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Electronic Supplementary Information

Efficient flash memory devices Based on non-conjugated ferrocene-containing copolymers

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Synthesis of VM1

4-Di-*p*-tolylamino-benzaldehyde (860 mg, 2.85 mmol) in dry THF was added into a mixture solution of potassium *t*-butoxide (480 mg, 4.28 mmol) and methyltriphenyl phosphonium iodide (1.73 g, 4.28 mmol). They were then stirred at r.t. for 24 h. The solution was poured into ice water and extracted with ethyl acetate. The organic layer was concentrated under reduced pressure and the product was then purified by column chromatography (silica). 80% yield. ^{1}H NMR (acetone-d_6, 400 MHz): δ 7.33~7.30 (m, 2H, Ar), 7.12~7.09 (m, 4H, Ar), 6.96~6.89 (m, 6H, Ar), 6.67 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.8 Hz, vinyl CH), 5.65 (dd, 1H, J_1 = 17.6 Hz, J_2 = 0.8 Hz, *trans*-vinyl C=CH$_2$), 5.10 (dd, 1H, J_1 = 10.8 Hz, J_2 = 0.8 Hz, *cis*-vinyl C=CH$_2$). ^{13}C NMR (acetone-d_6, 100 MHz): δ 148.86, 146.07, 137.32, 133.48, 131.94, 130.86, 127.91, 125.52 (Ar), 122.98 (vinyl CH), 112.02 (vinyl CH$_2$), 21.01 (CH$_3$).

Synthesis of VM2

80% yield. ^{1}H NMR (CDCl$_3$, 400 MHz): δ 8.04 (dd, 3H, J_1 = 12.3, J_2 = 8.1 Hz, Ar), 7.85 (d, 1H, J = 8.0 Hz), 7.47 (dd, 3H, J = 11.2, 7.8 Hz, Ar), 7.35 (t, 1H, J = 7.6 Hz, Ar), 6.73 (dd, 1H, J_1 = 17.6, J_2 =10.9 Hz, vinyl CH), 5.83 (d, 1H, J = 17.6 Hz, *trans*-vinyl C=CH$_2$), 5.34 (d, 1H, J = 10.9 Hz, *cis*-vinyl C=CH$_2$). ^{13}C NMR (CDCl$_3$, 100 MHz): δ 167.64, 154.18, 140.13, 136.06, 135.03, 132.88, 127.75, 126.78, 126.34, 125.18, 123.19 (Ar), 121.60 (vinyl CH), 115.62 (vinyl CH$_2$).

Synthesis of VM3

83% yield. ^{1}H NMR (tetrahydrofuran-d_8, 400 MHz): δ 7.21~7.18 (m, 2H, Ar), 7.15~7.13 (m, 1H, Ar), 7.08~7.06 (m, 1H, Ar), 6.90~6.86 (m, 2H, Ar), 6.83~6.81 (m, 1H, Ar), 6.59 (dd, 1H, J_1 = 17.6 Hz, J_2 = 10.8 Hz, vinyl CH), 5.62 (dd, 1H, J_1 = 17.6 Hz, J_2 = 0.8 Hz, *trans*-vinyl C=CH$_2$), 5.07 (dd, 1H, J_1 = 10.8 Hz, J_2 = 0.8 Hz, *cis*-vinyl C=CH$_2$), 3.34 (s, 3H, CH$_3$). ^{13}C NMR (tetrahydrofuran-d_8, 100 MHz): δ 143.71, 143.54, 133.82, 130.33, 125.32, 124.76, 123.61, 122.21, 121.60, 121.10, 120.26, 112.12 (Ar), 111.92 (vinyl CH), 109.19 (vinyl CH$_2$), 32.72 (CH$_3$).

Synthesis of FcCP1

VM1 (278 mg, 0.929 mmol), vinylferrocene (197 mg, 0.929 mmol) and AIBN (30 mg, 0.18 mmol) were delivered into a Fisher-Porter aerosol compatibility tube equipped with a valve. 8 mL dry toluene was then added into the tube to dissolve the mixture followed by degassing using three alternate freeze-thaw cycles. After degassing, the tube was placed in a constant-temperature bath controlled to 70 °C for 24 h. The reacted solution was added dropwise to hexane with rapid stirring to precipitate the copolymer. It was filtered and precipitated in hexane again followed by drying under vacuum to obtain the pure product in 50% yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.84 (br, 36H, triphenylamine H), 3.85 (br, 9H, Fc), 2.19 (br, 19H, CH_3). IR (KBr pellet, cm^{-1}): 3089 (C-H stretching, Fc), 1605 (C=C stretching, Ar), 1580 (C=C stretching, Ar), 1502 (C=C stretching, Ar), 1448 (C=C stretching, Ar), 1412 (C=C stretching, Fc), 1270 (C-N stretching), 1106 (C-C stretching, Fc), 1000 (C-C stretching, Fc), 813 (C-H bending, Fc), 504 (C-Fe stretching, Fc).

Synthesis of FcCP2

The synthetic procedures of **FcCP1** were applied using **VM2** instead of **VM1** to afford **FcCP2** in 60% yield. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.90~6.76 (m, 23H, Ar), 4.00 (br, 9H, Fc). IR (KBr pellet, cm^{-1}): 3060 (C-H stretching, Fc), 1607 (C=C stretching, Ar), 1562 (C=C stretching, Ar), 1483 (C=C stretching, Ar), 1453 (C=C stretching, Ar), 1413 (C=C stretching, Fc), 1107 (C-C stretching, Fc), 483 (C-Fe stretching, Fc).

Synthesis of FcCP3

The synthetic procedures of **FcCP1** were applied using **VM3** instead of **VM1** to get **FcCP3** in 58% yield. ^{1}H NMR (CD_2Cl_2, 400 MHz): δ 7.23~6.56 (m, 24H, Ar), 4.04~3.71 (m, 9H, Fc), 3.25 (br, 10H, CH_3). IR (KBr pellet, cm^{-1}): 3058 (C-H stretching, Fc), 1879 (C-H oop bending, para-substituted-Ar), 1763 (C-H oop bending, para-substituted-Ar), 1602 (C=C stretching, Ar), 1576 (C=C stretching, Ar), 1497 (C=C stretching, Ar), 1469 (C=C stretching, Ar), 1256 (C-N stretching), 1109 (C-C stretching, Fc), 1000 (C-C stretching, Fc), 813 (C-H bending, Fc), 485 (C-Fe stretching, Fc).

Table S1 Compositions of **FcCP1**−**FcCP3** calculated from ^{1}H NMR spectra

Polymer	ferrocene unit: aromatic moiety (mole ratio)
FcCP1	0.24 : 0.76
FcCP2	0.26: 0.74
FcCP3	0.23 : 0.77

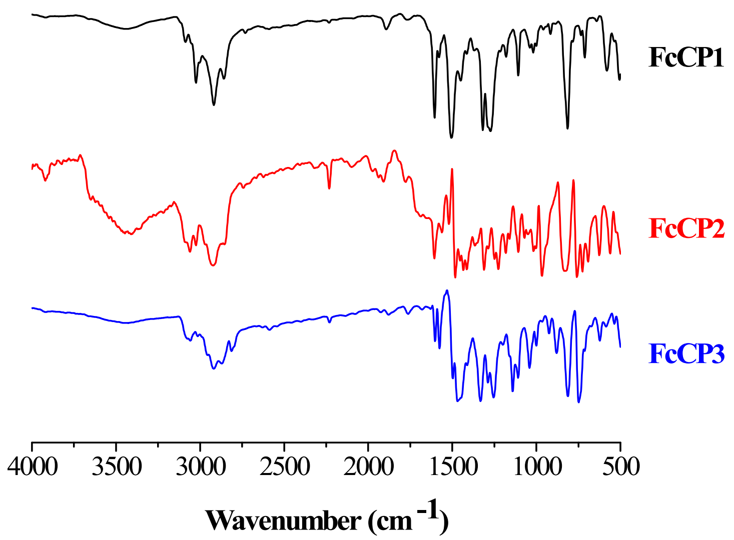


Figure S1. IR spectra of **FcCP1−FcCP3** using KBr pellet method

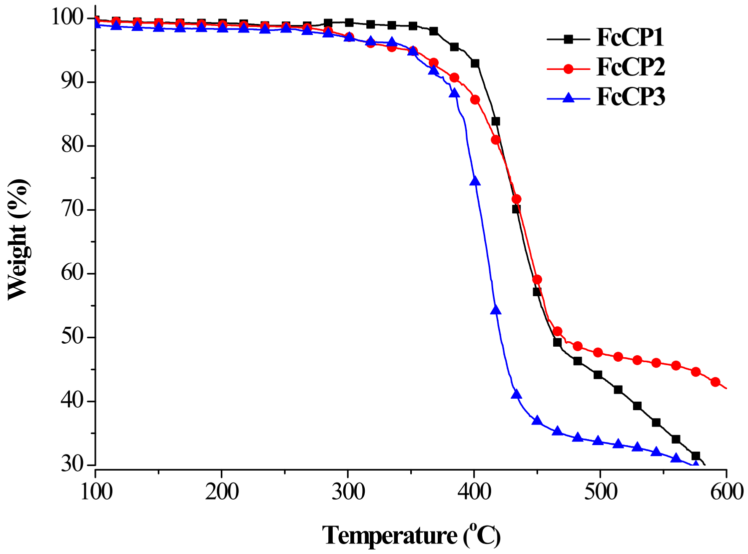


Figure S2. TGA curves of **FcCP1−FcCP3**

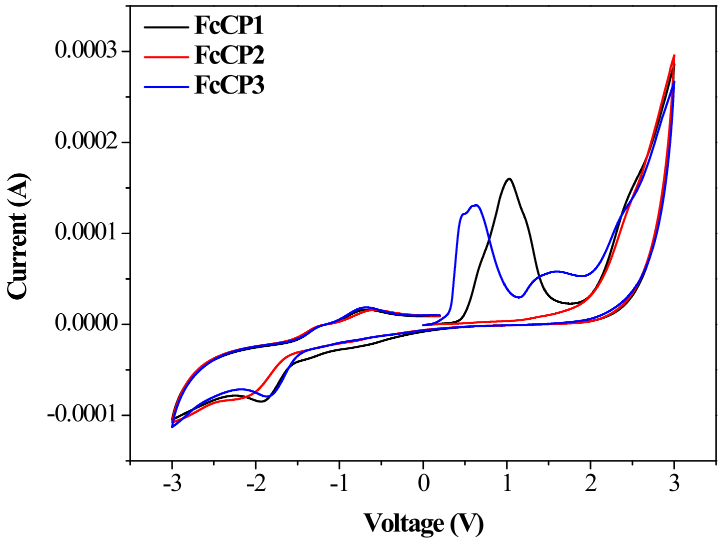
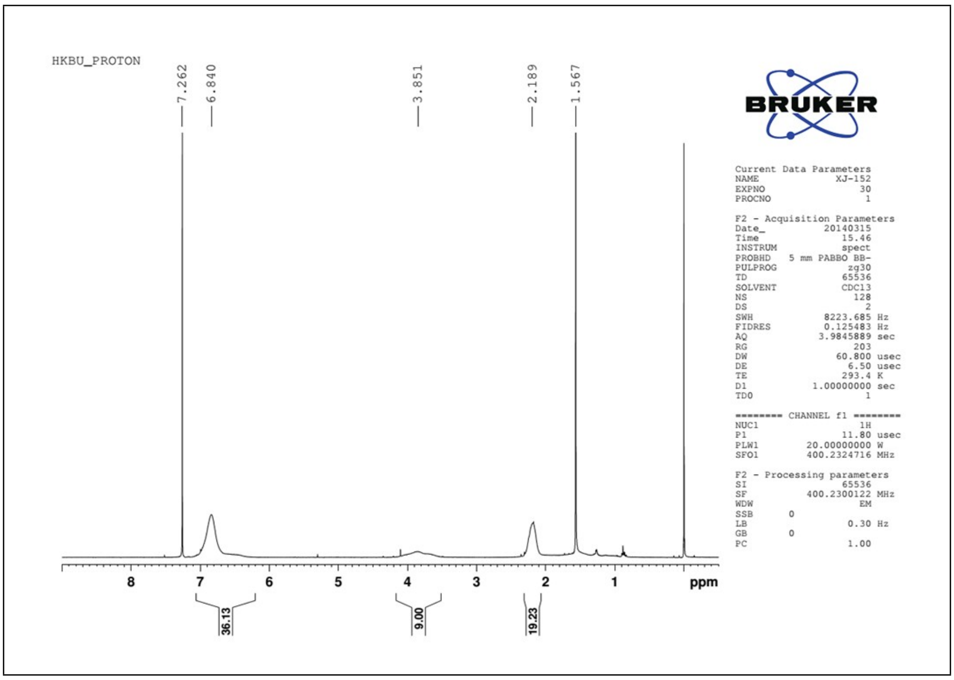


Figure S3. Cyclic voltammograms of **FcCP1−FcCP3** in thin layer electrodes on glassy carbon electrode under 0.1 M *n*-Bu_4NPF_6 acetonitrile solution at a scan rate of 50 mV s^{-1}



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PROCNO                   1

F2 - Acquisition Parameters
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PULPROG               zg30
TD                   65536
SOLVENT              CDC13
NS                     128
DS                       2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ               3.9845889 sec
RG                     203
DW                  60.800 usec
DE                    6.50 usec
TE                   293.4 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.80 usec
PLW1           20.00000000 W
SFO1           400.2324716 MHz

F2 - Processing parameters
SI                   65536
SF             400.2300122 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
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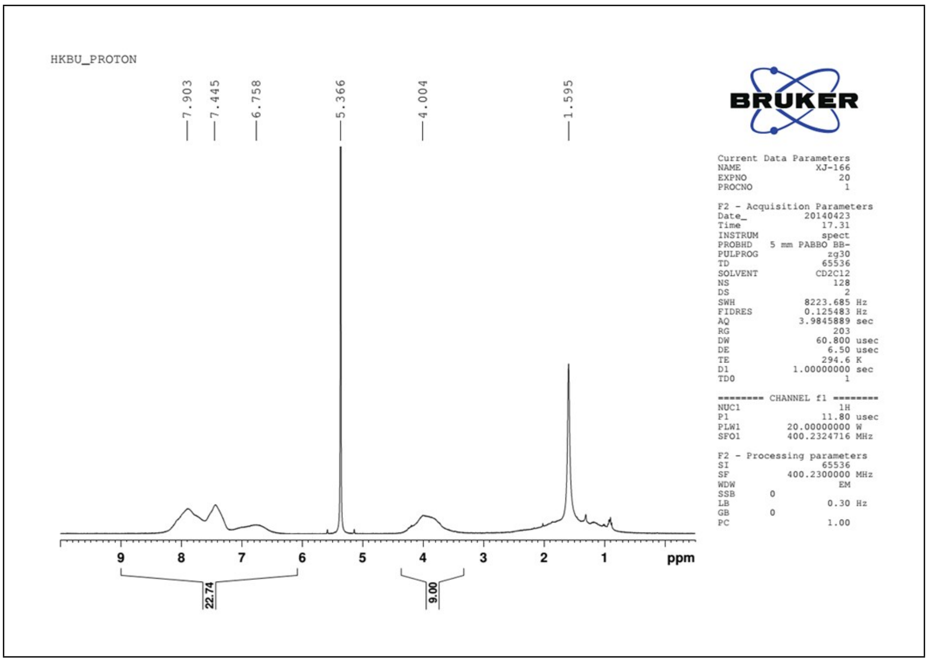
Figure S4. ^{1}H NMR spectrum of **FcCP1** in $CDCl_3$



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TD                   65536
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NS                     128
DS                       2
SWH               8223.685 Hz
FIDRES            0.125483 Hz
AQ               3.9845889 sec
RG                     203
DW                  60.800 usec
DE                    6.50 usec
TE                   294.6 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.80 usec
PLW1           20.00000000 W
SFO1           400.2324716 MHz

F2 - Processing parameters
SI                   65536
SF             400.2300000 MHz
WDW                     EM
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GB       0
PC                    1.00
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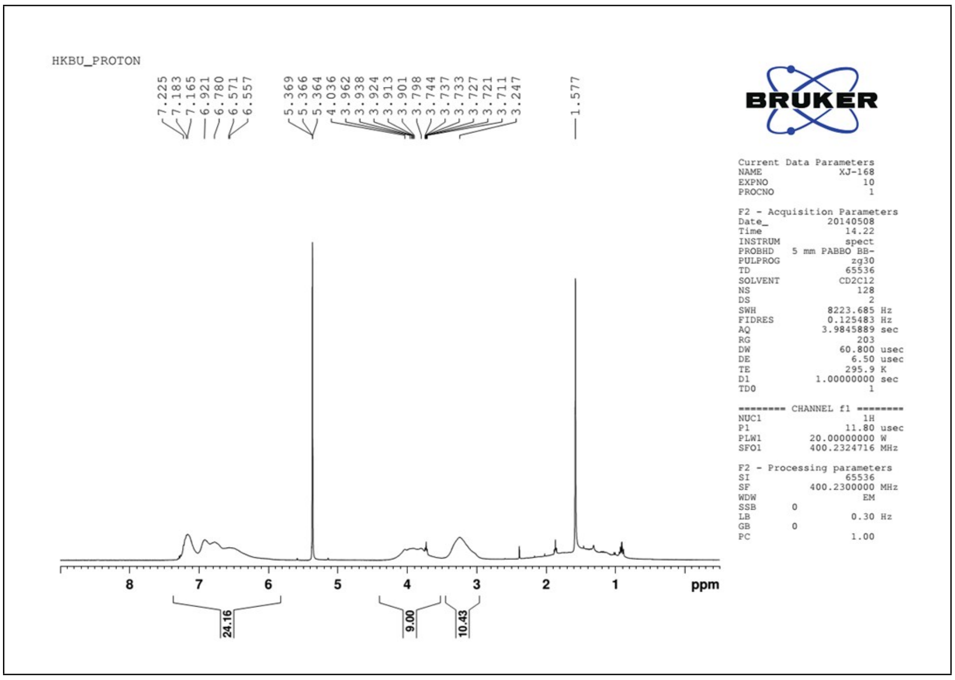
Figure S5. ^{1}H NMR spectrum of **FcCP2** in $CDCl_3$



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PROCNO                   1

F2 - Acquisition Parameters
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PULPROG               zg30
TD                   65536
SOLVENT             CD2Cl2
NS                     128
DS                       2
SWH              8223.685 Hz
FIDRES           0.125483 Hz
AQ              3.9845889 sec
RG                     203
DW                  60.800 usec
DE                    6.50 usec
TE                   295.9 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   11.80 usec
PLW1           20.00000000 W
SFO1           400.2324716 MHz

F2 - Processing parameters
SI                   65536
SF             400.2300000 MHz
WDW                     EM
SSB      0
LB                    0.30 Hz
GB       0
PC                    1.00
```

Figure S6. ^{1}H NMR spectrum of **FcCP3** in $CDCl_3$