

Steric effect of aromatic pendant groups and electrical bistability in π -stacked polymers for memory devices

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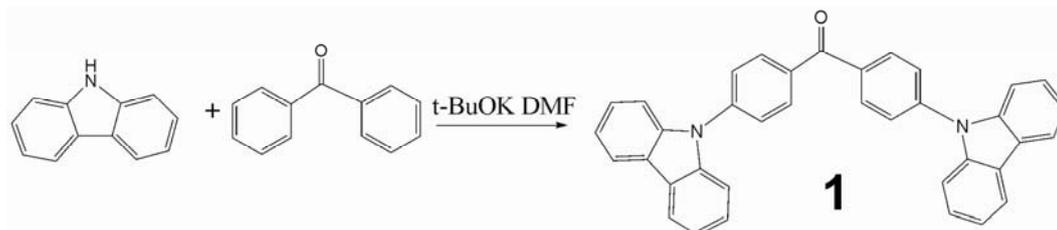
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Electronic Supplementary Information

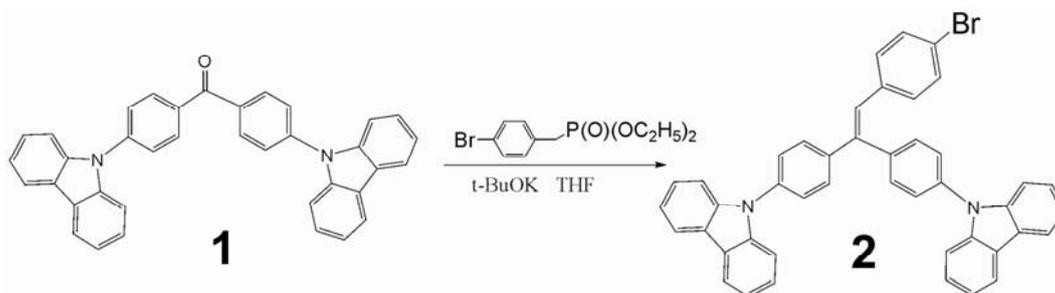
Procedures of synthesis of BC monomer (compounds 1, 2 and 3), PVK, PBC and PVK-PBC



Synthesis of bis(4-(9H-carbazol-9-yl)phenyl)methanone (Ref.[1])(1):

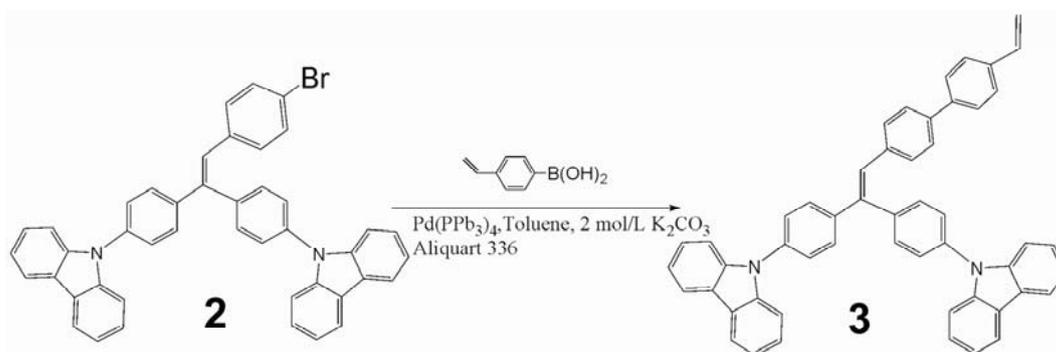
Carbazole (16.7 g, 100 mmol) was dissolved in anhydrous DMF (150 mL) in a flask fitted with a magnetic stirrer and condenser. Potassium tert-butoxide (11.8 g, 105 mmol) was added and the mixture was heated at 70 °C for 10 min and bis(4-fluorophenyl) methanone (10.9 g, 50 mmol) was added with stirring for 12 h. The mixture was cooled down to room temperature, poured into ice water, filtered, and the crude residue was recrystallized from acetone. A white powder was obtained (24.1 g, 94% yield). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 7.36 (t, 4 H), 7.48 (t, 4 H), 7.58 (d, 4 H), 7.82 (d, 4 H), 8.19 (d, 8 H); MS (FAB) m/z: 512 ([M]⁺, calcd for

$C_{37}H_{24}N_2O$, 512.6); Anal. calcd for $C_{37}H_{24}N_2O$: C 86.69, H 4.72, N 5.46; O 3.12,
found: C 86.72, H 4.68, N 5.44.



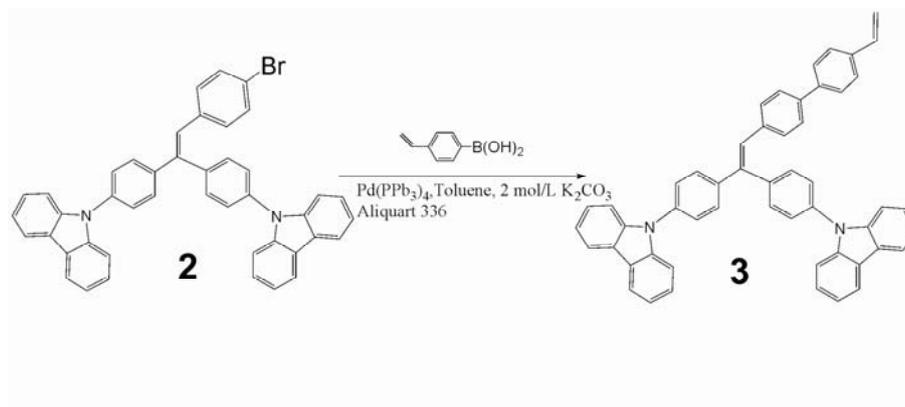
Synthesis of 9,9'-(4,4'-(2-(4'-bromophenyl)ethene-1,1'-diyl)bis(4-phenylene))bis(9H-carbazole) (Ref.[1]) (2)

A solution of compound 1 (10.3 g, 20 mmol) and diethyl-4-bromobenzylphosphonate (6.2 g, 20 mmol) in anhydrous tetrahydrofuran (100 mL) was stirred in N_2 at 0 °C. Potassium tert-butoxide (2.2 g, 20 mmol) was quickly added and the mixture was continuously stirred for 2 h at room temperature. The reaction mixture was precipitated into ethanol. Then the crude product was collected and washed with ethanol for three times. Having been recrystallized from dichloromethane-n-hexane (1:20 v/v), 11.6 g white powder was obtained (yield = 87%). 1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.05 (d, 2H), 7.11 (s, 1H), 7.27–7.57 (m, 16H), 7.58–7.71 (m, 6H), 8.10–8.24 (m, 4H); MS (FAB) m/z: 666 ($[M]^+$, calcd for $C_{44}H_{29}N_2Br$, 665.62); Anal. calcd for $C_{44}H_{29}N_2Br$: C 79.40, H 4.39, Br 12.00, N 4.21; found: C 79.42, H 4.42, N 4.16.



Synthesis of 9,9'-(4,4'-(2-(4'-vinylbiphenyl-4-yl)ethene-1,1-diyl)bis(4,1-phenylene))bis(9H-carbazole) (Ref.[1]) (3)

Compound 2 (3.3 g, 20 mmol) and 4-vinylphenylboronic acid (0.74 g, 5 mmol) were added into a solution containing 20 mL toluene, 5 mL K_2CO_3 (2 mol L^{-1}) and Aliquant336 (1 g). Then, the mixture was stirred in N_2 for 30 min. Tetrakis(triphenylphosphine)palladium (10 mg) was quickly added and the mixture was continuously stirred for 24 h at 90 °C. The reaction mixture was precipitated into ultra-pure water. The crude product was then collected from the organic phase, washed with ethanol for three times, recrystallized from dichloromethane-*n*-hexane (1:10 v/v) to obtain 2.1 g light-green powder in 87% yield. 1H NMR (300 MHz, $CDCl_3$) δ (ppm): 7.05 (d, 2H), 7.11 (s, 1H), 7.27–7.57 (m, 16H), 7.58–7.71 (m, 6H), 8.10–8.24 (m, 4H); MS (FAB) m/z : 666 ($[M]^+$, calcd for $C_{44}H_{29}N_2Br$, 665.62); Anal. calcd for $C_{44}H_{29}N_2Br$: C 79.40, H 4.39, Br 12.00, N 4.21; found: C 79.42, H 4.42, N 4.16.



The polymers, PVK, PBC and PVK-PBC, were synthesized by conventional free-radical polymerization with the respective monomers in essentially similar procedures. An illustrative example is provided for PVK-PBC.^[2]

A solution of VK (1 g, 6 mmol) and BC (2.1 g, 3 mmol) in anhydrous tetrahydrofuran (THF) (10 mL) was stirred in argon at room temperature. The initiator AIBN (13 mg, 0.08 mmol) was quickly added. Then, the mixture was stirred at reflux temperature for 36 h. The copolymer sample was purified by precipitation in methanol. The crude product was collected, and then washed with ethanol for three times.

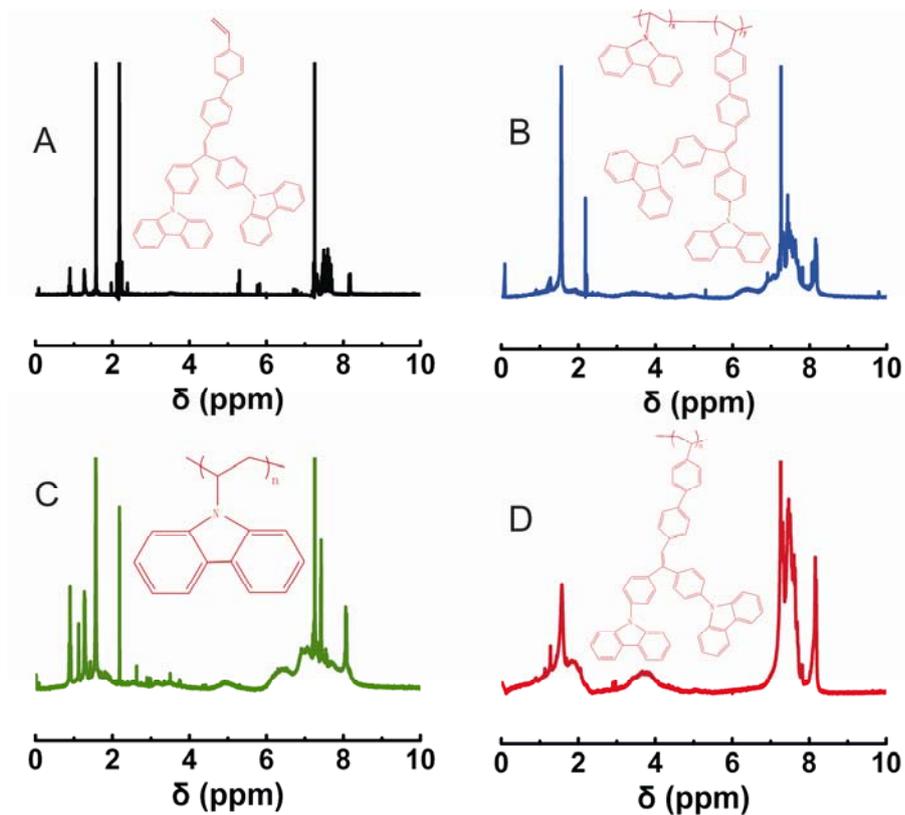


Figure S1. ^1H NMR spectra of (A) BC monomer, (B) PVK-PBC, (C) PVK and (D) PBC.

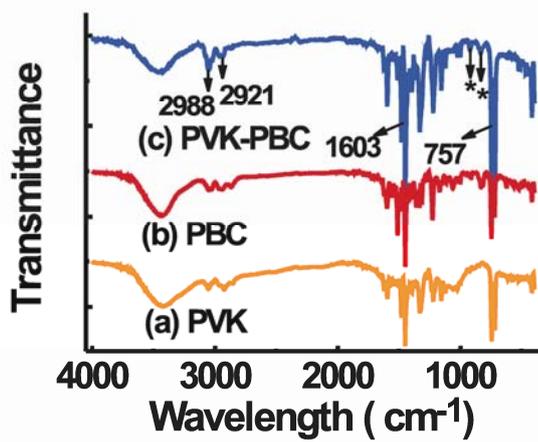


Figure S2. FTIR spectra of (a) PVK, (b) PBC and (c) PVK-PBC.

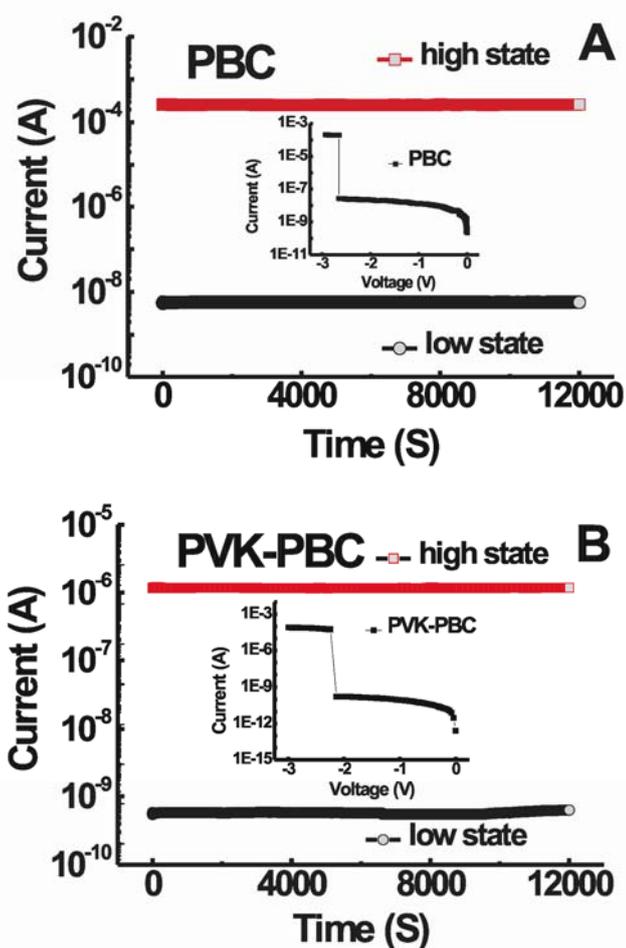


Figure S3. Effect of operation time (at -1 V) on the device current density in the OFF and ON states of (A) PBC and (B) PVK-PBC. The inset shows the ON-to-OFF state current ratio as a function of applied voltage for the same sweep.

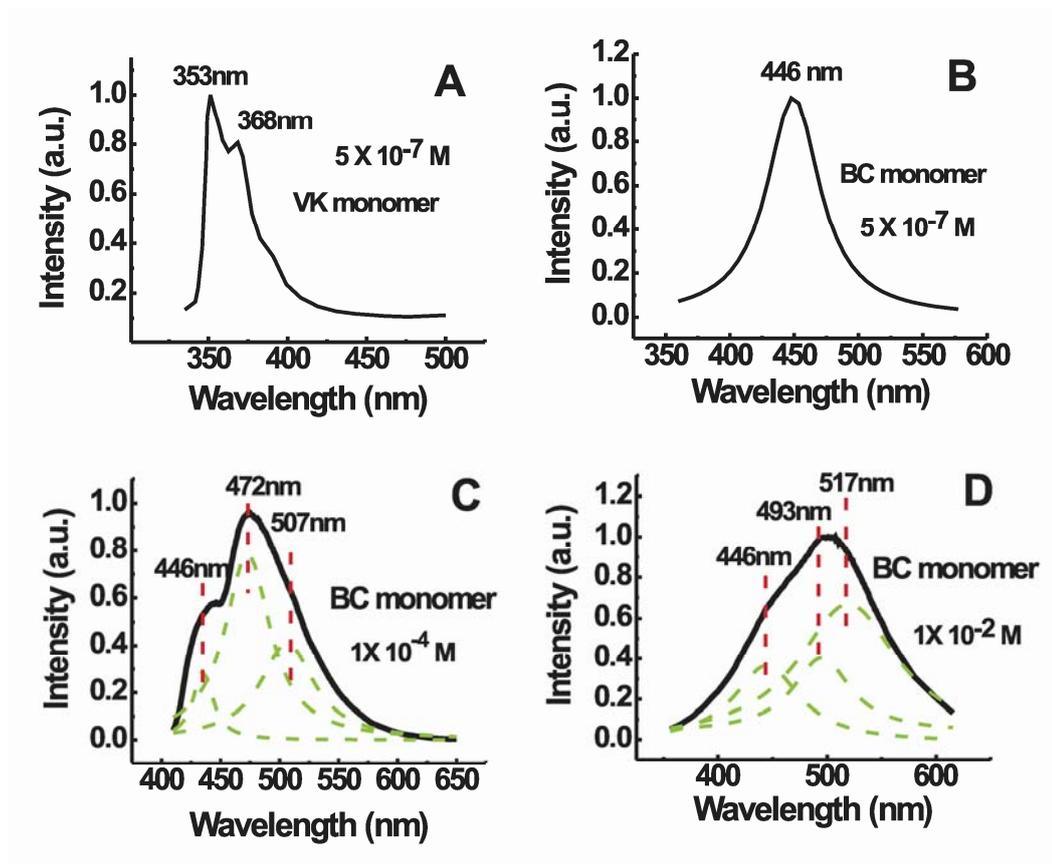


Figure S4. Fluorescence spectra of (A) VK (5×10^{-7} M), (B) BC monomer (5×10^{-7} M), (C) BC monomer (1×10^{-4} M) and (D) BC monomer (1×10^{-2} M) solutions in anhydrous THF.

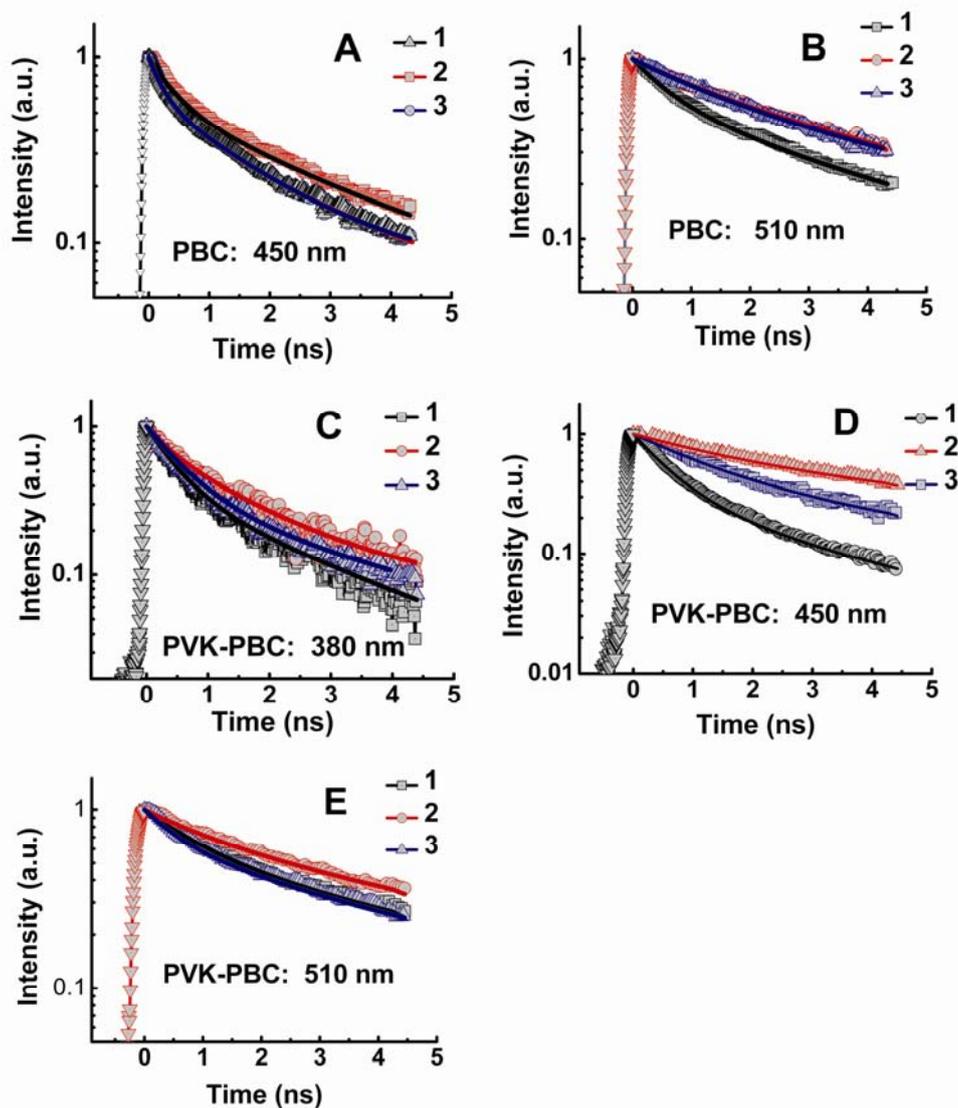


Figure S5. Room temperature fluorescence decay curves of (A, B) ITO/PBC/Al and (C, D and E) ITO/PVK-PBC/Al devices recorded under different external voltages: (1) 0 V, (2) -3 V and (3) 3 V.

Reference:

- (1) Z. Yang, Z. Chi, T. Yu, X. Zhang, M. Chen, B. Xu, S. Liu, Y. Zhang and J. Xu, *J. Mater. Chem.*, 2010, **20**, 7352.
- (2) Z. Yang, Z. Chi, T. Yu, X. Zhang, M. Chen, B. Xu, S. Liu, Y. Zhang and J. Xu, *J. Mater. Chem.*, 2009, **19**, 5541.