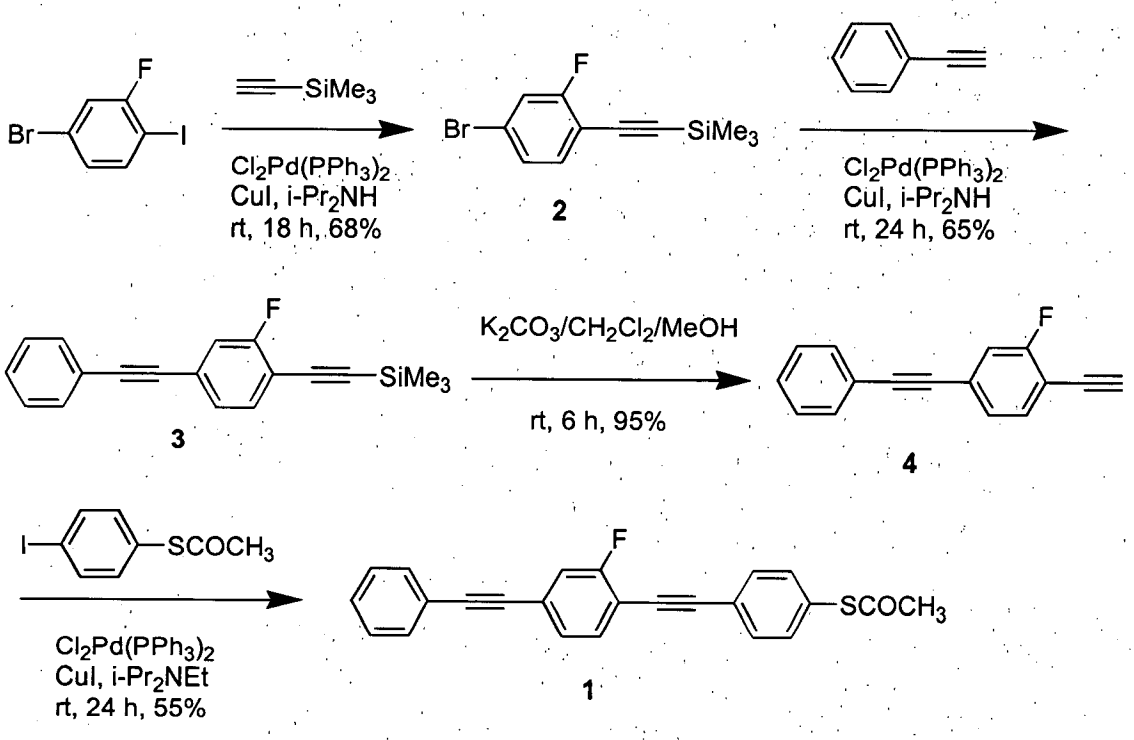
SUPPORTING INFORMATION

Synthesis of 2-fluoro-4-phenylethynyl-1-[(4-acetylthio)-phenylethynyl]benzene, **1**.



Compound 2. 1-Bromo-3-fluoro-4-iodobenzene (3.3g, 11 mmol) was added to THF (100 mL) at rt under argon, then $Pd(PPh_3)_2Cl_2$ (285 mg, 0.4 mmol), CuI(85 mg, 0.4 mmol) and iPr_2NH(3.54 g, 35 mmol) were added and stirred at rt for 10 minutes.[1,2] Trimethylsilylacetylene (3.35 g, 35 mmol) was added in one portion and the reaction was stirred at rt for 18 hours (TLC until all the starting material disappeared). The reaction mixture was poured into water (150 mL) and extracted with diethyl ether (3 x 100 mL). The combined organic layer was washed with brine (2 x 150 mL) and dried over $MgSO_4$. The mixture was then filtered and concentrated to remove solvent. The residue was then applied to a flash silica gel column and rinsed with pure petroleum ether to obtain **2** as a colorless oil (2.0 g, 68%). ^1H NMR ($CDCl_3$): δ 7.30-7.12 (3H, m), 0.26 (9H, s) ppm. (If the product is contaminated by side product 1-fluoro-2,5-bis(trimethylsilylacetylenyl)-benzene, it can be used directly in the next step reaction.)

Compound 3. Compound **2** (2.4 g, 8.86 mmol) was added to THF (40 mL) at rt under argon. CuI (33 mg, 0.17 mmol), $Pd(PPh_3)_2Cl_2$ (140 mg, 0.20 mmol) and iPr_2NH (1.02g, 10 mmol) were added, and the solution was stirred at rt for 10 minutes. Phenylacetylene (1.02 g, 10 mmol) was then added, and the reaction was stirred for 24 hours. The

reaction was worked up as above to obtain **3** as a colorless oil (1.68g, 65%). ^{1}H NMR ($CDCl_3$): δ 7.60-7.10 (8H, m), 0.25 (9H, s) ppm.

Compound 4. A mixture of **3** (1.46g, 5 mmol), methylene chloride (30 mL), methanol (30 mL) and potassium carbonate (4.14g, 30 mmoL) was stirred at rt for 6 hours. Solvent was then removed, and the residue was applied to a short silica gel column. Elution with petroleum ether gave **4** as a colorless oil (1.05 g, 95%). ^{1}H NMR ($CDCl_3$): δ 7.55-7.10 (9H, m), 3.32 (1H, s) ppm.

2-Fluoro-4-(4-phenylethynyl)-1-[(4-acetylthio)-phenylethynyl]benzene, 1. To a solution of S-acetyl-4-iodothiophenol[3] (900 mg, 3.24 mmol) in THF (80 mL) was added $Pd(PPh_3)_2Cl_2$ (140 mg, 0.20 mmol), CuI (33 mg, 0.17mmol) and iPr_2NEt (1.13 g, 8.2 mmol) under argon. The mixture was stirred for 10 minutes, and then compound **4** (1.05 g, 4.77 mmol) was added, and the reaction was stirred at rt overnight. Work-up was as in the preparation of **3** except the chromatography solvent was 33% methylene chloride in petroleum ether. The product **1** was obtained as a light yellow-white powder (659 mg, 55%). ^{1}H NMR ($CDCl_3$): δ 7.60-7.10 (12 H, m), 2.42 (3H, s) ppm. ^{19}F NMR ($CDCl_3$): δ -110.15 (q) ppm. ^{13}C NMR ($CDCl_3$): δ 193.70, 164.25, 160.90, 134.63, 133.64, 132.65, 132.12, 129.10(d), 128.85, 127.75(d),125.60 (d), 124.32, 122.94, 118.69(d), 112.01(d),95.58(d), 92.65, 88.32(d), 84.56, 30.71 ppm. MS (ion-trap): 371 (M+H).
Note: to remove trace iodine impurities, **1** (100mg) was dissolved in minimum amount of THF (about 2 ml), and water (25 mL) was added slowly with stirring (a precipitate appeared formed in this process). Stirring was continued for 0.5 h, and the solid was filtered, washed with water (3 x 5 mL), and dried to obtain pure **1** (99 mg).

References:

1. Chen, J.; Wang, W.; Reed, M.A.; Rawlett, A.M.; Price, D.W.; Tour, J.M.; Room-temperature negative differential resistance in nanoscale molecular junctions Appl. Physics Lett. 77, 1224-1226 (2000).
2. Pearson, D.L.; Tour, J.M. Rapid Syntheses of Oligo(2,5-thiophene ethynylene)s with thioester termini: Potential Molecular Scale Wires with Alligator Clips J. Org. Chem. 62, 1376-1387 (1997).
3. Wu, J.; Chi, C.; Wang X.; Zhao, X.; Wang, P. A one-pot procedure to prepare S-protected-4-iodothiophenols. Syn. Commun. 30, 4293-4298 (2000).

Table S1. Fragment dipole moments for OPE

	Fragment *L*			Fragment *C*			Fragment *R*		
Voltage (volts)	μ_x (D)	μ_y (D)	μ_z (D)	μ_x (D)	μ_y (D)	μ_z (D)	μ_x (D)	μ_y (D)	μ_z (D)
0.00	0.71014	0.94925	-0.00085	1.15894	-0.23413	0.00519	-1.17411	0.12517	-0.00284
0.50	-0.19946	0.96556	-0.00082	0.99033	-0.23306	0.00506	-2.02913	0.15747	-0.0036
0.75	-0.66423	0.97365	-0.00081	0.90645	-0.23258	0.00499	-2.46127	0.1737	-0.00398
1.00	-1.13631	0.98186	-0.00079	0.82269	-0.23204	0.00492	-2.89805	0.19017	-0.00436
1.25	-1.61755	0.9902	-0.00077	0.73914	-0.23142	0.00485	-3.34137	0.20696	-0.00476
1.50	-2.11016	0.99864	-0.00075	0.65596	-0.23073	0.00478	-3.79291	0.22415	-0.00516
1.75	-2.61682	1.00729	-0.00072	0.57329	-0.22997	0.00471	-4.2552	0.24188	-0.00557

Table S2. Fragment dipole moments for F-OPE

	Fragment *L*			Fragment *C*			Fragment *R*		
Voltage (volts)	μ_x (D)	μ_y (D)	μ_z (D)	μ_x (D)	μ_y (D)	μ_z (D)	μ_x (D)	μ_y (D)	μ_z (D)
0.00	0.24734	0.95753	0.00122	-0.39402	-1.31664	-0.00082	0.05401	0.14909	0.00015
0.50	-0.66381	0.96098	0.00128	-0.5622	-1.31737	-0.00083	-0.81483	0.16294	0.00011
0.75	-1.12884	0.96226	0.00131	-0.64491	-1.31748	-0.00084	-1.25354	0.16965	0.0001
1.00	-1.6015	0.96351	0.00133	-0.7276	-1.31756	-0.00085	-1.69621	0.17642	0.00008
1.25	-2.08352	0.96469	0.00136	-0.81014	-1.3176	-0.00086	-2.14469	0.18333	0.00006
1.50	-2.57709	0.96582	0.00139	-0.89245	-1.3176	-0.00086	-2.60081	0.1904	0.00005
1.75	-3.08471	0.9669	0.00142	-0.97437	-1.31755	-0.00087	-3.06694	0.19767	0.00003

Table S3. Fragment dipole moments for NO_2-OPE-NH_2

	Fragment *L*			Fragment *C*			Fragment *R*		
Voltage (volts)	μ_x (D)	μ_y (D)	μ_z (D)	μ_x (D)	μ_y (D)	μ_z (D)	μ_x (D)	μ_y (D)	μ_z (D)
0.00	-2.46473	0.77016	0.02257	-6.34742	-7.57551	0.75368	5.6084	0.27564	0.03085
0.50	-2.41244	0.78401	0.02317	-6.6538	-7.60536	0.75368	3.75113	0.34855	0.02067
0.75	-2.40505	0.79129	0.02346	-6.76234	-7.61876	0.75355	2.78842	0.38494	0.01544
1.00	-2.39627	0.7987	0.02375	-6.87693	-7.63192	0.75339	1.82167	0.42152	0.01019
1.25	-2.38547	0.80619	0.02405	-6.99794	-7.64485	0.7532	0.84817	0.45832	0.0049
1.50	-2.37192	0.81383	0.02435	-7.12581	-7.65736	0.75299	-0.13633	0.49555	-0.00044
1.75	-2.35473	0.82165	0.02467	-7.26126	-7.66951	0.75275	-1.13619	0.53334	-0.00585