temperature and 1.154 g (4 mmol) of N-(4-nitrophenyl)-carbazole was subsequently added to the solution portion-wise. The reaction temperature was controlled at 30 °C by using a water bath. The mixture was stirred at this temperature for 20 min and then poured into 150 ml of distilled water. The precipitate was collected by filtration, and washed with water. The product was purified by recrystallization from 1,2-dichlorobenzene to afford pure di-nitro compound 1 g with a yield of 75 %. FT-IR (KBr): 1510, 1332  $\text{cm}^{-1}$  ( $-\text{NO}_2$ ).  $^1\text{H}$  NMR (DMSO- $d_6$ , 600 MHz),  $\delta$ (ppm): 9.33(d, 1H, J=2.3 Hz), 8.56(m, 3H), 8.36(dd, J=9.1 Hz, J=2.3 Hz), 8.03(d, 2H, J=9.0 Hz), 7.47-7.66(m, 4H)

N-(4'-aminophenyl)-3-aminocarbazole (3,4'-DAPCz, 5).<sup>1</sup> In a 100 ml round-bottom flask equipped with magnetic stirring, 1 g of N-(4-nitrophenyl)-3-nitrocarbazole and 0.3 g 10 % Pd/C were

suspended in 30 ml of ethanol. Then, 20 ml of hydrazine monohydrate was added to the mixture dropwise. The solution was heated to reflux for 48 h and then was hot filtered to remove Pd/C. The solvent was evaporated under reduced pressure to afford a grey white power 0.574 g with a yield of 70 %. DSC (N<sub>2</sub>, 5 °C min<sup>-1</sup>): m.p.183 °C. FT-IR (KBr): 3346, 3422 cm<sup>-1</sup> (-NH<sub>2</sub>). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400MHz), δ(ppm): 7.97(d, 1H, J=7.7Hz), 7.25-7.33(m, 2H), 7.07-7.20(m, 4H), 6.99(d, 2H, J=8.6Hz), 6.72-6.80(m, 4H), 5.34(s, 2H), 4.78(s, 2H). MS (m/z): [M]<sup>+</sup> calc. for C<sub>18</sub>H<sub>15</sub>N<sub>3</sub>, 274.1. Found, 274.1. Elemental analysis: calc. for C<sub>18</sub>H<sub>15</sub>N<sub>3</sub> (%), C, 79.10; H, 5.53; N, 15.37. Found: C, 79.13; H, 5.58; N, 15.29.



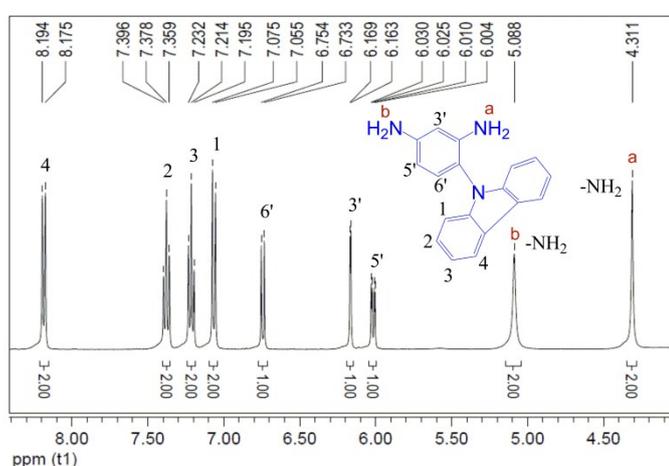
**Figure S2.** <sup>1</sup>H-NMR spectrum of the N-(3,4'-diaminophenyl)-carbazole (3,4'-DAPCz, **5**) measured in DMSO-d<sub>6</sub>.

### Synthesis of N-(2',4'-diaminophenyl)-carbazole (2',4'-DAPCz, **7**)

N-(2',4'-dinitrophenyl)-carbazole (2',4'-DNPCz, **6**).<sup>2</sup> The N-(2,4-dinitrophenyl)-carbazole was synthesized from carbazole and 1-fluoro-2,4-dinitrobenzene according to a previously reported procedure.<sup>2</sup> In a 100 ml round-bottom flask equipped with magnetic stirring, 2.058 g (15mmol) carbazole and 1.1g (8 mmol) potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) were dissolved in 20 ml of dimethyl sulfoxide (DMSO) and 2 ml (16mmol) of 1-fluoro-2,4-dinitrobenzene was added under nitrogen protection. The solution was heated at 120 °C for 24 h. After cooling, the solution was poured into

300 ml of cold water under stirring, and the precipitate was collected by filtration and washed by water and methanol. The crude product was recrystallized from ethanol to afford pure di-nitro compound as orange crystals 2.33 g with the yield of 70 %. FT-IR (KBr): 1540, 1340  $\text{cm}^{-1}$  ( $-\text{NO}_2$ ).  $^1\text{H}$  NMR (DMSO- $d_6$ , 600 MHz),  $\delta$ (ppm): 9.07(d, 1H,  $J=2.6$  Hz), 8.78(dd, 1H,  $J=8.7$  Hz,  $J=2.6$  Hz), 8.25(m, 3H), 7.45(t, 2H,  $J=7.2$  Hz), 7.36(t, 2H,  $J=7.5$  Hz), 7.25(d, 2H,  $J=8.2$ Hz).

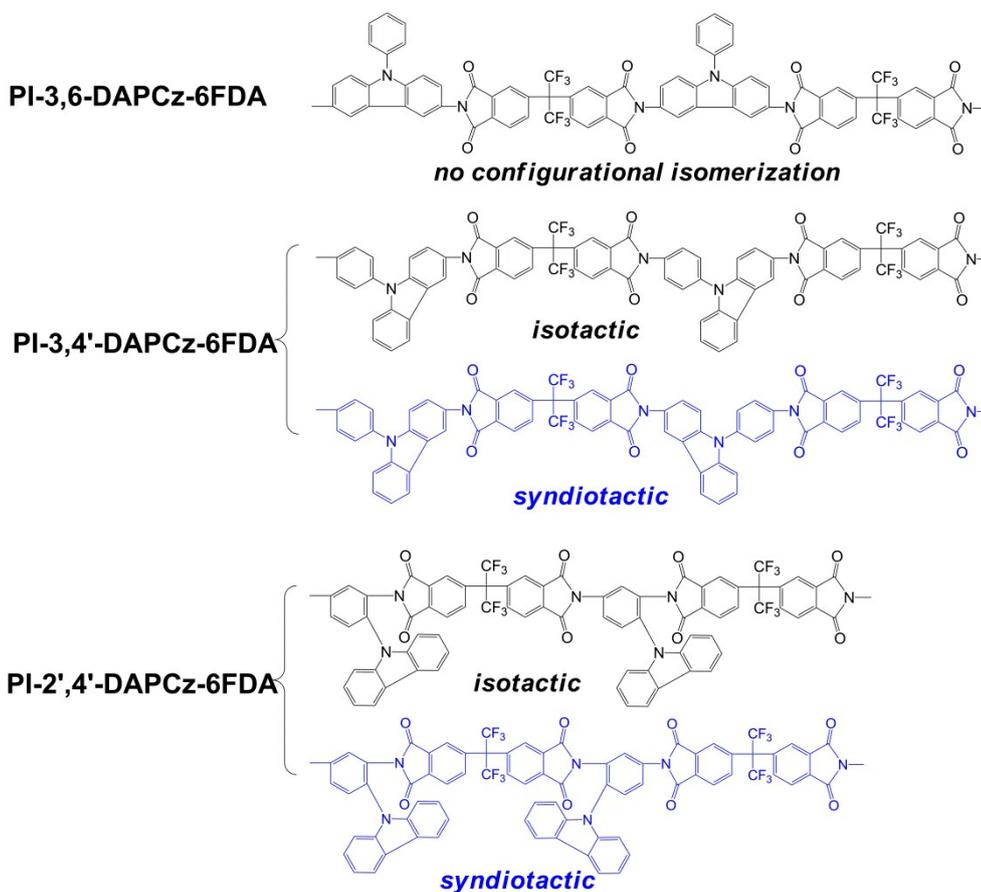
N-(2',4'-diaminophenyl)-carbazole (2',4'-DAPCz, **2**).<sup>2</sup> In a 100 ml round-bottom flask equipped with magnetic stirring, 1 g of N-(2,4-dinitrophenyl)-carbazole and 0.3 g 10 % Pd/C were suspended in 30 ml of ethanol, and 20 ml of hydrazine monohydrate was added dropwise to the mixture. The solution was heated to reflux for 48 h. The solution was filtered hot to remove Pd/C. The solvent was evaporated under reduced pressure to afford a grey white power 0.615 g with a yield of 75 %, DSC ( $\text{N}_2$ , 5  $^\circ\text{C}\cdot\text{min}^{-1}$ ): m.p.136  $^\circ\text{C}$ . FT-IR (KBr): 3363, 3446  $\text{cm}^{-1}$  ( $-\text{NH}_2$ ).  $^1\text{H}$  NMR (DMSO- $d_6$ , 400MHz),  $\delta$ (ppm): 8.18(d, 2H,  $J=7.7$ Hz), 7.38(t, 2H,  $J=7.3$ Hz), 7.21(t, 2H,  $J=7.4$ Hz), 7.06(d, 2H,  $J=8.1$ Hz), 6.73(d, 1H,  $J=8.3$ Hz), 6.16(d, 1H,  $J=2.3$ Hz), 6.00(dd, 1H,  $J=8.3$ Hz,  $J=2.3$ Hz), 5.09(s, 2H), 4.31(s, 2H). MS (m/z):  $[\text{M}]^+$  calc. for  $\text{C}_{18}\text{H}_{15}\text{N}_3$ , 274.1. Found, 274.1. Elemental analysis: calc. for  $\text{C}_{18}\text{H}_{15}\text{N}_3$  (%), C, 79.10; H, 5.53; N, 15.37. Found: C, 79.20; H, 5.63; N, 15.17.



**Figure S3.**  $^1\text{H}$ -NMR spectrum of the N-(2',4'-diaminophenyl)-carbazole (2',4'-DAPCz, **7**) measured

in DMSO-d<sub>6</sub>.

**Isomeric polyimide structures: draw at-, it-, st-**



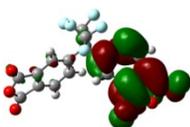
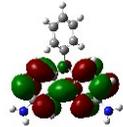
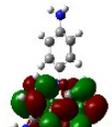
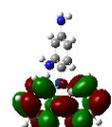
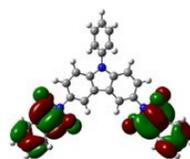
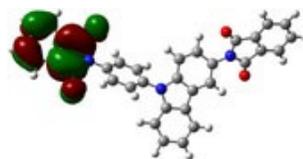
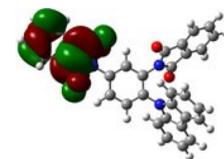
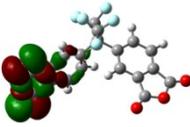
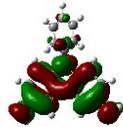
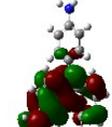
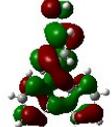
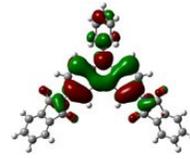
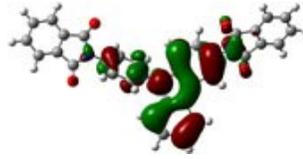
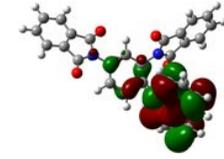
**Scheme S2.** Configurational structures of the PI-3,6-DAPCz-6FDA, PI-3,4'-DAPCz-6FDA and PI-2',4'-DAPCz-6FDA isomeric polyimides and their long-chain conformations obtained from MS modeling. The PI-3,6-DAPCz-6FDA has no configurational isomerization since the 3,6-DAPCz is structurally symmetrical, while both the PI-3,4'-DAPCz-6FDA and the PI-2',4'-DAPCz-6FDA intrinsically possess the isotactic, syndiotactic and atactic (not shown) stereoregular configurations due to the asymmetrical structures of the 3,4'-DAPCz and 2',4'-DAPCz. The atactic configurational structures were not shown in the Scheme.

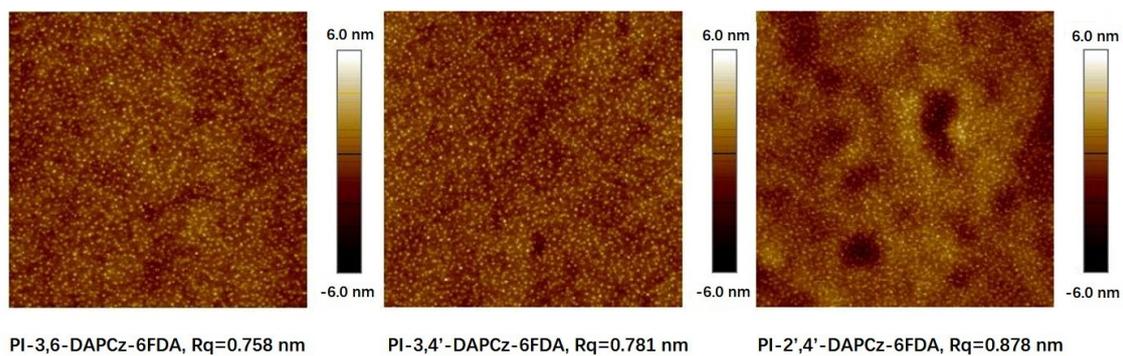
### References:

1. J. P. Chen and A. Natansohn, *Macromolecules* 32, 3171 (1999).

2. S. H. Hsiao, C. W. Chen and G. S. Liou, *J. Polym. Sci., Part A: Polym. Chem.* 42, 3302 (2004).

**Table S1.** The B3LYP/6-31G(d) simulation results for the 6FDA, isomeric diamines, and the model compounds of the isomeric polyimides

Compound	6FDA	3,6-DAPCz	3,4'-DAPCz	2',4'-DAPCz	PI-3,6-DAPCz-6FDA	PI-3,4'-DAPCz-6FDA	PI-2',4'-DAPCz-6FDA
LUMO levels	 -2.98 eV	 -0.41 eV	 -0.41 eV	 -0.33 eV	 -2.15 eV	 -2.42 eV	 -2.44 eV
HOMO levels	 -8.28 eV	 -4.49 eV	 -5.25 eV	 -4.66 eV	 -5.32 eV	 -5.30 eV	 -5.28 eV
Energy gap	5.30 eV	4.08 eV	4.84 eV	4.33 eV	3.17 eV	2.88 eV	2.84 eV



**Figure S4.** The AFM images of synthesized PI-3,6-DAPCz-6FDA, PI-3,4'-DAPCz-6FDA and PI-2',4'-DAPCz-6FDA films spin-coated on the ITO electrode. The scan size was 5 × 5 μm<sup>2</sup>.