

Electronic Supporting Information

A non-volatile resistive memory effect in 2,2',6,6'-tetraphenyl-dipyranylidene thin films as observed in field-effect transistors and by conductive atomic force microscopy

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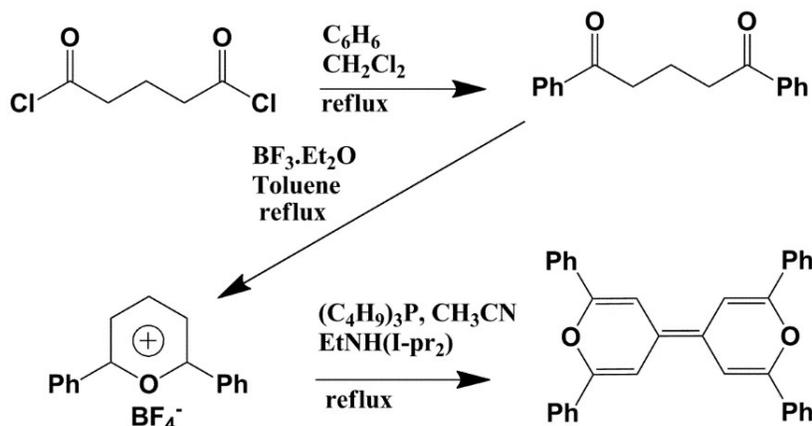
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Synthesis



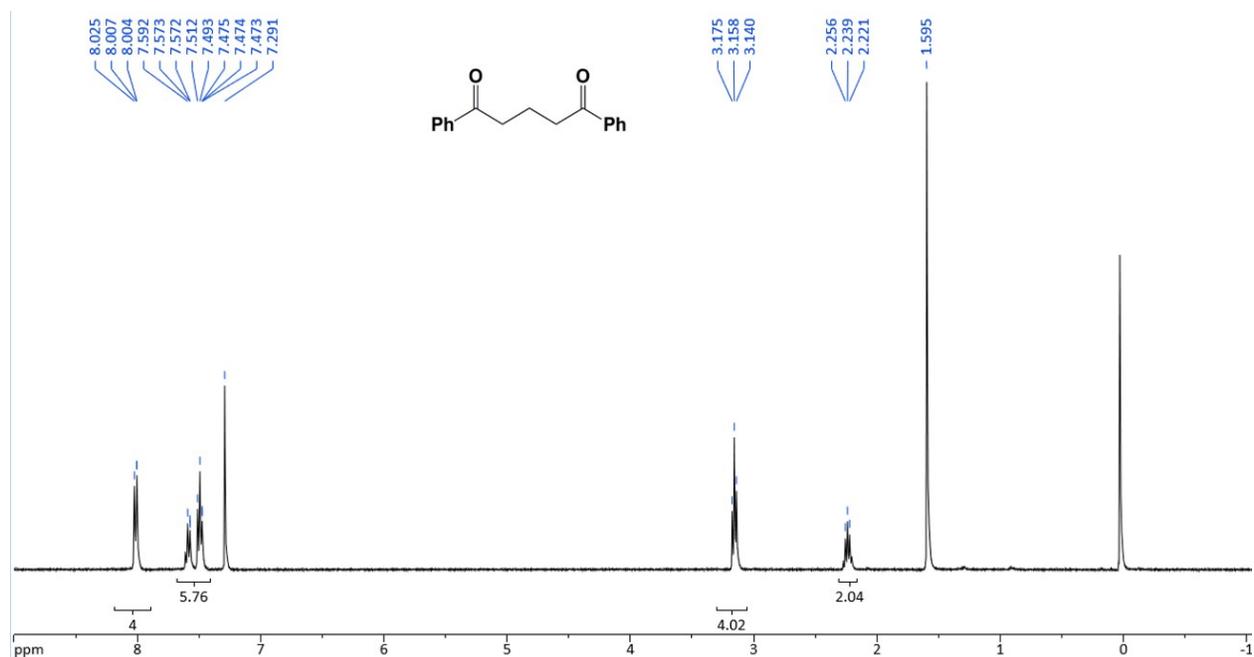
Scheme. S1. Synthetic pathway to 2,2',6,6'-tetraphenyldipyranylidene (DIPO-Ph₄).

Materials and synthesis

Glutaryl chloride, AlCl₃, BF₃·Et₂O, (C₆H₅)₃P, EtNH(i-pr)₂ and all solvents are purchased from commercial sources (Sigma-Aldrich, Alfa Aesar). All solvents are distilled under N₂ before utilization.

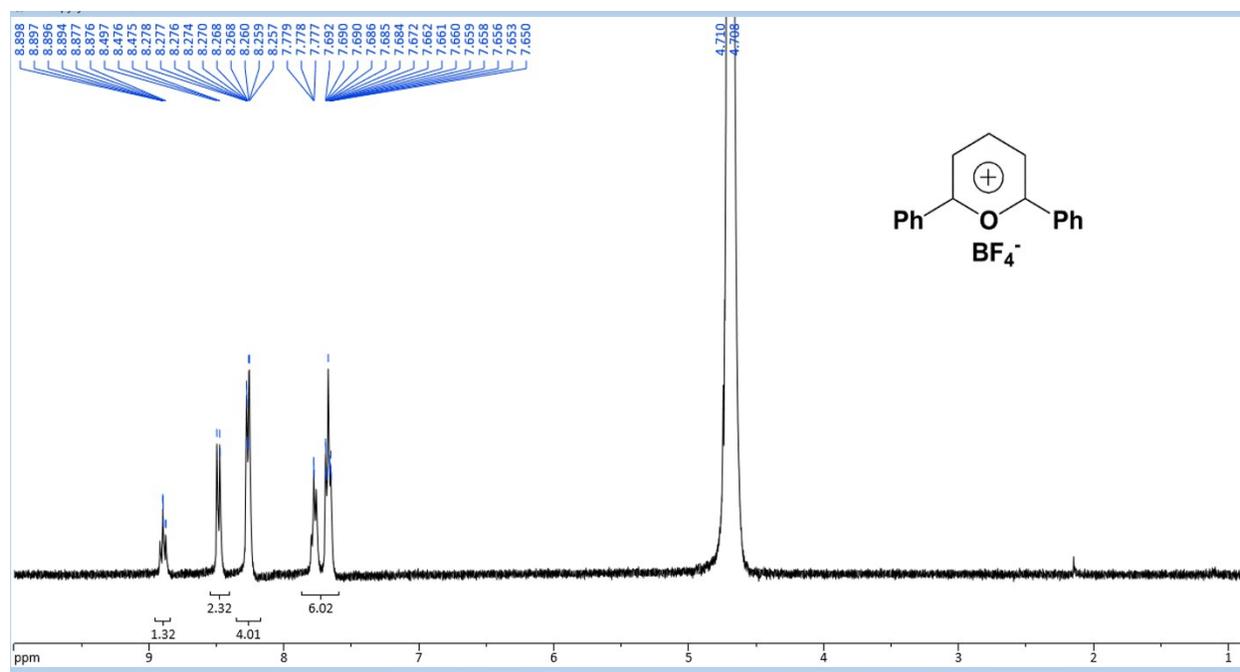
Synthesis of 1,5-diphenyl-1,5-pentadione

In a two-neck round bottom flask of 50 mL, AlCl₃ (150 mmol; 20.01 g) is dissolved in benzene under N₂. Glutaryl Chloride (60 mmol; 7.65 mL) is added dropwise to the solution and the mixture is stirred under reflux for 12 h. After return to ambient temperature, the mixture is poured into a diluted HCl solution (10 %). The organic phase is extracted with CH₂Cl₂ and dried over MgSO₄. The organic product is purified by column chromatography (hexane:ethyl acetate at a ratio=95:5) and a white solid is collected (12.01 g, yield=80 %). ¹H RMN (CDCl₃, 300 MHz) δ=8.00 (d, 4H), 7.57 (t, 2H), 7.47 (t, 4H), 3.15 (t, 4H), 2.23 (quint, 2H).



Synthesis of 2,6-Diphenylpyrylium fluoroborate

In a two-neck round bottom flask of 50 mL, 1,5-diphenyl-1,5-pentadione (13.7 mmol, 3.47 g) is dissolved in distilled toluene under N_2 . Then $BF_3 \cdot Et_2O$ (41.2 mmol, 5.09 mL) is added drop by drop to the solution. The slightly red solution is refluxed at $130^\circ C$ during 12 h process. After cooling down to room temperature, 5 mL of acetone is added to the solution and poured in 100 mL of diethyl ether. A yellow precipitate is filtered and dried overnight under vacuum (2.05 g; yield=46%). 1H NMR (D_2O , 300 Mhz) δ =ppm: 8.89 (t, 1H), 8.47 (d, 2H), 8.26 (d, 4H), 7.77 (t, 2H), 7.68 (t, 4H).



Synthesis of 2,2',6,6'-tetraphenyldipyrylium tetrafluoroborate (DIPO-Ph₄)

2,6-Diphenylpyrylium fluoroborate (8.21 mmol, 2.65 g) is dissolved in distilled CH₃CN (50 mL). (C₄H₉)P (16.4 mmol, 4.1 mL) is added to the solution and during 2 h at room temperature. EtNH(i-pr)₂ (41.06 mmol, 7 mL) is added to the yellow solution and the mixture is heated at 90°C under N₂ during 18 h. After the return to room temperature, the red solid formed is filtered and washed with ethyl acetate. The final compound is a dark red crystalline powder (m=1.62 g, yield=85%). mp=325°C. ¹H NMR (acetone, 500 MHz): δ = 8.02 (d, 8H), 7.51 (dd, 8H), 7.42(t, 4H), 7.18 (s, 4H); MS (ESI+): m/z 464.

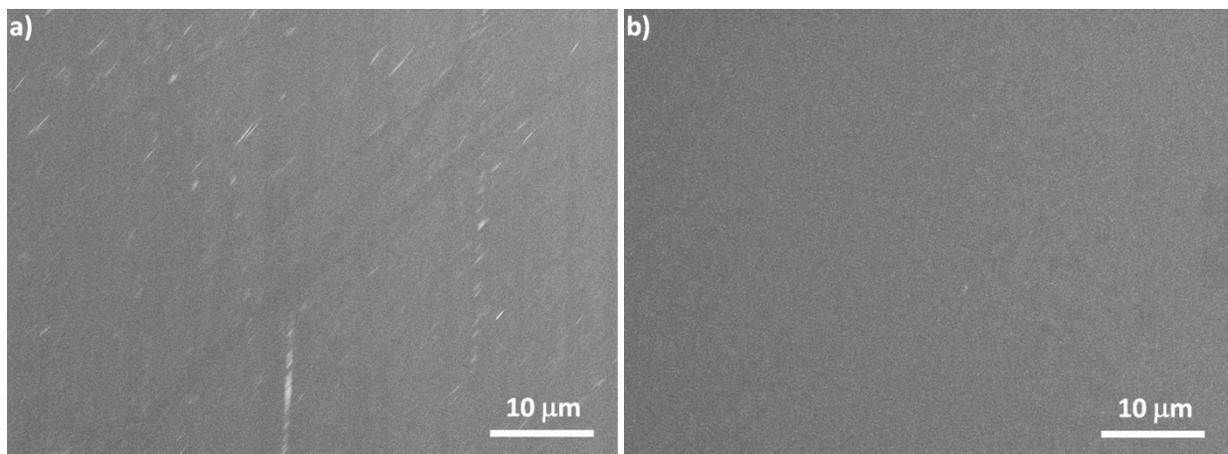


Fig. S1 SEM images of a 50 nm DIPO-Ph₄ thin film vacuum-deposited on a) a SiO₂/Si wafer and b) an HMDS-treated SiO₂/Si wafer. The DIPO-Ph₄ thin film deposited on a HMDS-treated wafer (right image) possesses a uniform surface with no pinholes.

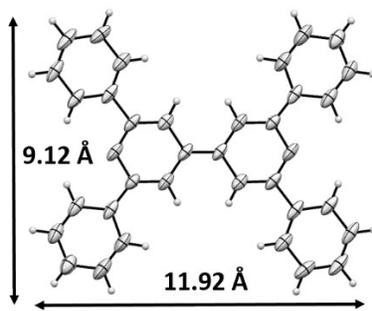


Fig. S2 ORTEP representation of the DIPO-Ph₄ molecule.

OFET characteristics

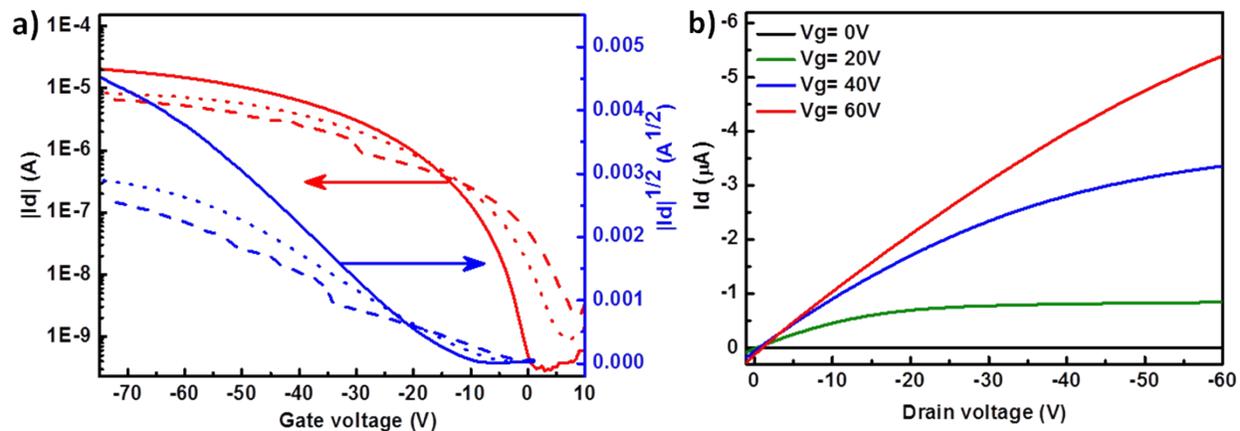


Fig. S3 a) Transfer curves (red) with their respective $(I_d)^{0.5}$ (blue) of the DIPO-Ph₄ based OFET with a 300 nm SiO₂ layer as the dielectric for different annealing temperatures, 200°C (straight line), 150°C (dots line) and no annealed (dash line). b) Output I_d/V_d curves of the corresponding 200°C annealed DIPO-Ph₄-based OFET.