Highly efficient polymerization via Sulfur(VI)-fluoride exchange (SuFEx): Novel polysulfates bearing a pyrazoline-naphthlamide conjugated moiety and their electrical memory performance

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Experimental section

Materials

4-bromo-1,8-naphthalic anhydride, n-Butylamine, p-hydroxybenzaldehyde, 4'-hydroxyacetophenone, imidazole, tert-butyldimethylsilyl chloride, hydrazine hydrate, bisphenol S, and 1,8-diazabicyclo[5.4.0]undec-7-ene [DBU] from TCI (Shanghai)Development Co., Ltd. were used as received without further purification. Sulfuryl fluoride (SO$_2$F$_2$) were purchased from Maui (Hangzhou) Electronic Chemicals Co., Ltd. All solvents and other reagents were purchased from Sinopharm Chemical Reagent Co., Ltd and used without further purification.

Synthesis of (E)-1, 3-bis (4-hydroxyphenyl) prop-2-en-1-one (BHPP).

4'-hydroxyacetophenone (16.32 g, 0.12 mol) was dissolved in sulfuric acid (2 mL). The solution of p-hydroxybenzaldehyde (12.2 g, 0.10 mol) in glacial acetic acid (60 mL) was added dropwise to the reaction mixture. The reaction mixture was stirred at room temperature for 24 hrs. The solution was then poured into 500 mL of ice water. The mixture was neutralized with proper amount of 1 M KOH solution. The resulting precipitate was filtered and the crude product was recrystallized twice in ethanol. The BHPP was finally isolated as a yellow powder (20 g, 83.3%). mp: 197-199 ºC. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 10.34 (s, 1H), 10.03 (s, 1H), 8.04 (d, J = 8.1 Hz, 2H), 7.75–7.64 (m, 3H), 7.61 (d, J = 15.3 Hz, 1H), 6.88 (d, J = 8.1 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H). $^{13}$C NMR (151 MHz, DMSO-$d_6$) $\delta$ (ppm) 187.48, 162.32, 160.25, 143.59, 131.36, 131.14, 129.89, 126.42, 118.97, 116.21, 115.73.
Figure S1a. $^1$H NMR spectrum of BHPP.

$^{13}$C NMR (125 MHz, deuteriochloroform) $\delta$ 187.98 (s), 180.37 (s), 158.27 (s), 145.59 (s), 130.36 (s), 131.14 (s), 129.87 (s), 128.45 (q), 119.85 (d), 119.31 (q), 113.73 (s).

Figure S1b. $^{13}$C NMR spectrum of BHPP
Synthesis of 6-(3,5-bis(4-hydroxyphenyl)-4,5-dihydro-1H-pyrazol-1-yl)-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione(MTPP-NI).

2-butyl-6-hydrazinyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (BHBO) was synthesized according to the previous literature. The BHBO (2.83 g, 10 mmol), BHPP (2.4 g, 10 mmol) and hydrochloric acid (5 mL) were dissolved in anhydrous ethanol (100 mL) and the resulting mixture was stirred at 85 °C for 24 hrs. Then the mixture was cooled to room temperature and filtered. The resulting pure product was dried in the vacuum oven overnight at 60 °C to give a red powder (4.05 g, yield: 80%). mp: > 250 °C. 1H NMR (400 MHz, DMSO-\(d_6\)) \(\delta\) (ppm) 10.00 (s, 1H), 9.74 (d, \(J = 8.5\) Hz, 1H), 9.41 (s, 1H), 8.47 (d, \(J = 7.0\) Hz, 1H), 8.14 (d, \(J = 8.5\) Hz, 1H), 7.86–7.63 (m, 3H),
7.15 (d, J = 8.1 Hz, 2H), 6.90 (t, J = 9.3 Hz, 3H), 6.67 (d, J = 8.2 Hz, 2H), 5.83 (s, 1H), 4.04–3.81 (m, 3H), 3.18 (d, J = 17.5 Hz, 1H), 1.57 (s, 2H), 1.31 (d, J = 7.0 Hz, 2H), 0.90 (t, J = 7.1 Hz, 3H). $^1$H NMR (151 MHz, DMSO-d$_6$) δ (ppm) 164.03, 163.08, 159.78, 157.30, 153.89, 145.79, 134.86, 132.33, 131.43, 131.11, 130.49, 128.69, 127.59, 124.89, 122.78, 122.67, 122.02, 116.17, 116.14, 111.86, 110.63, 64.80, 42.53, 30.15, 20.25, 14.15.

Figure S1d. $^1$H NMR spectrum of MTPP-NI.

Figure S1e. $^{13}$C NMR spectrum of MTPP-NI
Synthesis of 6-(3,5-bis(4-((tert-butyldimethylsilyl)oxy)phenyl)-4,5-dihydro-1H-pyrazol-1-yl)-2-butyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (MTPP-NITBS).

MTPP-NI (1.012 g, 2 mmol) and imidazole (0.354 g, 5.2 mmol) were dissolved in dichloromethane (40 mL). And then the solution of tert-butyldimethylsilyl chloride (0.97 g, 4.8 mmol) in the dichloromethane (4 mL) was dropwise added into the reaction mixture. The reaction mixture was allowed to stir at room temperature for 24 hrs. After the reaction was completed, the mixture was extracted with ethyl acetate and washed successively with sodium bicarbonate solution and water. The solution was removed by rotary evaporation in vacuum. And the product was purified by silica-gel column chromatography to give a pale yellow powder with a yield of 1.1 g (75%). mp: 168-170 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm) 9.65 (d, J = 8.6 Hz, 1H), 8.59 (d, J = 7.2 Hz, 1H), 8.25 (d, J = 8.4 Hz, 1H), 7.66 (t, J = 8.6 Hz, 3H), 7.15 (d, J = 8.2 Hz, 2H), 6.89 (d, J = 8.4 Hz, 2H), 6.73 (d, J = 8.1 Hz, 3H), 5.56 (dd, J = 11.0, 7.6 Hz, 1H), 4.19–4.05 (m, 2H), 3.80 (dd, J = 17.0, 11.4 Hz, 1H), 3.20 (dd, J = 17.0, 7.3 Hz, 1H), 1.72–1.61 (m, 3H).
2H), 1.40 (dd, J = 15.0, 7.4 Hz, 2H), 1.03 – 0.86 (m, 21H), 0.22 (s, 6H), 0.12 (s, 6H).

$^{13}$C NMR (151 MHz, CDCl$_3$) δ (ppm) 164.76, 163.95, 157.48, 155.44, 151.89, 145.93, 134.40, 132.81, 132.34, 131.18, 130.68, 127.74, 126.98, 124.93, 124.42, 123.27, 122.37, 120.69, 120.51, 120.42, 120.25, 113.47, 110.51, 65.58, 42.59, 39.97, 30.24, 25.68, 25.63, 25.56, 25.53, 20.40, 18.26, 18.11, 13.85, -4.37, -4.46.

Figure S1g. $^1$H NMR spectrum of MTPP-NITBS

Figure S1h. $^{13}$C NMR spectrum of MTPP-NITBS
The MTPP-NISO$_2$F was synthesized following a similar method according to the literature. MTPP-NI (1.012 g, 2 mmol) and triethylamine (0.53 g, 5.2 mmol, 0.73 mL) were dissolved in dichloromethane (20 mL) in a dry 2 L three-necked flask. Then reaction flask was sealed with a rubber stopper, drained of air, and an air bag filled with SO$_2$F$_2$ gas was introduced. And the reaction mixture was allowed to vigorously stir under SO$_2$F$_2$ atmosphere for 12 hrs at room temperature. After the reaction was completed, the volatiles were removed by rotary evaporation, and the mixture was extracted with ethyl acetate and washed successively with diluted hydrochloric solution, sodium bicarbonate solution and water. The solution was removed by rotary evaporation in vacuum. And the product was purified by silica-gel column chromatography to give a light yellow powder with a yield of 1.07 g (80%). mp: 113-115 ºC. $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$ (ppm) 9.56 (d, J = 8.4 Hz, 1H), 8.47 (d, J = 6.7 Hz, 1H), 8.18 (d, J = 7.9 Hz, 1H), 8.01 (d, J = 7.8 Hz, 2H), 7.81 (t, J = 7.6 Hz, 1H), 7.73 (d, J = 7.7 Hz, 2H), 7.64 (d, J = 7.5 Hz, 2H), 7.56 (d, J = 7.7 Hz, 2H), 7.02 (d, J = 8.1 Hz, 1H), 6.14 (t, J = 9.2 Hz, 1H), 4.03 (dd, J = 30.8, 18.4 Hz, 3H), 3.40 (dd, J = 18.1, 7.1 Hz, 1H), 1.66 – 1.45 (m, 2H), 1.30 (dd, J = 13.5, 6.5 Hz, 2H), 0.88 (t, J = 6.6 Hz, 3H). $^{13}$C NMR (151 MHz, DMSO-d6) $\delta$ (ppm) 163.92, 163.08, 151.62, 150.49, 149.36,
145.17, 142.14, 134.13, 132.69, 132.16, 131.29, 130.24, 129.24, 129.10, 125.75, 123.25, 122.31, 122.20, 122.16, 122.04, 114.08, 111.65, 64.64, 42.05, 30.09, 20.21, 14.11.

Figure S1j. $^1$H NMR spectrum of MTPP-NISO$_2$F

Figure S1k. $^{13}$C NMR spectrum of MTPP-NISO$_2$F
**Figure S11.** The Mass spectrum of MTPP-NISO$_2$F

**Synthesis of 4, 4’-Dihydroxydiphenylsulfone bissilyether (NSOTBS)**

Bisphenol S (2.50 g, 10 mmol) and imidazole (1.8 g, 26 mmol) were added in a three neck round bottom flask with 20 mL dichloromethane as the solvent and stirred for 10 min. Then, a solution of the tert-Butyldimethylsilyl chloride (3.6 g, 24 mmol) in dichloromethane (10 mL) was dropped slowly for 30 mins. This reaction was allowed to stir for 24 hrs. After completed, the solvent was removed in vacuum and the residue was complete dissolved in ethyl acetate. The solution was washed by saturated sodium bicarbonate solution and saturated salt water in sequence. The organic solvent was evaporated using a rotary evaporator. The desired product was purified by column chromatography on silica gel. The target intermediate is a white solid with a yield of 87 %. mp: 129-131°C.
$^1$H NMR (400 MHz, DMSO) $\delta = 7.81$ (d, J=8.4, 4H), 7.03 (d, J=8.4, 4H), 0.93 (s, 18H), 0.21 (s, 12H). $^{13}$C NMR (75 MHz, DMSO) $\delta = 159.80$ (s, 1H), 134.62 (s, 1H), 129.95 (s, 4H), 121.07 (s, 4H), 25.82 (s, 8H), 18.35 (s, 2H), -4.23 (s, 3H).

Figure S1m. $^1$H NMR spectrum of NSOTBS

Figure S1n. $^{13}$C NMR spectrum of NSOTBS
Synthesis of PolyTPP-NI and CPTPP-NI via the SuFEx Click Reaction.

Synthesis of PolyTPP-NI.

MTPP-NITBS (367 mg, 0.5 mmol) and MTPP-NISO2F (335 mg, 0.5 mmol) were dissolved in N,N-dimethylformamide (2 mL). Then the catalyst DBU (15.2 mg, 0.1 mmol) was added dropwise into the reaction mixture and stirred for 24 hrs at room temperature. The mixture was poured into methanol and the precipitate was filtered. An orange powder was obtained and dried under vacuum with a yield of 520 mg (89.2%).

Synthesis of CPTPP-NI.

NSOTBS (340 mg, 0.5 mmol) and MTPP-NISO2F (335 mg, 0.5 mmol) were dissolved in N,N-dimethylformamide (2 mL). DBU (15.2 mg, 0.1 mmol) was dropwise
added into the reaction mixture, and the resulting mixture was stirred for 24 hrs at room
temperature. The mixture was poured into methanol and the precipitate was filtered.
A orange powder was obtained and dried under vacuum with a yield of 396 mg (90.0%).

**Characterization:**

$^1$H NMR spectra were measured by Agilent 400 or 600 MHz NMR spectrometers with
CDCl$_3$, DMSO-$d_6$ or DMF-$d_7$ as the solvent and tetra-methylsilane (TMS) as the
internal standard at ambient temperature. The molecular weights and polydispersity
index (PDI), relative to PS (Mn =25000) were measured using Waters1515 GPC with
DMF as a mobile phase at a rate of 1 mL·min$^{-1}$ and with column temperature of 30 °C.

UV-visible absorption spectra were determined using a Shimadzu RF540
spectrophotometer. Room temperature emission spectra were recorded using an
Edinburgh-920 Fluorescence spectrophotometer. HPLC-ION TRAP MS was
performed on an amazon SL ion trap mass spectrometer (Bruker Daltonics, Bremen,
Germany) and LC-MS was performed on an Agilent 1200/6220 eluting with CH$_3$OH.
All electrical measurements of the device were characterized under ambient conditions,
without any encapsulation, using a Keithley 4200-SCS semiconductor parameter analyzer.
Cyclic voltammetry (CyV) measurements were carried out in 0.1 M
acetonitrile solution of tetra-n-butylammonium hexafluoro-phosphate (TBAPF$_6$) with
a CHI-660C electrochemical workstation containing a platinum gauze auxiliary
electrode and an Ag/AgCl reference electrode. The DFT and MD simulations of MTPP-
NI, PolyTPP-NI were implemented using the Materials Studio software package. For
the electronic properties of the repeat unit, the BLYP functional with Grimme
correction was chosen to optimize the geometrical structure in the vacuum by the
Dmol3 module. All the electron core treatments and DNP 4.4 basis were set during the
whole calculation. The convergence standard of 2.0*10$^{-5}$ Ha energy and 0.004 Ha/Å
maximum force was enough to ensure the accuracy of calculations.

**Fabrication of memory devices:**

Firstly, indium tin oxide (ITO) glass was cleaned by using a sequence of deionized
water, acetone and anhydrous ethanol for 20 minutes after each other. The MTPP-NI
thin films were evaporated under vacuum using a vacuum deposition apparatus to take
35 mg of MTPP-NI on the furnace with the degree of vacuum set to 3*10$^{-4}$ Pa. MTPP-
NI in the evaporator furnace was slowly sublimated to the ITO glass surface. A
cyclopentanone solution of PolyTPP-NI (10 mg.mL$^{-1}$) was spin-coated onto the ITO-
glass substrate using a spin coater at a rotational speed of 2000 rpm for 30 seconds. The
organic molecule films were annealed in a vacuum chamber at 10$^{-5}$ torr and 80 °C for
10 hrs. The CPTPP-NI thin films were prepared using the same process as PolyTPP-NI.

Scheme S1. The synthesis and chemical structures of MTPP-NI and PolyTPP-NI. TBSCl=tert-Butyldimethylsilyl chloride, Imid=Imidazole, DMF=N,N-Dimethylformamide, DBU=1,8-Diazabicyclo[5.4.0]undec-7-ene.

Scheme S2. The synthesis and chemical structures of CPTPP-NI.

Scheme S3. The mechanism of SuFEx reactivity. Solvent: polar aprotic (CH$_3$CN, DMF, NMP); Catalyst: DBU (10-30 mol %); SiR$_3$ = SiMe$_3$ (< 4 h, RT); SiR$_3$ = SiMe$_2$tBu (4-18 h, RT to 80°C).
### Table S1 Comparison of polymerization conditions [a]

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[a] Unchanged polymerization conditions: 20%DBU, 24 h.

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**Fig. S2.** The change curve of polymer molecular weight over time in DMF at 20 °C

*Thermal stabilities*
The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energy levels can be calculated from the CyV measurement results and the UV visible absorption spectra via the following equations: 3

\[ E_{\text{HOMO}} = -[E_{\text{ox (onset)}} + 4.80 - E_{\text{Foc}}] \]

\[ E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}} \]

where \( E_{\text{ox}} \) is the onset oxidation potential, \( E_{\text{Foc}} \) is the external standard potential of the ferrocene/ferrocenium ion couple and \( E_{\text{g}} \) represents the band gap determined from UV-visible absorption. The \( E_{\text{Foc}} \) is 0.43 eV from the CyV measurement with the bare ITO glass substrate without any organic films.
The optical band gaps of the MTPP-NI, PolyTPP-NI and CPTPP-NI films estimated from the absorption edges were 2.12, 2.33 and 2.34 eV, respectively. The onset oxidation (Eox) measured from the CyV curves for the thin films of MTPP-NI, PolyTPP-NI and CPTPP-NI were 0.71 eV, 0.72 eV and 0.69 eV, respectively. The HOMO energy levels of MTPP-NI, PolyTPP-NI and CPTPP-NI were determined to be -5.08 eV, -5.09 eV and -5.06 eV. In addition, the LUMO energy levels of MTPP-NI, PolyTPP-NI and CPTPP-NI were determined to be -2.96 eV, -2.76 eV and -2.72 eV.

The opto-electronic properties and calculated energy levels for each of the compounds are summarized in Table S2.

**Fig. S4** Typical I–V curves for ITO/active layer/Au memory devices of a) PolyTPP-NI, b) CPTPP-NI, c) MTPP-NI at compliance currents of 0.001 A.

**Table S3.** HOMO, LUMO and ESP of PolyTPP-NI, CPTPP-NI and MTPP-NI

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**Fig. S5** The IV-characteristics of (a) MTPP-NI, (b) PolyTPP-NI, (c) CPTPP-NI by continuing sweeps across 0 V with arrows indicating the direction of the sweep.

**Fig. S6** The IV-characteristics of (a) MTPP-NI, (b) PolyTPP-NI, (c) CPTPP-NI by sweeping with different delay times (5 minutes later and 10 minutes later respectively) after switching off the applied bias.
Fig. S7 The IV-characteristics of (a) MTPP-NI by scanning from Scan from positive voltage direction and (b) PolyTPP-NI, (c) CPTPP-NI starting from negative voltage direction.

Fig. S8 The simulated molecular structure and corresponding dipole moment of (a) PolyTPP-PC (2.02 D), (b) CPTPP-PC (3.20 D).
**Fig. S9** Accompanying GPC Traces for Table S1. Effect of solvent (NMP) on polymer molecular weight of PolyTPP-NI.
Fig. S10 Accompanying GPC Traces for Table S1. Effect of solvent (THF) on polymer molecular weight of PolyTPP-NI.
**Fig. S11** Accompanying GPC Traces for Table S1. Effect of solvent (DMF) on polymer molecular weight of PolyTPP-NI.

![Graph showing GPC traces for PolyTPP-NI with DMF solvent effect]

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**Fig. S12** Accompanying GPC Traces for Table S1. The temperature effect on polymer molecular weight of PolyTPP-NI.

![Graph showing GPC traces for PolyTPP-NI with temperature effect]


**Fig. S13** Accompanying GPC Traces for Table 1 and Figure S2. Effect of reaction time on polymer molecular weight of PolyTPP-NI.

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**Fig. S14** Typical I-V curves of the MTPP-NI based device with different thickness, (a) M-1(35nm), (b) M-2(52nm), (c) M-3(91nm) and AFM images of the (d,g) M-1(35nm), (e,h) M-2(52nm), (f,i) M-3(91nm).

**Fig. S15** Typical I-V curves of the PolyTPP-NI based device with different thickness, (a) P-1(37.5nm), (b) P-2(55.1nm), (c) P-3(106nm) and AFM images of the (d,g) P-1(37.5nm), (e,h) P-2(55.1nm), (f,i) P-3(106nm).
Fig. S16 Typical I-V curves of the CPTPP-NI based device with different thickness, (a) C-1(44.2nm), (b) C-2(59.8 nm), (c) C-3(96.7nm) and AFM images of the (d,g) C-1(44.2nm), (e, h) C-2(59.8 nm), (f, i) C-3(96.7nm).

Fig. S17 Typical I-V curves of the ITO/MTPP-NI/Al which prepared in a similar way (spin-coated onto the ITO-glass substrate using a spin coater) as for the polymeric materials. (a cyclopentanone solution of MTPP-NI (10 mg.mL⁻¹) was spin-coated onto
the ITO-glass substrate using a spin coater at a rotational speed of 2000 rpm for 30 seconds).

We have prepared a device with the electro-active layer MTPP-NI in the same way as for the polymeric materials. And the $I-V$ performance showed that the device also exhibits a SRAM electron storage behavior (Fig. S17).